

Noble Metal Nanoparticle-Containing Photoactive Nanofibres for Photovoltaic Applications



Ryan M. Schofield
The Queen's College
University of Oxford

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Preface

This thesis is an account of work I conducted as a postgraduate student at the Department of Materials, University of Oxford. No part of this thesis has been submitted for a degree at this University or any other. Work conducted by other authors has been acknowledged and appropriate references provided.

Work presented in this thesis has been published in the following scientific journals or presented at the following conferences:

- **R. M. Schofield**, B. M. Maciejewska, S. Dong, G. T. Tebbutt, D. McGurty, R. S. Bonilla, H. E. Assender and N. Grobert. Driving fiber diameters to the limit: nanoparticle-induced diameter reductions in electrospun photoactive composite nanofibers for organic photovoltaics. *Adv. Compos. Hybrid. Mater.*, 6:229, 2023. <https://doi.org/10.1007/s42114-023-00788-0>
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Abstract

Achieving greater light-harvesting in thin photoactive layers remains critical to alleviating the absorption-extraction trade-off presented by organic photovoltaics (OPVs) - a flexible, lightweight, and low-cost alternative to silicon.

Herein, plasmonic nanoparticles are introduced to electrospinning solutions containing the electron donor polymer poly(3-hexylthiophene) (P3HT) and auxiliary polymer poly(ethylene oxide) (PEO), inducing viscosity/conductivity modulation and enabling the fabrication of record-low diameters of P3HT nanofibres with diameters of 55 nm, 30% lower than prior reports. Viscosity reduction is a time-dependent process allowing thinner fibres to be electrospun as the solution ages.

Electrospinning offers an impressive degree of chain alignment wherein anisotropic features orient along the fibre axis. For dissolved polymer, the chains are extended along the fibre. In crystalline regions, diffraction studies reveal the backbones are orthogonal to the axis. Crystallites assembled in solution before electrospinning grow in the $\pi - \pi$ direction, and this anisotropy results in the observed backbone orientation.

Upon nanoparticle-induced diameter reductions, polymer alignment increases, providing optimal overlap of the transition dipole moment with the electric field vector of light, promoting photon-harvesting. Champion nanowebs provide up to 60% additional exciton generation versus a conventionally spin-coated thin-film.

A novel plasmon-active nanofibrous active layer is prepared by infiltration of the nanoweb with an electron acceptor. Photoluminescence quenching indicates that fibres offer competitive exciton dissociation levels of 95 – 97 %, whilst ultra-fast transient absorption confirms quenching translates into enhanced charge carrier populations with longer lifetimes. Compounded with absorption enhancements, $\sim 135\%$ greater polaron populations were estimated 1 ns after photo-excitation in the presence of AgNPs prepared in-situ.

Proof-of-principle OPVs present efficiency approaching that of the bulk heterojunction, whilst AgNPs raise open-circuit voltage. Further work is required to achieve high-quality acceptor infiltration for effective carrier extraction. As the nanoparticle - PEO interaction dictates electrospinning, this platform is easily adapted to other contemporary semiconducting polymers.

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List of Abbreviations

% RH	% Relative Humidity
< P₂>	Hermans' Orientation Factor
β	Azimuthal angle
θ	Scattering angle
A	Absorptance
ADF	Annular Dark Field
AFM	Atomic Force Microscopy
AM1.5G	Air Mass 1.5 Global - global horizontal irradiance spectrum
AZO	Al-doped ZnO
BET	Brunauer-Emmett-Teller
BF	Brightfield
BHJ	Bulk heterojunction
BVM	Bragg Vector Map
CoP(3DDT)-(C₆₀HT)	poly[3-dodecylthiophene-co-3-(6-fullerenylhexyl)thiophene]
DCM	dichloromethane
DMF	N,N-dimethylformamide
EDX	Energy-dispersive X-ray [Spectroscopy]
EQE	External Quantum Efficiency
EX	Exciton
FDTD	Finite-Difference Time-Domain
FEG	Field Emission Gun
FF	Fill Factor
FRET	Förster resonance energy transfer
fs-TAS	Femtosecond-Transient Absorption Spectroscopy
FT-IR (ATR)	Fourier-Transform Infrared (Attenuated Total Reflectance)
FWHM	Full width at half maximum
GI	Grazing-incidence
GI-WAXS	Grazing-incidence Wide Angle X-ray Scattering
GSB	Ground State Bleach
HOMO	Highest occupied molecular orbital
IDTBR	(5Z,5'Z)-5,5'-((7,7'-(4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(benzo[c][1,2,5]thiadiazole-7,4-diyl))-bis-(methanylylidene)) bis(3-ethyl-2-thioxothiazolidin-4-one)
IP	In-plane
IPA	isopropanol
IPCE	Incident Photon to Current Efficiency
IR	Infrared

ITO	indium tin oxide
J_{MP}	Current density at Maximum Power Point
J_{SC}	Short circuit current density
J-V	Current density-voltage
LUMO	Lowest unoccupied molecular orbital
LSPR	Local Surface Plasmon Resonance
MDMO-PPV	poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene]
MEH-PPV	poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene]
NF	Nanofibre
NFA	Non-Fullerene Acceptor
NIR	Near Infrared
NP	Nanoparticle
OA	oleylamine
OFET	Organic Field-Effect Transistor
OOP	Out-of-plane
OPV	Organic Photovoltaic
P	Polaron
P3HT	poly(3-hexylthiophene)
PC₇₁BM	[6,6]-Phenyl-C71-butyric acid methyl ester
PCBM	[6,6]-phenyl-C61-butyric acid methyl ester
PCDTBT	poly[N-9'-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3',-benzothiadiazole)]
PCE	Power Conversion Efficiency
PCE12	poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene)) -alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl) benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)]
PCL	poly(ϵ -caprolactone)
PDCBT	poly[2,2''-bis[[[(2-butyloctyl)oxy]carbonyl][2,2':5',2'':5'',2'''-quaterthiophene]-5,5''-diyl]
PDF	Pairs Distribution Function
PDI	Polydispersity Index
PDINO	N,N'-Bis(N,N-dimethylpropan-1-amine oxide)perylene-3,4,9,10-tetracarboxylic diimide
PEDOT:PSS	poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate)
PEG	poly(ethylene glycol)
PEO	poly(ethylene oxide)
PIA	Photo-induced absorption
PL	Photoluminescence
PM6	poly[(2,6-(4,8-bis(5-(2-ethylhexyl-3-fluoro)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene)) -alt-(5,5-(1',3'-di-2-thienyl-5',7'- bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)]
PML	Perfectly matched layer
PMMA	poly(methyl methacrylate)
P_{MP}	Maximum Power Point
PP	Polaron Pair

PTB7	poly [[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]]
PTFE	poly(tetrafluoroethylene)
PV	Photovoltaic
PVAc	poly(vinyl acetate)
PVP	poly(vinyl pyrrolidone)
pXRD	Powder X-ray Diffraction
QCM	Quartz Crystal Microbalance
R	Reflectance
RCP	Representative Concentration Pathway
RMS	Root Mean Square
RRa	Regiorandom
RR	Regioregular(ity)
S₀	Ground electronic state
SAED	Select-area Electron Diffraction
SATW	Super Atmospheric Thin Window
SE	Stimulated Emission
SEM	Scanning Electron Microscopy
SNR	Signal-to-noise ratio
S_n	The n th excited electronic state
SPR	Surface Plasmon Resonance
STEM	Scanning Transmission Electron Microscopy
T	Transmittance
TAS	Transient Absorption Spectroscopy
TEM	Transmission Electron Microscopy
T_g	Glass transition temperature
TGA	Thermogravimetric Analysis
UV	Ultraviolet
vDF	virtual Dark-field Image
V_{MP}	Voltage at Maximum Power Point
V_{OC}	Open circuit voltage
w/w	weight by weight
wrt	with respect to
wt%	weight %
XRD	X-ray Diffraction

1

Introduction

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1.1 Meeting a Sustainable Energy Demand

Supplying energy to an inflating global population is the most pressing concern of our generation, and yet existing technologies are inadequate at meeting this demand whilst fulfilling net-zero targets. Despite record deployments of renewable technologies, fossil fuels still fulfil over 75% of global energy consumption, [1] and consequently, global energy-related CO₂ emissions rose by 0.9% in 2022, to unprecedented levels of 36.8 Gt annum⁻¹.

Climate change and the desire for energy security encourage progression towards low-carbon alternatives. However, to induce true change, the cost of this energy must be comparable to legacy fossil fuels. From 2010 to 2022, energy generated by photovoltaics (PVs) saw 83% global-average reduction in cost, surpassing grid parity and costing 29% less than the cheapest fossil fuel-derived energy. [2, 3] Sunlight delivers a magnitude of

energy that dwarfs the world’s energy demand with just 1 h of sunlight incident upon the Earth equating to the entire year’s consumption. [4] Therefore, solar PV holds the potential to make a significant contribution towards clean and sustainable energy with low operating costs, low emissions and a source of energy at point-of-use.

Emerging PVs based upon thin-films offer an attractive alternative to conventional silicon PVs. Tailorable light harvesting by organic semiconductors provides a lightweight, flexible device processed simply from solution or vapour at low temperatures. [5, 6] Their fast deposition and compatibility with roll-to-roll processing allows them to be formed cheaply from Earth-abundant elements, and resultantly deliver an energy payback time of just 10 weeks. [7] Whilst perovskite devices have led third-generation PVs in terms of efficiency, OPVs have been touted to fill strategic niches essential to enabling commercialisation, such as photovoltaic windows, [8] indoor light harvesting, [9] or agrivoltaics [10]. Also, OPVs do not possess environmental and toxicity concerns like lead halides [11]. Moreover, they are considered a highly sustainable PV option with easy end-of-life treatment, during which redundant panels can be used as a solid fuel. [12]

OPV device efficiencies have exceeded 19% in lab settings in recent years, [13] largely owing to the emergence of non-fullerene acceptors (NFAs). [14] Real-world stabilities of 20+ years have been predicted for the most stable systems, [15] whilst T_{80} (time taken for PCE to reduce to 80% of its initial value under 1 Sun illumination for 5.5 h day⁻¹) [16] of > 2 years has already been achieved for state-of-the-art devices. [17] Arguably, driving the efficiency higher is no longer the primary focus. Instead, researchers feel that greater light harvesting, and device efficiencies, must next be achieved using lower-cost, chemically simpler and stable polymers/molecules. [6] As the synthesis of novel absorbers can take many years, and the materials considered most desirable will change regularly, research into adaptable processing methods is deemed attractive. Ideally, said research would also focus on the use of green solvents. [18]

1.2 Conjugation in Organic Semiconductors

In its ground state, a carbon atom possesses a $1s^2 2s^2 2p^2$ electron configuration with two unpaired electrons (in p-orbitals), yet is observed to create four bonds. [19] The

promotion of an electron from the 2s to the unoccupied 2p orbital yields the required four unpaired electrons, however, the s-orbital and three p-orbitals in the valence shell still inadequately describe the nature of its bonding with other atoms. To understand the characteristics of carbon bonding, particularly a carbon-carbon double bond, one must introduce the concept of orbital mixing to produce molecular orbitals with both s- and p- character, namely three degenerate sp^2 orbitals, while the third p-orbital remains un-hybridized. (Figure 1.1a) These new orbitals possess an intermediate ‘shape’ and energy to the un-hybridised atomic orbitals. [20] Whilst other orbital mixing is possible, sp^2 hybridisation is the most relevant to organic semiconductors.

When two sp^2 -hybridized carbons bond in ethene, an sp^2 orbital from each carbon overlaps to form a σ -bond, Figure 1.1a. The remaining two sp^2 orbitals may bond with additional atoms in a trigonal planar configuration. The orientation of the p-orbitals from each carbon atom means that a π -bond also forms via side-on interaction between the p-orbital ‘lobes’ above and below the molecular plane.

The sp^2 and p-orbitals may interfere constructively or destructively producing bonding and anti-bonding orbitals, respectively (Figure 1.1b). In the molecular energy diagram of benzene, the six sp^2 atoms produce three π and π^* orbitals, and form a ring containing alternating single and double carbon-carbon bonds, known as conjugation. In reality, these bonds are equal in length, as the p-orbitals interact to form a large molecular orbital ‘delocalised’ across the entire molecule. As the number of carbon atoms in the conjugated system increases, the highest occupied molecular orbital - lowest unoccupied molecular orbital (HOMO - LUMO) gap is reduced, and the π and π^* orbitals form almost-continuous bands, analogous to the valance and conduction bands in inorganic semiconductors. [19]

At some point, the reduction in the HOMO-LUMO energy separation introduces semiconducting behaviour, and the resultant optical properties, when the energy gap is comparable to photons in visible to near-infrared (IR) regions.. Charge transport properties of organic semiconductors is also linked to conjugation, as electrons (or ‘holes’) can be delocalised across the series of alternating single-double bonds. [21]

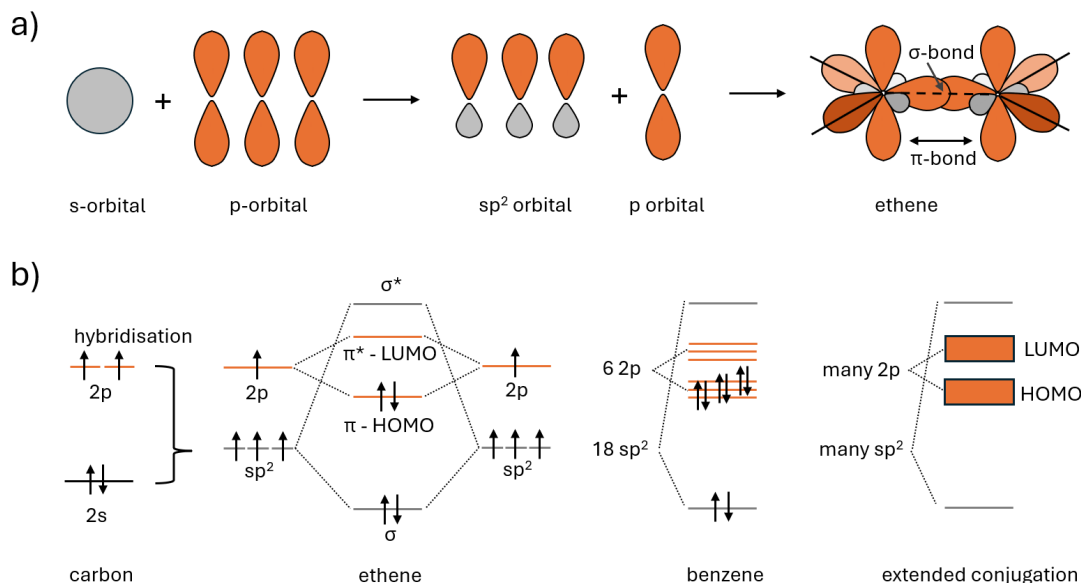


Figure 1.1: (a) Diagram of sp^2 hybridisation of s-orbitals and p-orbitals, and the formation of a double bond (σ -bond and π -bond) between two sp^2 hybridised carbon atoms e.g. in ethene. (b) Energy level diagram of ethene, benzene, and extended conjugated carbon systems, e.g. poly(p-phenylene vinylene) (PPV). Constructive and destructive interference of the sp^2 orbital overlap causes energy splitting into (σ) and anti-bonding (σ^*) orbital, shown in grey, whilst the π -bonding and π^* anti-bonding orbitals, in orange, arise from the p-orbital interaction. The magnitude of energy splitting between the (σ) and (σ^*) orbitals is larger as it is affected by the degree of atomic orbital overlap. With enough carbon atoms, continuous bands of π and π^* bonds are formed. Adapted from reference [19].

1.3 Photophysics and Principles of OPV Operation

When sunlight passes through the window electrode of an OPV, wavelengths with energy exceeding the HOMO - LUMO gap of the photoactive material may be absorbed, with a valent electron being promoted to the LUMO, leaving a hole in the HOMO. (Process 1, Figure 1.2 - 1.3)

Absorption (and emission) are often represented in a Jablonski diagram [22] (Figure 1.4a), where photo-excitation induces the promotion of an electron from the ground state (S_0) to the first excited state (S_1). For each electronic state, there are a number of vibrational energy levels separated by small energy gaps (approximately 0.1 eV). [23]

The probability of a radiative transition (absorption or emission) is determined by three main factors: the dipole factor, vibrational factor, and spin selection rules. This is largely beyond the scope of this thesis, but the selection rules can be summarised as below.

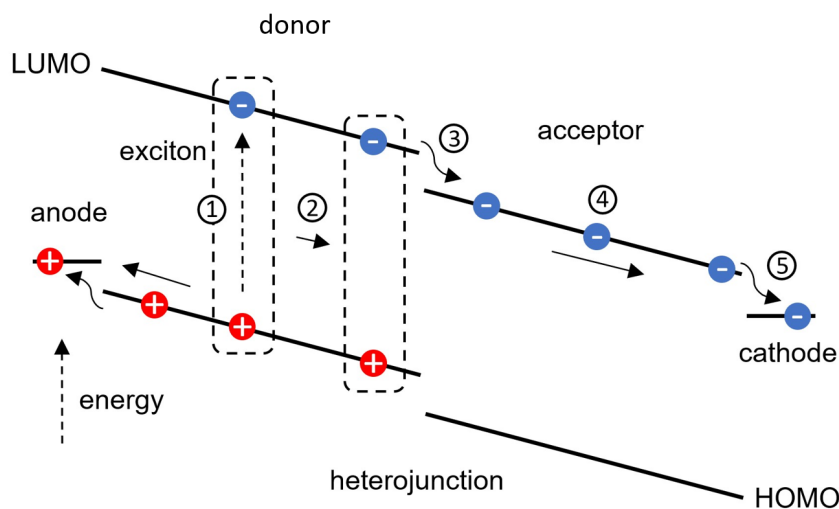


Figure 1.2: Energy band diagram of an OPV cell under the short-circuit condition demonstrating the fundamentals of exciton generation and separation, and charge extraction.

Firstly, the intensity of a transition is affected by a dipole factor. In brief, for a transition to be optically allowed, this electronic factor must be non-zero. This occurs when the transition involves a change in spatial symmetry (or parity) of the electronic wavefunction. [20] The strength of the transition is then influenced by the overlap between the initial and final electronic wavefunctions. In organic semiconductors, the π - π^* transition is dipole-allowed with good overlap of the orbital wavefunctions, being delocalised over the same region of the molecule. [23, 20]

The Franck-Condon principle describes the relative intensities of vibronic (electronic + vibrational) transitions commonly observed in the optical spectra of organic semiconductors. Electronic transitions occur on faster time-scales (10^{-15} s) than atoms rearrange, as electrons are three orders of magnitude less massive than protons or neutrons. [20] As the molecular geometry of the excited state at equilibrium usually differs from the ground state, an accompanying vibrational excitation often occurs to better match the nuclear positions of the initial ground state. In Figure 1.4b, the vertical transition is the most probable, though this rarely corresponds to a transition involving the lowest vibrational state (0-0). [23]

Finally, the spin selection rule dictates that a transition is allowed if the spin of the initial and final state is the same, to conserve angular momentum. Otherwise, the spin

factor is zero, and the transition is suppressed. [20]

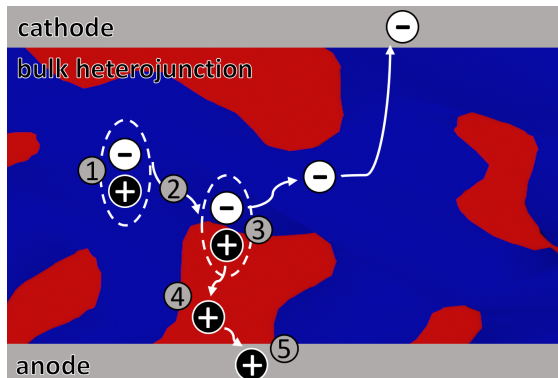


Figure 1.3: Schematic diagram demonstrating the procession from exciton formation to extracted charge within a bulk heterojunction OPV device.

The excited electron and hole form a coulombically-associated ‘Frenkel exciton’. [24] The attraction between the oppositely-charged species is significantly higher than in inorganic semiconductors, being confined to a single conjugated π -system with low polarizability, resulting in a binding energy of 0.1 – 1 eV. [24, 25, 26] The selection rules dictate that photo-excitation primarily produces singlet excitons, where the excited and ground-state electron are paired with the opposite sign, rather than a triplet state (same spin orientation). [27]

Immediately after excitation, excitons will be vibrationally ‘hot’, but the excited electron rapidly thermalizes (internal conversion) within 10^{-12} s to the ground vibrational level of the first excited electronic state. [28]

As a neutral excited species, excitons diffuse between organic molecules (Process 2, Figure 1.2 - 1.3) via processes including Förster resonance energy transfer (FRET). [21] In FRET, when a exciton donor relaxes to the ground state, its energy is non-radiatively transferred to an acceptor via resonance. [29] By these processes, the exciton travels a distance of just $\sim 5 - 20$ nm (the exciton diffusion length) [30] before the electron recombines with the hole, quenching the potential charge carriers either radiatively (photoluminescence, or PL) or non-radiatively. As the exciton undergoes internal conversion before recombination, the energy of the emitted photon is lower than that absorbed, resulting in Stoke’s shift of the (0-0) transition (Figure 1.4b-c).

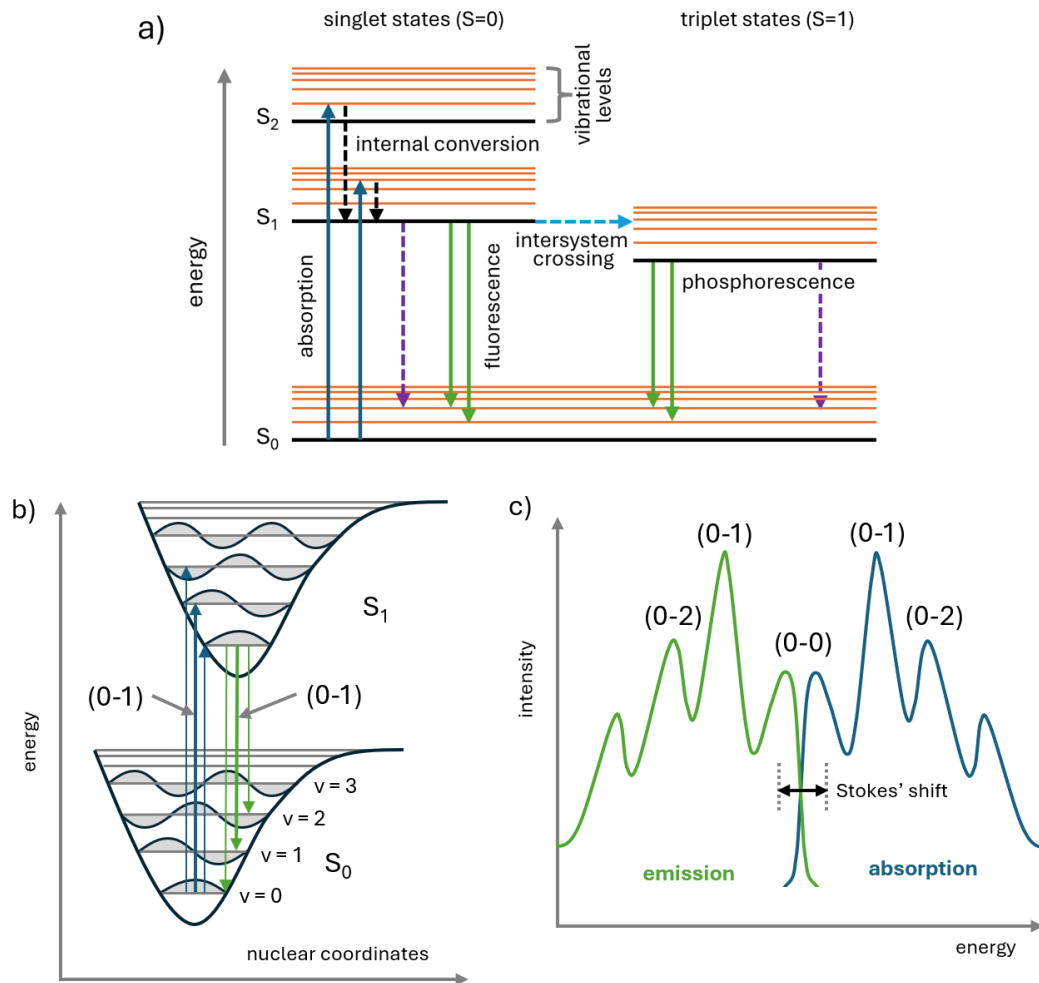


Figure 1.4: (a) Jablonski diagram showing the possible processes following photo-excitation. Solid lines represent radiative processes such as fluorescence and phosphorescence, while non-radiative pathways are represented by dashed lines. (b) Potential energy curves for the ground and first excited states of a simple diatomic molecule. Due to the fast time-scale of excitation, there is no initial molecular rearrangement, resulting in a favourable (0-1) vibronic transition in the presented scenario. (c) Corresponding absorption and emission spectra generated by the molecule given in (b) showing the difference in energy between absorption, and relative intensities of vibronic transitions under the Frank-Condon Principle.

[23] Alternatively, singlet excitons may undergo intersystem crossing to produce triplet excitons, however this is uncommon in regioregular(RR)-P3HT. [31]

However within an OPV device, if the electron-hole pair reaches the heterojunction, the interface between the electron donor and acceptor materials, it may instead be separated into free charge carriers. For effective photovoltaic performance, short diffusion lengths demand strict restrictions on the donor and acceptor domain sizes within the active layer.

At the heterojunction, the electron in the donor material LUMO travels down the

electrical gradient into the acceptor material LUMO. (Process 3, Figure 1.2 - 1.3) Meanwhile, the hole remains associated with the donor material HOMO. Dissociation proceeds via an intermediate charge-transfer state, where the charges reside on different molecules (electron on an acceptor molecule, and hole in the donor material), but are still weakly-bound and not yet ‘free’. [20]

Following separation, the charge carriers travel to the collection electrodes driven by the applied electrical field and carrier concentration gradient. (Process 4, Figure 1.2 - 1.3) Charge transport generally proceeds via thermally-activated hopping, rather than a band-like mechanism as in inorganic semiconductors. The interaction of a charge carrier with the surrounding environment can polarize nearby orbitals, forming a charged quasi-particle known as a polaron. [32] This distortion can localise/trap the charge, meaning polaronic transport requires an additional reorganisation energy. [33] A polaron pair represents the analogous charge-transfer intermediate of coulombically-bound negative and positive polarons.

Once the charge carriers are transported to the electrodes, they are ultimately extracted into the external circuit, producing a current. (Process 5, Figure 1.2 - 1.3)

1.4 Conventional OPV Active Layer Architectures

The simplest structure of an organic photoactive layer is the bilayer junction. This architecture involves the sequential deposition of an electron donor film onto an acceptor film, or vice versa. (Figure 1.5) Excitons which reach the heterojunction are separated efficiently, however, if excitons are generated a distance of greater than one exciton diffusion length from the interface, recombination is likely to occur instead. This imparts an intrinsic restriction to the thickness of the bilayer. An oversimplification of this architecture, ignoring inter-diffusion of the two materials, would suggest a limit of each film to the exciton diffusion length of the semiconducting material (~ 10 nm). This leads to processing difficulties, but also means that light absorption is low, setting up a trade-off between optical absorption and internal quantum efficiency.

To help OPVs reach efficiencies required for commercialisation, the bulk heterojunction (BHJ) was developed. [34] The BHJ features a donor and acceptor blend which undergo

nanoscale phase separation to generate a 3D structure containing bi-continuous pathways to increase the heterojunction surface area. (Figure 1.5) For effective exciton dissociation, the domains should be small enough so that all excitons are formed within one diffusion length of an interface.

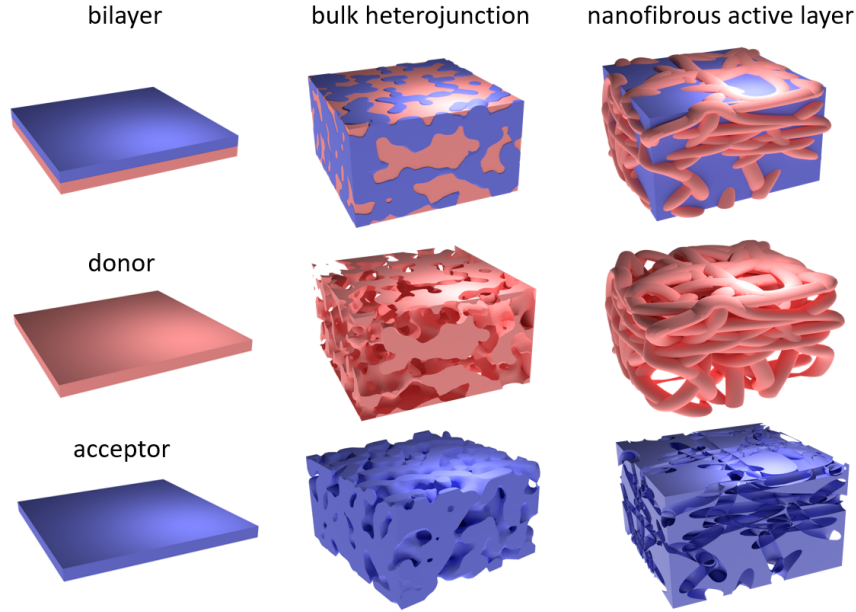


Figure 1.5: Schematic of donor and acceptor domains in bilayer, bulk heterojunction and nanofibrous active layer architectures.

This allows the BHJ to present optimal efficiencies at 100 – 200 nm, [35, 36] beyond the capability of the simplified bilayer system, meaning more of the incident light can be absorbed. However, at this thickness there is still insufficient material to harvest the full intensity of incident light. [36, 37]

Further, pathways for charge transport within the BHJ can be long and therefore inefficient. [38]. In extreme cases, phases may become discontinuous or isolated. [9, 39] Even at its increased thickness, processing continuous thin-films of ~ 100 nm is complex and can present shorting issues. These issues typically become more pronounced upon scale-up from the small area devices produced within laboratories. Hole mobility within polymers is generally an order of magnitude lower than electron mobility in fullerenes or NFAs, and this imbalance can lead to space-charge build-up. [36] Achieving the desired domain size, morphology and crystallinity required for higher efficiency devices typically requires

thermal [40, 41, 42] or solvent [43, 44, 45] annealing. These processes are energy-intensive and have limited compatibility with plastic substrates. Stability of the thermodynamically-unstable phase separation is also a concern, lowering device performance due to the migration and aggregation of the photoactive materials over time. [46]

Whilst they possess intrinsic advantages, OPVs have struggled to overcome the barrier to commercialisation. The low volumes produced by technologies emerging into the marketplace from the research environment, alongside the inferior efficiency of organic devices versus conventional silicon or emerging perovskite PVs, communicated in Figure 1.6, attenuates their cost benefit. [47] This uncompetitive efficiency arises from the incomplete photon harvesting by organic semiconductors at the thickness required for efficient charge extraction. Current record-performance devices present short circuit currents of 80% of the theoretical limit, with a significant photocurrent loss of 20% originating from insufficient absorption. [48, 49] Increasing the active layer may encourage further absorption, but to the detriment of charge extraction. Therefore, a major area of OPV research focusses on increasing absorption by the same mass of the photoactive material. Within this work, a processing change and optimisation strategy is developed to produce desirable influences upon the nanostructure of organic semiconductor materials towards promoting photon harvesting.

Synthesizing novel donor semiconductors is time-consuming and resource-intensive, [50, 51] therefore, developing process changes to form new materials with existing absorbers may offer a straightforward and universally-adaptable approach to promoting the efficiency and commercialisation potential of OPVs. The work presented here focusses upon polymeric electron donors. OPVs based on small molecule donors and acceptors possess advantages with reproducibility and lower batch-to-batch variation, [52] and following substantial research efforts, their device performance has improved steadily in recent years. However, small molecule systems can crystallise excessively or highly miscible donor and acceptor components can render control over the phase separation difficult. [53] Polymers also retain greater mechanical and film-forming properties. Vacuum processing of large molecules such as polymers is relatively limited, slower and more costly, and the performance of vacuum-deposited systems has generally lagged behind its solution-processed peer. [54, 55]

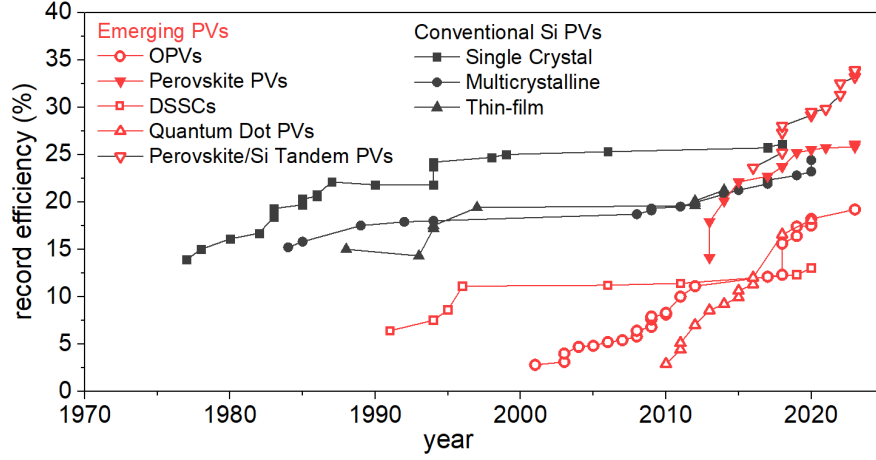


Figure 1.6: A timeline of record efficiency PVs based upon silicon and emerging technologies. Produced using data from reference [47].

1.5 A Review of Electrospun Photoactive Nanofibres in OPVs

One such approach to increasing the light-harvesting capabilities of polymeric semiconductors is to produce high aspect ratio nanofibres by the solution-processing method, electrospinning. Electrospinning is a facile, from-solution method capable of producing continuous polymer fibres with diameters between tens of nanometres and several microns. [56] Nanofibre mats can be collected over large areas (up to several hundred cm^2) from a single nozzle. The technique involves low material wastage compared to other deposition techniques such as spin-coating, and needle-less spinning holds potential compatibility with roll-to-roll scale-up. [57, 58]

A charged polymer solution is delivered to a needle tip, and a high voltage is applied between this and a grounded collector. (Figure 1.7) The voltage causes the formation of a Taylor cone due to electrostatic repulsion and surface tension. [59, 60] At some critical point, the voltage induces a jet to erupt from the droplet. During its travel to the collector, the solvent evaporates, and the jet is stretched and decreases in diameter until a fibre is formed.

Devices containing electrospun organic semiconductors display performance enhancements arising from superior light absorption and greater charge transport mobility, and when implemented effectively, have presented greater device efficiencies than their BHJ

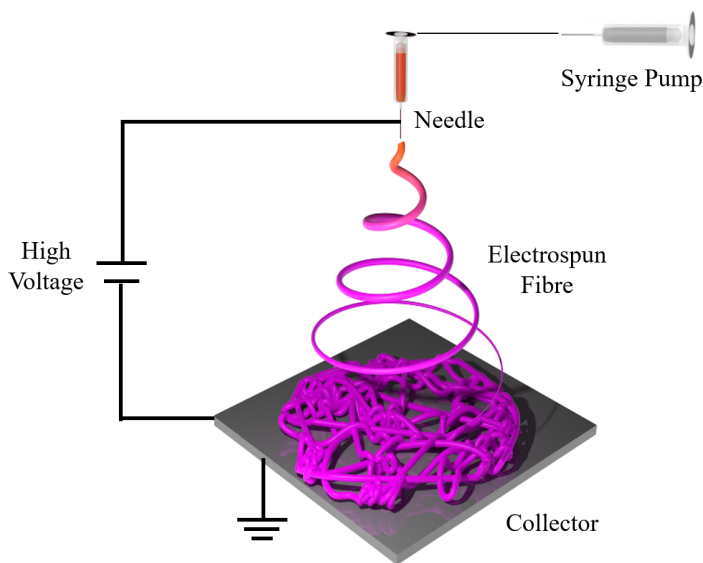


Figure 1.7: Schematic of the electrospinning rig used to produce P3HT nanofibres.

counterparts. Fibres may either be introduced into the BHJ [61, 62, 63] or used to produce an alternative architecture, the nanofibrous active layer. [64, 65, 66] (Figure 1.5) Here, the fibres serve as the donor domains and the interstitial space is infiltrated by the acceptor material, historically [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM), forming bicontinuous pathways.

The advantages of electrospun polymer over spin-coated domains generally stem from polymer chain alignment induced by the shear and elongational forces experienced by the jet during electrospinning. Resultantly, nanofibres have reportedly increased the absorption of light by a fixed volume of photoactive material. Typically, the planarization of the polymer backbones results in a red-shift in the absorption spectrum, [61, 62, 67] which can result in additional harvesting and sometimes offers a better overlap with solar emission. [63] Additionally, Bedford et al. described how the chain alignment along the fibre translates into a greater proportion of polymer laying parallel to the substrate plane, as the fibres lay flat on the collector. [61, 62, 68] This configuration is advantageous for absorption as the polymer is orientated so that the $\pi - \pi^*$ transition dipole moment (along the backbone) has an effective overlap with the electric-field vector of light impinging normal to the substrate. [68, 69]

Beyond light-harvesting, electrospinning provides greater hole mobility along the fibre axis. Within P3HT, charge transport is fastest along the backbone (the (001) direction), followed by along the (0k0) $\pi - \pi$ stacking direction. Transport is slowest in the (h00) lamellar stacking direction due to attenuation by insulating alkyl side chains. [70] Therefore, electrospinning-induced alignment may orient the polymer crystallites so that mobility and transport along the fibre axis would be enhanced. The along-chain preference generally results in electrospun nanowebs containing a mixture of edge-on ((h00) axis normal to the substrate) and face-on ((0k0) axis normal to the substrate) orientations with respect to (wrt) the substrate. Spin-coated P3HT films (from chlorobenzene) often favour an edge-on configuration, allowing the alkyl side-chains to present at the film-air and film-substrate interfaces. [71]

As charge extraction occurs vertically, at the top and bottom of the solar cell, the dominant edge-on orientation in films presents the slowest hole mobility in the required vertical direction. Therefore, previously reported electrospun fibres may provide favourable configurations for long-range lateral transport, while face-on crystallites provide essential vertical charge transport.

Electrospinning can also provide a ‘templating effect’ where the polymer alignment in the early stages of fibre formation may facilitate a higher extent of crystallinity in P3HT fibres versus their thin-film equivalent. [67] As the crystalline regions in P3HT films are not fully percolated, transport must partially occur through amorphous domains, with an additional energy barrier to charge transfer between these regions. Under this model, a greater degree of crystallinity acts to reduce the distance that charges must travel through this rate-limiting amorphous content. [72, 73, 74, 75]

Combined, these advantages allow nanofibrous devices to harvest more light, produce and extract additional charges, and ultimately enhance energy generation. Enhanced efficiency typically arises from an increased short-circuit current (J_{SC}) (approximately proportional to light absorption [76, 77]) and fill factor (FF) (linked to resistance within the device [76, 78]). The addition of P3HT:PCBM or fullerene-grafted polythiophene (poly[3-dodecylthiophene-co3-(6-fullerenylhexyl)thiophene], CoP(3DDT)-(C₆₀HT)) nanofibres

to a BHJ generated 33% and 60% relative improvements in power conversion efficiency (PCE) respectively. [61, 63] (Figure 1.8a and e)

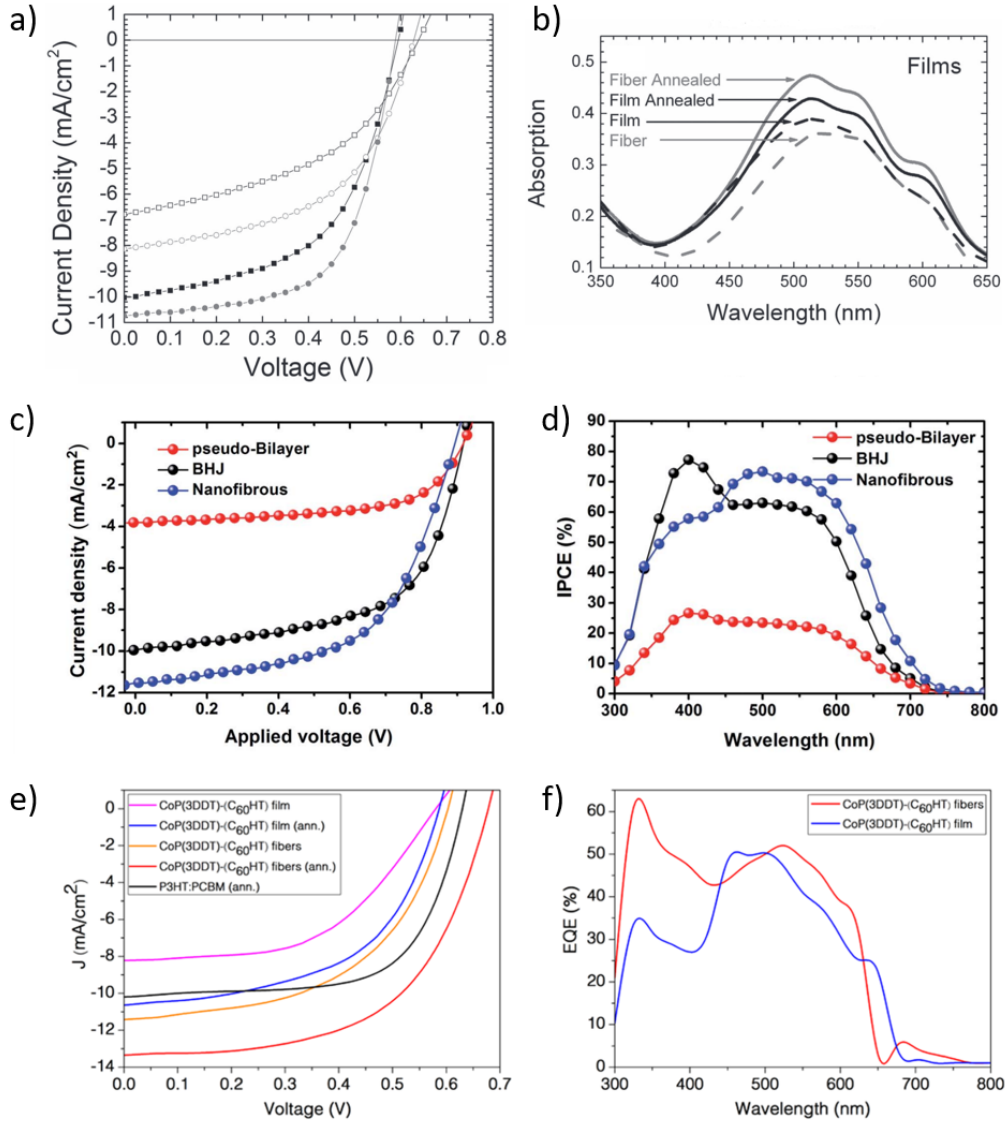


Figure 1.8: Fibre-containing BHJ or nanofibrous active layer device enhancements versus the BHJ. (a) Current density – voltage (J-V) curves for as-cast (unfilled) and annealed (filled) BHJs (squares) and P3HT:PCBM fibre-containing BHJ (circles) devices measured under AM1.5 conditions at 100 mW cm⁻². (b) Visible absorption spectra of BHJ and P3HT:PCBM fibre-containing BHJ. Reprinted with permission from reference [61]. 2012 WILEY-VCH Verlag GmbH Co. KGaA, Weinheim. (c) J-V characteristics and (d) IPCE spectra of devices prepared containing a PCDTBT:PC₇₀BM bilayer, BHJ and nanofibrous heterojunction. Reprinted with permission from reference [64]. Copyright 2014 The Royal Society of Chemistry. (e) J-V characteristics of BHJ films and fibre-containing CoP(3DDT)-(C₆₀HT) BHJ devices. (f) EQE spectra of the film and fibre-based CoP(3DDT)-(C₆₀HT):PCBM BHJ devices. Reprinted with permission from reference [63]. Copyright 2017 American Chemical Society.

In Figure 1.8c, analogous enhancements were shown with poly[N-9'-hepta-decanyl]-2,7-

carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3',- benzothiadiazole)] (PCDTBT) nanofibrous active layers, generating a 16% increase in J_{SC} , translating into a 7% relative PCE enhancement. [64] Greater fibre light-harvesting can also be observed within absorption spectra, (Figure 1.8b) and a greater conversion of light to collected charge carriers has been reported from Incident-Photon-to-Current Efficiency (IPCE) and External Quantum Efficiency (EQE) analysis (Figure 1.8d and f) A non-exhaustive selection of fibre-induced device enhancements are presented in Appendix Table A.1.1.

As electrospinning enhancements are achieved solely by a change in processing methodology, they offer a versatile approach, adaptable to a number of donor-acceptor systems. Often donor polymers are combined with a sacrificial auxiliary polymer ‘template’ to enable electrospinning. Therefore, other donor polymers can be spun using similar conditions resulting in the equivalent advantages without the need for the laborious synthesis of novel polymers.

1.6 Thesis Structure

To begin, Chapter 2 contains a full description of experimental and characterisation procedures, alongside details of data processing and analysis discussed within experimental chapters. The results are then presented and discussed in three experimental chapters (Chapters 3 - 5). Each experimental chapter commences with a further background review of the relevant literature and concepts, offering external context for benchmarking and context for how the project was planned. Finally, Chapter 6 summarises the major conclusions of this thesis and offers future research directions. Below, an abridgement of the experimental chapters is presented.

1.6.1 Experimental Chapter Summaries

Whilst device enhancements have been achieved upon nanofibre introduction, the ideal nanofibre for photovoltaic applications remains elusive. In Chapter 3, the importance of the donor fibre diameter presented in literature is reviewed, and a novel strategy for reducing the diameter of this class of electrospun fibres is presented, involving the addition of Ag/Au NPs in the presence of the auxiliary polymer, PEO. Effects

of nanoparticle addition upon the spinning solution and the as-spun fibres is investigated to isolate the contributing factors towards the time-dependent diameter reductions. The realisation of newly-achievable fibre diameters via a potentially universal method is a promising step towards marrying the optoelectronic benefits of nanofibres with the charge separation efficacy of the BHJ.

Chapter 4 opens by discussing the characterisation options used previously in literature to explore polymer alignment and structure, and offers rationale for the selection of techniques used within this work. Chapter 4 investigates how the electrospinning fabrication process imparts a unique internal nano-structure to the ultra-thin P3HT nanofibres. Using polarized light alongside X-ray and electron diffraction studies, the mechanism of how elongational effects align the amorphous and crystalline polymer on both bulk nanowebs and individual fibres is elucidated. The potential impact of the proposed nano-structure upon the fibres' photovoltaic performance is discussed versus thin-films and previously reported fibrous polymer.

Whilst the promise of previously reported fibre-based OPVs has been reviewed in Section 1.4, Chapter 5 provides background for the mixed reception of nanoparticle introduction to OPV active layers in literature. Within this chapter, photovoltaic promise of the nanoparticle-containing fibres is experimentally evaluated. Fibres spun from increasingly-aged solutions are found to offer greater light-harvesting properties owing to polymer alignment and plasmonic effects. Versus the BHJ, electrospun fibres deliver increased exciton generation. PL quenching and ultra-fast transient optical studies are conducted on nanofibrous active layers to investigate the dissociation of excitons into charge carriers. Nanoparticles generally introduce recombination mechanisms, however here, metal addition may provide longer polaron lifetimes without evidence of charge trapping. Finally, proof-of-principle devices are tested and it is discussed how the morphology of the PCBM infiltration layer currently limits charge extraction.

2

Materials and Methods

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2.1 Fabrication

In this section, the electrospinning of nanoparticle-containing P3HT fibres and their incorporation into novel plasmonic nanofibrous active layers, and finally OPVs, is described. The classical P3HT:PCBM system is well-studied, making it the logical choice to develop an adaptable fibre platform, whilst PEO produces competitively low fibre diameters. P3HT is also cheaper, chemically simpler, and more air-stable than its modern counterparts. [79] The rationale for the choice of nanoparticles is provided in Section 3.3.

2.1.1 Nanoparticle Synthesis

2.1.1.1 In Situ Synthesis of PEO-reduced AgNPs

PEO-reduced AgNPs were prepared by silver salt (AgNO_3) addition to dilute PEO solutions in chloroform or chloroform:N,N-dimethylformamide (DMF). The salt is subsequently reduced by PEO producing an orange-brown colour after >12 h. Analogous AgNPs have been reported to form within aqueous poly(ethylene glycol) (PEG) or PEO solutions. [80, 81, 82]

2.1.1.2 Synthesis of Oleylamine-Capped NPs

OA-capped AgNP synthesis was carried out by a modified ‘solvent-free’ protocol, based upon the approach developed by Hiramatsu and Osterloh. [83] AgNO_3 (100 mg, 0.6 mmol, Sigma Aldrich) was dissolved in a minimum of oleylamine (2 mL, 4.3 mmol, 70%, Sigma Aldrich) for 0.5 h in a sealed vial purged with N_2 .

Meanwhile, oleylamine (15 mL, 32 mmol) was heated to 175 °C in a round bottom flask attached to a Schlenk line. A freeze-thaw method was used to remove dissolved O_2 from the reagents. The silver solution was then rapidly injected into the heated oleylamine leading to an instantaneous colour change from light to dark yellow, and eventually to black. The reaction was maintained at 175 °C for 10 minutes, before cooling slowly to room temperature. Methanol (50 mL, Sigma Aldrich) was added to precipitate the product, and the nanoparticles were collected by centrifugation (4000 rpm, 20 minutes). The particles were washed three times with methanol before being redispersed in chloroform to produce a yellow-black dispersion of 10 mg mL^{-1} .

Analogously, OA-capped AuNPs could be prepared using tetrachloroauric acid (HAuCl_4 , Sigma Aldrich) (100 mg, 0.3 mmol) in place of AgNO_3 to produce a red-black dispersion.

2.1.2 Nanofibre Synthesis

2.1.2.1 Spinning Solution Preparation

All solvents used in fibre synthesis or active layer fabrication were degassed with N_2 on a Schlenk line using a freeze-thaw method prior to use.

To produce P3HT/PEO nanofibres, 900 kDa PEO (17.5 mg, Sigma Aldrich) and P3HT (7.5 - 12.5 mg, 49 kDa, RMI-001E, Rieke Metals) was added to chloroform (3.189

mL, 4.75 g) and dissolved at 40 °C for 1 h to produce a transparent orange solution. DMF (0.264 mL, 0.25 g, Sigma Aldrich) was then added drop-wise under vigorous stirring to prevent precipitation of the polymeric material, producing a 95: 5 w/w chloroform: DMF solvent mixture. The resultant solution was stirred for up to 96 h at 40 °C.

To prepare a nanoparticle-containing spinning solution, AgNO₃ (1.75 mg, 0.01 mmol) was dissolved into the DMF before addition. Alternatively, OA-capped Ag or AuNPs (1.75 mg) were added simultaneously to DMF. For PEO nanofibres, the solution was prepared without P3HT, and DMF addition could be increased up to 92: 8 w/w chloroform: DMF if desired.

2.1.2.2 Substrate Preparation

Nanofibres were directly electrospun onto aluminium foil, silicon wafer or indium tin oxide (ITO)-coated glass. Aluminium foil was cut into squares and used without further preparation. Silicon wafers (15 x 20 mm) and ITO-coated glass (15 x 20 mm, Ossila, ~ 100 nm ITO) were cleaned by sonication in a dilute detergent (Decon 90) solution, followed by sonication in deionised water, acetone, and isopropanol (IPA) for 15 minutes each, rinsing between each medium change. Substrates were dried under N₂ flow and finally ultraviolet (UV)-Ozone treated for 15 minutes. The prepared ITO possessed a sheet resistance of ~20 Ω square⁻¹.

2.1.2.3 Electrospinning

The spinning solution was drawn into a syringe and delivered at 1 mL min⁻¹ through a flat-tip stainless steel needle (27-gauge, Terumo) using a syringe pump. A collection substrate was placed on top of a grounded, stainless steel plate collector. 23 kV was then applied between the needle and collector at a separation distance of 20 cm. These conditions were determined using starting parameters used by Kim et al. [67] and altered to achieve the lowest fibre diameter whilst retaining uniformity (parameter optimisation is not presented in this thesis). Electrospinning was carried out under a N₂ atmosphere inside a glovebox at ambient temperature (20 – 22 °C). Fibres could also be produced in air given a low humidity of <20% relative humidity (RH). Above this, solvent evaporation slowed and the fibres appeared to be wet upon collection.

2.1.2.4 PEO Removal

After electrospinning P3HT/PEO nanofibres, PEO was selectively removed. To prevent delamination, the nanofibres were first ‘fixed’ to the substrate by heating the nanowebs above the glass transition temperature (T_g) of PEO, at 70 °C for 2 minutes. PEO was then dissolved in IPA (50 mL) at 70 °C by submerging the samples for 1 h. As a non-solvent for P3HT, upon removing the sample from the hot IPA, virgin P3HT nanofibres are yielded. Samples are finally dried under N_2 flow or vacuum.

2.1.3 Device Fabrication: ITO/AZO/active layer/ MoO_3 /Al

2.1.3.1 Electron Transport Layer

For the electron transport layer, an Al-doped ZnO dispersion in IPA (AZO, 1 - 2.5 wt%, Sigma Aldrich) was spin-coated onto a clean ITO-coated glass at 5000 rpm for 30 s and annealed at 120 °C for 5 minutes under N_2 (1 ppm O_2 and H_2O). Charge transport layer and electrode deposition was conducted by Alanood Aljaghwan at the University of Warwick.

2.1.3.2 Nanofibrous Active Layer

To produce the nanofibrous active layer, PCBM was dissolved in dichloromethane (DCM, Sigma Aldrich) at 14 mg mL^{-1} or semi-orthogonal solvent mixtures (50:50 v/v DCM:chloroform or DCM:chlorobenzene (Sigma Aldrich)) at 20 mg mL^{-1} for 1 h at room temperature. The acceptor solution was filtered to remove any undissolved material or aggregates.

The nanofibres were directly electrospun onto the AZO layer for 120 s and then washed in 70 °C acetonitrile for 0.5 h (IPA was avoided as it would dissolve the AZO layer). Using an Ossila spin-coater, 30 μL of the PCBM solution was dispensed onto the centre of the substrate at 200 rpm. This speed was maintained for 5 s to allow for spreading and infiltration of the solution before increasing to 1500 rpm (1500 $rpm\ s^{-1}$ acceleration) for 40 s. Alternatively, 20 μL of semi-orthogonal solution could be spin-coated on top by dynamically dispensing the solution at 1500 rpm, rotated for 40 s.

2.1.3.3 Bulk Heterojunction Active Layer

P3HT (20 mg) and PCBM (20 mg) was dissolved in chlorobenzene (1 mL, Sigma Aldrich) overnight at 40 °C before filtering through a 0.22 μm PTFE filter. 30 μL of the solution was dynamically spin-coated onto the ITO-coated glass (1500 rpm, 40 s) and annealed at 120 °C for 20 minutes.

2.1.3.4 Thermal Evaporation of the Hole Transport Layer and Electrical Contacts

Full-area deposition of the hole transport layer, MoO_3 (8 - 9 nm, 99.97%, Sigma Aldrich) on top of the active layers was conducted by thermal evaporation under vacuum (5×10^{-6} mbar) at a rate of 0.1 - 0.2 $\text{\AA s}^{-1}$ from a boron nitride crucible. 160 nm Al (99.999%, Kurt J. Lesker) electrodes were then evaporated from a tungsten boat through a shadow mask to form 6 device pixels. Initial deposition rate was limited to 0.3 $\text{\AA s}^{-1}$ for the first 10 nm to produce a conformal layer. Deposition was conducted using a glovebox-integrated CreaPhys Organic molecular evaporator fitted with a MBraun eVap bell-jar controlled via an Inficon SQM-160 monitoring unit. Thickness was monitored using a quartz-crystal microbalance (QCM) adjacent to the sample holder.

2.2 Characterisation

The general characterisation procedures described hereafter were selected for their suitability in the analysis of polymeric materials at the nanoscale. The preference for polarized UV-Vis, X-ray diffraction and 4D-STEM to determine polymer ordering/structure in Chapter 4 is considered in detail in Section 4.2. However, in short, they produce complementary measurements upon bulk nanowires and individual fibres, whilst avoiding the degradation of beam-sensitive materials. The techniques used to elucidate the photovoltaic potential of the materials in Chapter 5 were selected for their ability to handle diffuse light scattering. Additionally, photoluminescence and transient absorption was used to explore the potential of the novel active layer, without the bottleneck of charge extraction, given poor morphology of the current PCBM infiltration layer. Further details are supplied in the main text.

2.2.1 Microscopy

2.2.1.1 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) imaging was conducted using JOEL JSM-840F and Zeiss Merlin Field Emission Gun (FEG) SEMs using secondary electrons for surface topology information. 6 nm of Pt was sputter-coated (Cressington 208HRD) onto the specimens before imaging to prevent charging. SEM micrographs were taken at an accelerating voltage of 4 - 6 kV. A working distance of 14 and 8.5 mm were used for the 840F and Merlin instruments, respectively. Nanofibre widths, the fibre diameter in the plane of the substrate, were determined through at least 100 unbiased counts from the SEM micrographs using ImageJ software. The thickness of Pt coating was not removed from quoted diameters.

2.2.1.2 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) images were collected using a JOEL JEM-3000F with an accelerating voltage of 200 kV. Images were collected in both brightfield (BF) (direct beam minus the scattered intensity) and annular dark field (ADF) (the image formed from a region of scattering) modes. Nanoparticle d-spacings (distance measured across many peaks, divided by the number of spacings) was calibrated using carbon nanotubes of known carbon d-spacing.

Nanofibres were directly electrospun onto lacey carbon, 400-mesh TEM grids allowing the specimens to be imaged over the vacuum. Where required, PEO was removed by submerging the grid in 70 °C IPA. Nanoparticles were drop-cast onto the same grids from dilute dispersions in chloroform. All specimens were dried under vacuum prior to analysis. For infiltration studies, PCBM was spin-coated on top of the fibres deposited upon a continuous, carbon film TEM grid used for additional support. TEM imaging was conducted by George Tebbutt, Dr Barbara Maciejewska and Dr Dillon McGurty.

2.2.1.3 Energy-Dispersive X-ray Spectroscopy

Energy-Dispersive X-ray (EDX) analysis was conducted using an Oxford Xmax 150 EDX detector fitted to a Zeiss Merlin SEM (collected at 20 kV) at a working distance of 8.5 mm or Oxford Instruments EDS detector with a super atmospheric thin window

fitted to a JOEL JEM-3000F (collected at 200 kV). Line scans and mapping modes were collected using the software Aztec for ~ 20 minutes.

2.2.1.4 Scanning Transmission Electron Microscopy

Scanning Transmission Electron Microscopy (STEM), a TEM mode in which the beam is rastered over the specimen, was used on a JOEL JEM-3000F at 200 kV to acquire EDX data and imaging atomic mass contrast between metals and polymer. Additionally, a Zeiss a-STEM (STEM-in-SEM) detector was used at an accelerating voltage of 20 kV equipped to a Zeiss Merlin FEG SEM. This allowed for low magnification transmission images and location selection for EDX.

2.2.1.5 Atomic Force Microscopy

Atomic Force Microscopy (AFM) was used to determine the vertical diameter of the nanofibres, and evaluate fibre encapsulation and surface roughness upon PCBM infiltration. 5×5 or $10 \times 10 \mu\text{m}$ (512 lines) scans were carried out on an Agilent 5400 AFM in tapping mode with a speed of 0.5 lines s^{-1} .

Root Mean Square (RMS) roughness and the average waviness were determined using the software Gwyddion, with a threshold of 0.025 applied to a series of $5 \mu\text{m}$ line profiles with 5 pixel width.

2.2.1.6 Scanning Electron Nanobeam Diffraction

Scanning electron nanobeam diffraction or 4D-STEM was acquired using a JOEL ARM 300 CF fitted with ultra-high-resolution pole piece, cold field emission gun, and aberration correction at the probe-forming and image-forming optics, located at Diamond Light Source. The experiment was run at an accelerating voltage of 300 kV at a low electron dosage of $\leq 6 \text{ e}^- \text{ \AA}^{-2}$ to prevent damage of the beam-sensitive polymer. To limit total exposure to the beam-sensitive samples, fibres were chosen and imaged using a ‘blind selection’ approach.

The highly-focussed beam of high energy electrons ($\sim 0.8 \text{ mrad}$ convergence semi-angle) is scanned across the sample over the vacuum and a quad-chip Merlin Medipix direct electron detector (Quantum Detectors) was used to record a 2D image of the diffracted probe at each rastered position. The resultant datacube contains diffraction

images measuring 512 x 512 pixels at 256 x 256 probe positions (dwell time of 1 ms pixel⁻¹). The 4D-STEM datasets were collected by Dr David Hopkinson.

Fibre samples were prepared by directly electrospinning onto lacey carbon TEM grids and removing PEO by submerging the grid in 70 °C IPA.

Data was processed using py4DSTEM (0.14.8) [84, 85] and the workflow is discussed in Section 4.5.3. Python code was initially provided by Dr Mohsen Danaie and adapted for analysis of P3HT fibres.

2.2.2 Spectroscopy

2.2.2.1 UV-Visible-NIR Spectroscopy

Absorbance measurements of solutions or non-scattering dispersions were carried out in quartz cuvettes using a Varian Cary 5000 UV-Visible-NIR spectrophotometer between 300 – 800 nm wavelength, at a scan rate of 100 nm min⁻¹. Here, in transmission mode, absorbance is calculated by the decadic logarithm of the reciprocal of the transmittance. [86]

Nanofibre or thin-film samples produce non-negligible scattering therefore absorptance (A), the ratio of flux absorbed by a material, [87] was determined through combined total (specular + diffuse) transmittance (T) and reflectance (R) spectroscopy. These measurements were conducted using an Ocean Optics Flame Miniature Spectrometer, equipped with DH-2000-BAL UV-VIS-NIR light source and ISP-50-8-R-GT integrating sphere between 350 - 800 nm with an acquisition time of 30 s. A self-absorption correction was not conducted.

Absorptance was then calculated by the relation [88]:

$$A(\%) = 100 - T(\%) - R(\%) \quad (2.1)$$

Samples were deposited by electrospinning and/or spin-coating directly onto ITO-coated glass. Absorptance comparisons could be made by the analysis of thin-films and nanofibres of the same mass (0.20 ± 0.01 mg of P3HT), determined using a Mettler Toledo Excellence Plus Balance (Readability ± 0.01 mg).

2.2.2.2 Polarized Absorption Spectroscopy

Using Polarized Absorption Spectroscopy, it is possible to elucidate molecular orientation in anisotropic materials by comparing the relative intensities of electronic transitions as a function of the polarization angle. Absorption is dependent on the orientation between the molecule and electric field vector of radiation. [89] The absorption probability is proportional to the square of the cosine of the angle between the polarization of light and the transition dipole moment, and is maximised when polarized along the dipole moment. [90] As the $\pi - \pi^*$ transition dipole moment is known to be oriented along the P3HT backbone, molecular orientation may be determined. The degree of alignment is then given by the linear dichroism between the absorption of parallel and perpendicularly polarization light.

$$A(\%) = 100 - T(\%) - R(\%) \quad (2.2)$$

To investigate the dependence of absorption with different polarization, a visible light film polarizer (400 - 700 nm, Thorlabs) was placed between the light source and sample, at the entrance to the integrating sphere. The polarizer was orientated so that the light was linearly polarized along (parallel to, $\parallel$) and across (perpendicular to, $\perp$) the axis of aligned samples. Aligned nanowebbs were produced using a rotating drum collector with ITO-coated glass substrates fixed to its surface.

2.2.2.3 Transient Absorption Spectroscopy

Femtosecond - Transient Absorption Spectroscopy (fs-TAS) is an pump-probe technique used to track changes in a materials' optical properties over time. First, a population of molecules within a sample is excited by an intense excitation (pump) pulse. The absorption spectra of excited species may be then be investigated using a lesser power, probe pulse, incident on the sample after a short time decay. Negative changes in optical density (ΔOD) in the TAS spectra correspond to either ground state bleach (GSB) or stimulated emission (SE), while positive values arise from photo-induced absorption (PIA), Figure 2.1. By varying the temporal delay between the pump and probe pulse, researchers

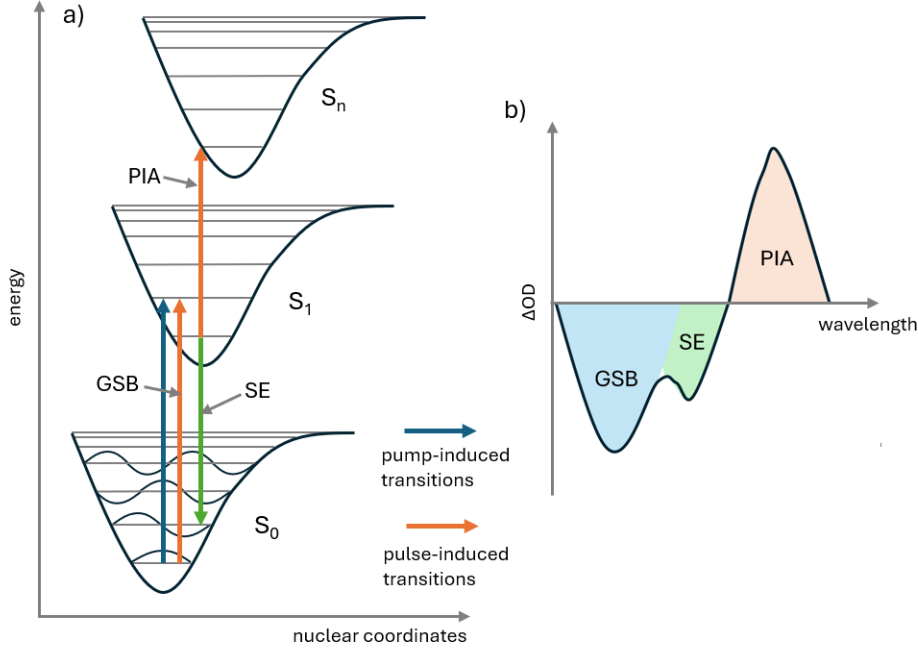


Figure 2.1: (a) Energy band diagram showing the photo-excitation induced by pump pulse (blue arrow), and the subsequent transitions induced by the probe pulse (orange arrows) resulting in ground state bleach (GSB) and photo-induced absorption (PIA) signals. Stimulated emission (SE), shown in green, originates from the relaxation of excitons following their formation by the pump pulse. (b) Schematic illustration of a typical TAS spectrum showing the change in optical density (ΔOD) caused by GSB, PIA, and SE signals. Adapted from Reference [91]

may produce snapshots to elucidate the lifetimes and populations of photoinduced species such as excitons, polaron pairs, and free polarons.

For fs-TAS studies, fibres and active layers were built upon z-cut quartz windows (13 mm circle, 2 mm thick). As fibres cannot be easily spun onto insulating substrates, a self-supporting fibre web was collected over a small gap for 120 s. Subsequently, the quartz was lifted through the web from beneath. PCBM backfill was then conducted via spin-coating of a 14 mg mL⁻¹ DCM solution. Once mounted, N₂ was continuously blown over the sample which was found to prevent photo-oxidation with no gradual bleach.

Femtosecond 12 W pulses (1 kHz, 40 fs, 800 nm) were generated by a Ti-sapphire regenerative amplified laser system (Spectra-Physics Dual Ascend Pumped Spitfire Ace) seeded by a Mai Tai (Spectra-Physics) and split to produce a 2.5 W and 1 W beam fraction. Details can be found in reference [92].

The 2.5 W fraction seeded an optical parametric amplifier (TOPAS-prime with UV extension, Light Conversion) and the excitation wavelength was tuned to 520 nm. This

pump pulse was focussed onto the sample with a beam diameter of 790 μm (as per its $1/e^2$ definition) and power of 180 μW , providing a fluence of 74 $\mu\text{J cm}^{-2}$. $\sim 5\%$ of the 1 W fraction was used to generate a white light continuum ($\sim 330 \text{ nm} - 1025 \text{ nm}$) when passed through a CaF_2 window. A filter was then used to subtract light between 740 - 850 nm to prevent overexposure of the detector by the 800 nm fundamental laser. The relative polarization between the pump and probe pulses was set to 54.7° to negate molecular reorientation effects.

Pump-probe delays between -0.5 ps and 3 ns were varied by moving a hollow gold retroreflector along a motorized delay stage (Newport M-IMS500CCHA). Changes to optical density (ΔOD , given by Equation 2.3) after photo-excitation were determined using a fibre-coupled spectrometer (Avantes, AvaSpec-ULS1650F) from dark backgrounds and unpumped spectra.

$$\Delta OD = OD_{(t)} - OD_{(t=0)} \quad (2.3)$$

The spectra were chirp corrected using the KOALA package (Appendix Figure A.2.1). Decays at select wavelengths were fitted using a tri-component exponential decay function with an additional term to describe the initial photo-excitation using OriginPro. Measurements were recorded at the Warwick Centre for Ultra-fast Spectroscopy (WCUS) alongside Dr Jack Woolley.

2.2.2.4 Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy measures light emission from a sample following excitation by a laser (Figure 1.4). This is measured under steady-state conditions when the sample has reached dynamic equilibrium with continuous illumination. Herein, emission is measured before and after the P3HT fibre mat is infiltrated by an electron acceptor. Quenching of radiative emission following infiltration is used to estimate the exciton population separated into charge carriers at the donor:acceptor interface.

A 450 nm diode laser (PicoHarp, LDH-D-C-405M) was used to photo-excite the samples on a continuous wave setting at 9900 mW cm^{-2} . The resultant PL was collected and coupled into a grating spectrometer (Princeton Instruments, SP2558) which directed

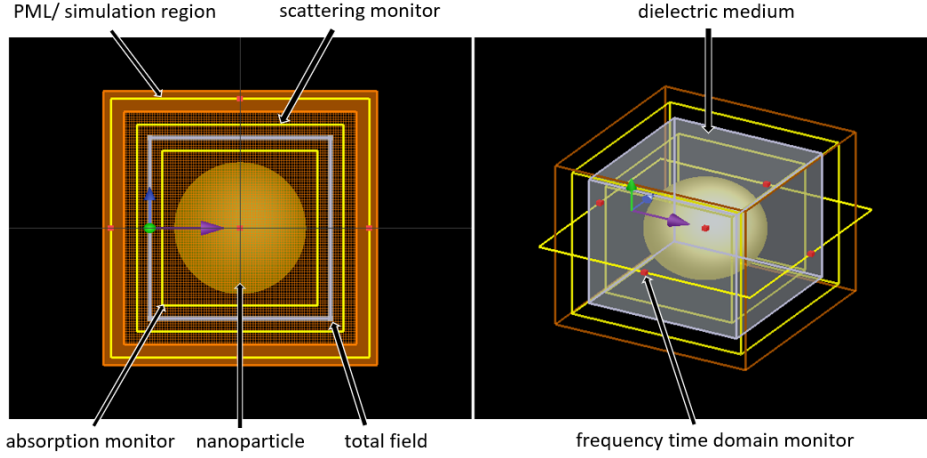


Figure 2.2: 2D and 3D projections of the FDTD simulation set-up showing the positioning of the particle, PML boundaries, total field (light injection region) and cross-section monitors.

the spectrally dispersed PL onto a silicon iCCD (intensified charge coupled device, PI-MAX4, Princeton Instruments). Samples were mounted in a vacuum cell at $\sim 10^{-2}$ mbar. PL measurements were conducted by Karim Elmostekawy.

2.2.2.5 Finite-Difference Time-Domain Simulations

Finite-Difference Time-Domain (FDTD) simulations were run using Lumerical FDTD (Ansys Ltd). Ag and Au NPs represented by ‘Johnston and Christy’ models were positioned within a isotropic, scalar dielectric medium with a refractive index of 1.44 (chloroform) or 1.95 (refractive index of P3HT near to absorption onset).

Simulations were run at 300 K with a 0.1 nm mesh step size until an energy cut-off was reached. The cubic simulation domain with 18 nm sides was enclosed by perfectly matched layer (PML) boundary conditions. A total field/scatter field domain with side length 16 nm was positioned inside and a 200 - 900 nm plane wave was injected along the x-axis, polarized along y.

Spatially resolved, near-field electric field intensity at key wavelengths was visualised using a 2D frequency domain monitor. To measure scattered light intensity, a cubic ‘cross section’ optical power monitor was placed between the PML boundary and total field as this region only contains light scattered from the particle. For absorption, the monitor was positioned within the total field. The scattering and absorption cross-sections were calculated using the software’s built-in computations.

2.2.2.6 Fourier-Transform Infrared Spectroscopy

Fourier-Transform Infrared (FT-IR) was conducted using a Varian Excalibur FTS 3500 FT-IR Spectrometer in Attenuated Total Reflectance (ATR) mode. Transmission spectra were recorded between 500 – 4000 cm^{-1} and averaged over 64 scans. Absorption found in all spectra at 2300 - 2400 cm^{-1} is ascribed to the asymmetric stretching of ambient CO_2 . [93]

2.2.3 Solution Properties

2.2.3.1 Solution Conductivity

Electrolytic conductivity of spinning solutions (primarily ionic) was determined using a temperature-compensated potentiometric method using an Oakton CON 550 Benchtop Conductivity Meter fitted with a $K = 0.1$ cell at ambient conditions (20 - 22 $^{\circ}\text{C}$).

2.2.3.2 Solution Viscosity

The viscosity of spinning solutions was evaluated using a Brookfield DV2T viscometer equipped with HA torque spring and CP4-41Z cone spindle. Flow curves were generated (viscosity vs shear rate) between 10 – 120 rpm (or 20 s^{-1} – 240 s^{-1}) or a single point reading was collected at 60 s^{-1} shear rate for comparison between solutions. Due to the ‘detection’ limit, PEO concentrations were increased to 1.5 wt% to ensure a spring torque of $>10\%$ was generated for accurate assessment. [94]

2.2.3.3 Tensiometry

The surface tension of spinning solutions was elucidated using the pendant drop technique employed using an Ossila Contact Angle Goniometer and a 21-gauge flat-tip needle. Due to the volatility of chloroform, the needle was lowered into a cuvette before the pendant droplets were formed to slow evaporation. The silhouette of the suspended droplet at equilibrium is used for drop shape analysis with a simplified D_s/D_e method originally proposed by Andreas. [95, 96] Surface tension is given by:

$$\gamma = (\Delta\rho g D_e^2)/H \quad (2.4)$$

The surface tension γ in N m^{-1} is determined through its relation to the density difference between the liquid and surrounding medium (air), $\Delta\rho$, acceleration due to

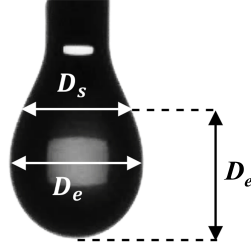


Figure 2.3: Optical image of a pendant drop of the PEO spinning solution with annotated definitions of D_e and D_s used for drop shape analysis.

gravity, g , the equatorial diameter of the droplet, D_e , and a correction factor, H , related to the dimensions of the drop. H is determined by:

$$H^{-1} = 0.345(D_s/D_e)^{-2.5} \quad (2.5)$$

where D_s is the diameter at a height of D_e from the bottom of the pendant drop. The correction factor was verified using solvents of known surface tension. The known outer diameter of the needle (0.413 mm) was used to calibrate the dimensions of the pendant drop in ImageJ software. The density of the spinning solution was taken to be equivalent to a 92:8 w/w chloroform:DMF solvent mixture.

2.2.4 Physical Analysis

2.2.4.1 Powder X-Ray Diffraction

Powder X-ray diffraction (pXRD) was conducted with a Bruker D8 Eco ADVANCE diffractometer in reflection mode with Ni-filtered Cu $K\alpha$ radiation. Scattering was recorded with a 1D detector in an out-of-plane (OOP) direction. Samples were deposited onto zero-background Si substrates with equal P3HT mass (~ 2 mg). P3HT d-spacing was determined from the XRD diffractograms by first removing the background and fitting peaks with a PearsonVII function. D-spacing was then calculated by the condition for constructive X-ray interference, as described by Bragg's Law [97]:

$$n\lambda = 2d\sin\theta \quad (2.6)$$

where n is an integer, λ is the X-ray wavelength, θ is the incident angle and d is the crystal d-spacing.

Assuming that the source of peak broadening is due to the crystallite size rather than defects, the average crystallite size can be estimated using the Scherrer equation [98].

$$D = k\lambda/\beta\cos(\theta) \quad (2.7)$$

where D is the average crystallite size in the scattering direction, k relates to the shape factor (taken to be 0.9) and β is the full width at half maximum (FWHM) in radians.

pXRD samples were submitted to Oxford Materials Characterisation Service for data collection.

2.2.4.2 Grazing Incidence 2D X-ray Diffraction

Grazing incidence X-ray diffraction (GI-XRD) was measured using a Rigaku SmartLab X-ray diffractometer equipped with a PhotonMax 9 kW rotating anode source using Cu K α radiation and a HyPix-3000 2D semiconductor detector at a sample-to-detector distance of 150 mm. Incident end optics included a parallel beam slit, 5 mm spot size height-limiting slit and 1.0° in-plane (IP) parallel slit collimator.

OOP diffraction was measured in 0.04° steps between 0 and 30° 2θ at a rate of $\sim 5^\circ 2\theta \text{ min}^{-1}$ at an asymmetric grazing incidence of 0.2° θ . The 2D detector was offset by $+12^\circ 2\theta_\chi$ to capture IP diffraction between $-2^\circ \sim +26^\circ 2\theta_\chi$.

Alternatively, the detector was used in 1D mode to measure the evolution of (100) scattering as the sample is rotated about 180° ϕ . Here, the size limiting slit was increased to 15 mm to allow the full sample to be illuminated throughout the ϕ rotation.

GI-XRD was used to determine preferential crystallite orientation within thin-films and electrospun nanofibres. To do so, fibre-to-fibre aligned nanowebs were analysed when the fibre axes were oriented parallel and perpendicular to the incident X-ray beam. Background subtraction and determination of the degree of fibre/crystallite alignment by Hermans' orientation factor is described in Section 4.5.2. For this, IP, OOP and azimuthal profiles were extracted as presented in Figure 4.21c. I am grateful to Dr Gyula Zilahi for assistance setting up the 2D GI-XRD optics.

2.2.4.3 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) is first employed to determine the proportion of PEO (and P3HT) within electrospun nanofibres before and after washing in 70 °C IPA, and later, to determine an estimate for nanoparticle retention upon washing.

To determine PEO content, nanofibre mats (~ 1 mg) were dynamically heated using a Perkin Elmer Pyris TGA 8000 from ambient conditions to 900 °C at 10 °C min⁻¹ under a N₂ flow of 20 mL min⁻¹. Alternatively, the nanofibres could be held at an isotherm of 370 °C for 1 h after heating from ambient temperature at 10 °C min⁻¹.

To assess nanoparticle retention, the nanofibre mats were heated under air flow of 40 mL min⁻¹ to 900 °C at 10 °C min⁻¹. The residual mass at 900 °C of washed samples with and without nanoparticle addition were compared to determine the remaining silver content.

2.2.4.4 Brunauer-Emmett-Teller Analysis

Brunauer-Emmett-Teller (BET) analysis was used to probe the influence of fibre diameter reductions upon the specific surface area of nanowebs using a Micromeritics Gemini VII BET surface area analyser and N₂ absorptive. 100 mg samples were degassed under vacuum for >10 h prior to analysis. Samples were submitted to Oxford Materials Characterisation Service for analysis.

2.2.5 Device Characterisation

2.2.5.1 Current Density-Voltage Characteristics

J-V characteristics of proof-of-principle OPVs were recorded by placing devices beneath an ABET technologies Sun 2000 Solar Simulator inside a glovebox, used to deliver AM 1.5G solar illumination at 100 mW cm⁻². A voltage sweep of -0.2 V to +1 V was performed by a Keithley 2400 Sourcemeter, and current was measured using LabView software. Measurements were taken through a pixel mask with an area of 0.012 cm². These measurements were assisted by Alanood Aljaghvani.

Under dark current conditions, ideal PVs present diodic behaviour. However under illumination, superposition of the dark current with the photoinduced current is measured, allowing measurement of power and PCE.

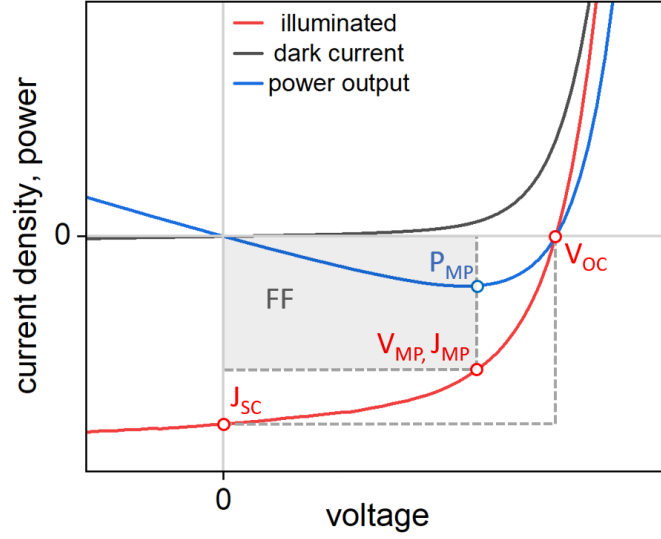


Figure 2.4: Annotated J-V plot of a typical solar cell displaying the key parameters used in determining photovoltaic performance.

Key parameters such as the open-circuit voltage (V_{OC}) may be found at the intercept between the curve and the voltage axis, and the short-circuit current density (J_{SC}) at the current-intercept. The maximum power point (P_{MP}) can be found at the ‘knee’ of the J-V curve and provides the conditions under which the cell delivers optimal power output. The Fill Factor (FF) is a measure of ‘squareness’ to the J-V curve and is given by:

$$FF = \frac{P_{MP}}{J_{SC}V_{OC}} \quad (2.8)$$

Ultimately, PCE is calculated by:

$$PCE = \frac{J_{SC}V_{OC}FF}{P_{in}} \quad (2.9)$$

where P_{in} is the illumination input power.

2.2.5.2 External Quantum Efficiency

External Quantum Efficiency (EQE) is a measure of the ratio of photons incident upon the device to collected charge carriers extracted into the external circuit. EQE measurements were performed upon the champion devices using a Bentham Instruments PVE 300 instrument between 300 - 900 nm. A sample is illuminated with a particular wavelength

using a monochromator, and the generated photocurrent is measured for each wavelength. EQE analysis was conducted by Alanood Aljaghwan.

3

Driving Diameters of Electrospun P3HT Nanofibres to the Limit

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3.1 Highlights

Whilst nanofibre introduction has demonstrated enhanced device efficiency in several systems, the ideal nanofibre for photovoltaic applications has not been achieved. Due to their low entanglement in solution, it is intrinsically difficult to electrospin conjugated polymers. When they have been electrospun, the resultant nanofibres are generally several

times larger than the typical active layer, and in cases where they are sufficiently small, they are larger than exciton diffusion lengths. A comprehensive list of fibre diameters and spinning conditions can be found in Appendix Table A.1.1.

This chapter discusses a novel and unrivalled approach to producing thinner electrospun P3HT nanofibres through nanoparticle introduction. These nanoparticles manipulate the spinning solution properties, resulting in a dynamic diameter reduction as the solution ages. To elucidate the mechanism for this diameter reduction, the influence of nanoparticle addition upon the spinning solution, the electrospinning process, and resultant fibres is studied with PEO, the auxiliary polymer used to enable P3HT electrospinning.

Through nanoparticle-induced viscosity reductions, all three types of tested nanoparticle were able to deliver similar and significant reductions in the diameters of PEO and P3HT/PEO nanofibres, lowering spinnable diameters by 40% and 30%, respectively. Electrical conductivity is identified as a secondary influence although possibly necessary to retain a uniform morphology at the reduced viscosity levels. After removal of the insulating polymer, this approach produces the lowest-dimension of P3HT nanofibres obtained by electrospinning to date at just 55 nm (diameter normal to the substrate).

3.2 Background

3.2.1 Importance of Photoactive Fibre Diameter

Polymer entanglement is a prerequisite to effective electrospinning, required to provide sufficient viscosity to resist the elongational forces acting upon the electrospinning jet to yield uniform nanofibre morphologies (of homogeneous diameter without beading). [99] However, due to the rigid-rod configuration of conjugated polymers in solution, and hence low viscosities (< 7 mPa.s [100, 101, 102]), with ideal values on the order of 1 - 20 Pa.s, [103] electrospinning fibres of this polymer class is inherently difficult.

Even still, the production of uniform photoactive fibres was achieved by Lee et al. using high concentration P3HT solutions dissolved in chloroform. [104] Although fibres could be obtained from 11 - 20 wt% solutions, the high evaporation rate of the volatile solvent meant that the needle became blocked within seconds and the fibre morphology was inconsistent, as in Figure 3.1a. To alleviate this issue, a sheath of pure chloroform

could be fed through the outer needle of a coaxial spinning setup to encompass the polymeric solution supplied through the inner needle. This prevented the phase separation of P3HT at the end of the nozzle, enabling continuous production of P3HT fibres as in Figure 3.1b. Chan and co-workers demonstrated that by dissolving 10 - 12 wt% P3HT in hot chloroform and then cooling the solution, crystallites formed and subsequently cross-linked/gelled, providing the entanglement necessary for spinning. The resultant fibres spun from the pure P3HT solution were on the order of 1 μm . [105]

However, the diameter of these fibres is ill-suited for incorporation into PVs. In fact, many reports of photoactive nanofibres are several times larger than the typical active layer thickness, and too large for effective exciton dissociation. [63, 66, 104, 105, 106, 107, 108] As the fibre diameters increase, a larger proportion of excitons are produced further than one exciton diffusion length from the surface of the fibre, and are therefore quenched, reducing device efficiency. A simplistic model, ignoring inter-diffusion upon the backfill of the PCBM acceptor, would suggest that the fibres should not exceed twice the exciton diffusion length (~ 20 nm), ensuring all excitons are formed within one diffusion length of the donor-acceptor interface. Therefore, whilst nanofibre introduction has already demonstrated numerous advantages over thin-films, including device efficiency, a universal strategy for producing and controlling ideal nanofibres for PV applications remains unrealised.

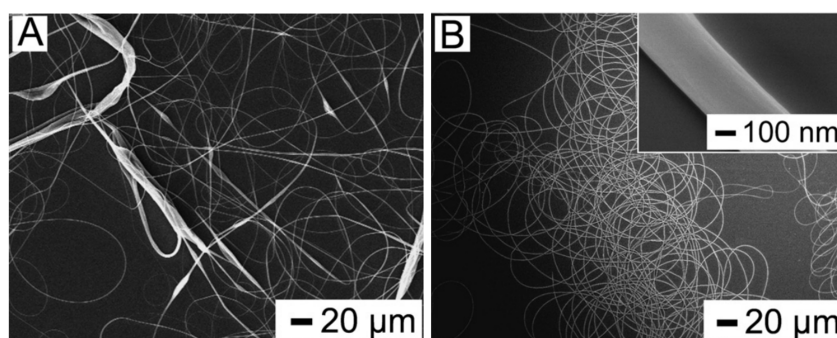


Figure 3.1: SEM micrographs of (a) discontinuous fibres prepared by mono-axial electrospinning of P3HT in a chloroform solution, and (b) continuous fibre production once additional solvent is fed through the outer nozzle of a co-axial spinneret. Reprinted with permission from reference [104]. Copyright 2009 The Royal Society of Chemistry.

The more commonplace approach to spinning conjugated polymers is to combine the

conjugated polymer with a more easily electrospinnable polymer, such as high molecular weight poly(vinyl pyrrolidone) (PVP), [109, 110] poly(ϵ -caprolactone) (PCL) [61, 104], poly(methyl methacrylate) (PMMA), poly (vinyl acetate) (PVAc) [111] or poly(ethylene oxide) (PEO) [63, 64, 65, 67, 112, 113, 114, 115]. This may be either blended into the conjugated polymer solution and spun monoaxially, or, used as a sheathing solution to template the electrospinning of the low viscosity core solution.

The spinning solution will generally contain a high ratio of auxiliary to conjugated polymer and the resultant fibres are comprised of 40 - 90 wt% of the insulating polymer. These polymers adopt random-coil configurations when dissolved in solution, leading to greater degrees of entanglement than generated with conjugated polymers. Hence, viscous solutions can be obtained even with low polymer concentrations, enabling production of thinner fibres. [116] The auxiliary polymer may also partially disrupt the rigid-rod conformation of the conductive polymer, inducing additional entanglement. Therefore, conjugated/insulating polymer co-electrospinning presents a facile approach to enabling the continuous formation of photoactive polymer nanofibres, and by optimising the polymer ratio and overall polymer concentration, one can begin to control the diameter. In the literature, the auxiliary polymer approach has produced fibres up to 7 μm wide, however the lowest reported P3HT fibre diameter achieved (spun from a chloroform-based solution) was obtained using a 50:50 wt% P3HT to PCL ratio, yielding fibres of 250 - 350 nm. [104]

It is important to note that the auxiliary polymer must then be removed by selective dissolution in an orthogonal solvent to regain the charge transport properties of the final material. This is due to the polymer's insulating properties, having a HOMO-LUMO gap of > 3.0 eV. [116] This can be an energy-intensive and lengthy post-processing treatment which can cause damage, degrading the fibre structure. In cases where the removal is incomplete, fibre conductivity may be attenuated, far lower than that of the pure semiconductor. However, the use of auxiliary polymers presented a step-change which allowed for a multitude of studies into conjugated polymer electrospinning and the realisation of P3HT nanofibres with diameters lower than OPV active layers, enabling their introduction into photovoltaic devices.

Later, addition of a polar co-solvent would represent the next leap forward in advancing the suitability of photoactive nanofibres for OPV applications. Due to the essentially non-conductive nature of conjugated/auxiliary polymer solutions, and the low dielectric constant of the chloroform solvent, the electric-field generates relatively weak elongational forces upon the charged electrospinning jet, resulting in inadequate stretching. Through the addition of a polar co-solvent, Kim et al. were able to produce the lowest reported diameter of P3HT nanofibres, at 80 nm. [65, 67] A 13.3 wt% addition of DMF and acetic acid (2:1 mol/mol or 9.4:3.9 w/w) induced a seven-fold increase in the electrical conductivity of P3HT/PEO spinning solutions to $0.33 \mu\text{S cm}^{-1}$, increasing the elongational forces upon the fibre as it travels to the collector. DMF was selected for its high dielectric constant of 36.7 and conductivity of $3.43 \mu\text{S cm}^{-1}$, (chloroform: 4.8 and $0 \mu\text{S cm}^{-1}$ respectively) whilst acetic acid provided additional viscosity. [67, 117] Beyond the electrolytic conductivity of the solvent, the polar solvent promotes greater dissociation of ions through favourable solvent-ion interactions. [23] In the absence of co-solvent, Kim et al. collected fibres of 700 nm before bead formation occurred below a critical threshold. However, through the incorporation of a maximum-allowable DMF:acetic acid addition, uniform fibres were synthesised down to 110 nm diameters, reducing to 80 nm after PEO removal, the lowest reported diameter of P3HT fibres by any prior approach, imaged in Figure 3.2a-b. [67] Further co-solvent addition was limited due to insolubility of the polymeric material in the non-solvents, meaning fibres became increasingly beaded beyond this addition point. Repeatability of this study has been an issue, with lesser diameter reductions being achieved by other groups and within my own reproducibility study discussed in section 3.4.1. Other reports using PEO and up to 15 wt% DMF:acetic acid have yielded minimum P3HT fibre diameters of 315 and 200 nm. [66, 113] It has also been shown to be less effective with P3HT:PCBM and CoP(3DDT)-(C₆₀HT) nanofibres, producing diameters of 150 and > 730 nm respectively. [62, 63]

However, using this mechanism to a greater level of success, Kim et al. would later produce uniform PCDTBT nanofibres of 20 nm (Figure 3.2c - d) by the optimisation of spinning solution conductivity, representing the first instance where electrospun fibres

of photoactive polymers possess a diameter comparable to twice the exciton diffusion length of the material. [65]

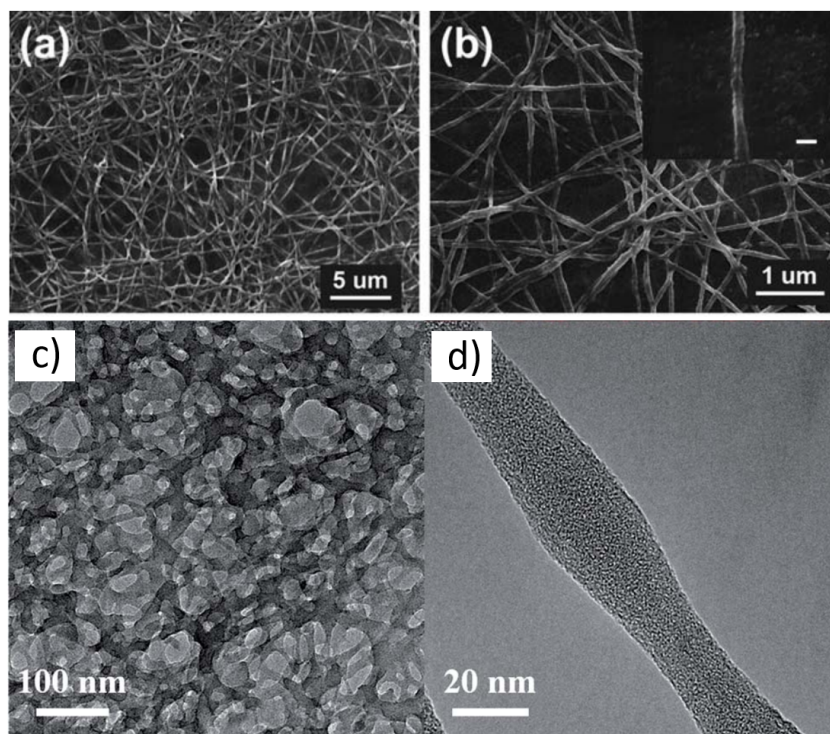


Figure 3.2: SEM micrographs of thin P3HT nanofibres achieved by electrospinning in conjunction with PEO and polar co-solvent addition under (a) low magnification and (b) high magnification. Reprinted with permission from reference [67]. Copyright 2011 The Royal Society of Chemistry. TEM micrographs of PCDTBT nanofibres with a diameter comparable to twice the exciton diffusion length, achieved by co-solvent addition, under (c) low and (d) high magnification. Reprinted with permission from reference [64]. Copyright 2014 The Royal Society of Chemistry.

Additional considerations should be made when designing the ideal electrospun nanofibre for photovoltaic applications, such as inter-diffusion upon acceptor infiltration, the morphology, and polymer orientation within the fibre; the picture is more complex than the exciton diffusion length alone. Kim et al. determined that the fibre diameter was strongly influenced by the ambient humidity. [65] Higher humidity reduces the solvent evaporation rate, which in turn reduces the fibre diameter by providing more time for stretching in flight. However, concurrently, beads were periodically formed along the fibre length, due to instability caused by low evaporation rates. At 20 %RH, the nanofibres were uniformly 81 nm in diameter which was reduced to 38 nm when spun at 50 %RH, but possessed 250 nm beads along its length. Large, bulk-like beads

contribute high exciton recombination rates [65] and can cause shorting issues, being of similar size to the active layer.

80 nm P3HT nanofibres synthesised were surprisingly capable of exciton dissociation with nearly 100% photoluminescence (PL) quenching upon infiltration of the nanoweb with PCBM, despite the carrier pathways being 4x longer than the exciton diffusion length. [67] This phenomenon is explained by the formation of a pseudo-BHJ interphase from diffusion of the P3HT fibre and backfilled PCBM into the opposing domains. [118, 119]. Most works using orthogonal solvents such as dichloromethane (DCM) to deposit PCBM onto P3HT films to create bilayers, report this mixed interphase [120, 121] which is heavily influenced by thermal annealing. [122] One report quantified this interphase region to be around 40 nm thick, [121] meaning that nanofibres up to 100 nm in diameter (interphase + twice the diffusion length) may be sufficiently thin to allow for complete exciton dissociation.

Whilst the width of the intermixed region may be different in electrospun polymer, the ideal fibre diameter for PV applications may not require a radius comparable to the exciton diffusion length. Furthermore, there is research to suggest that electrospun and self-assembled fibrous P3HT possess longer exciton diffusion lengths than their BHJ equivalent. [123, 124, 125]

Additionally, Yoon et al. demonstrated that the polymer orientation found within larger diameter fibres may provide an advantage of their own. [66] This research found favourable performance for devices based upon 650 nm over 315 nm nanofibres, although perhaps neither diameter allows for effective charge separation. [67] This improvement was ascribed to a change in the major crystallite conformation of P3HT in contact with the PCBM following diffusion into the fibres. In thinner 315 nm fibres, the air-interface led to an edge-on conformation throughout. However, in the thicker fibre, a face-on orientation existed at the core. After diffusion, PCBM could interact with the face-on orientation deemed to provide an increase in V_{OC} . These findings suggest a compromise for the ideal diameter of photoactive nanofibres - a balance between favourable orientation and shorter exciton diffusion pathways. In any case, a reproducible and universal strategy to producing fibres with reduced diameters is vital to promoting efficient charge separation whilst

understanding and controlling the nanostructure to harness the ultimate photoelectric potential of electrospun active layers.

Interestingly, diameter reduction mechanisms have been demonstrated within AgNP-containing PEO fibres, where nanoparticle addition provided increased solution conductivity. [80] Here, 0.3 wt% AgNO₃ addition, which is subsequently reduced in situ by PEO chains to produce nanoparticles, (hereafter referred to as PEO-reduced AgNPs), increased the electrical conductivity of a 4 wt% 600 kDa PEO aqueous solution by 26x, from 91 to 2365 $\mu\text{S cm}^{-1}$. This produced a reduction in fibre diameters from 313 nm to 197 nm, akin to effects observed with inorganic salt addition, even following the reduction of the ions to metallic silver. Meanwhile, the fibre morphology improved ‘tremendously’, allowing easy electrospinning of previously unspinnable PEO concentrations.

Noble metal nanoparticles themselves present an alternative approach to increasing the light harvesting capability of a given volume/mass of photoactive material. Enhancements generally arise from two major mechanisms. The first mode, light scattering, involves incumbent light taking a longer pathlength through the active layer following a scattering event at a particle, thereby increasing the probability of absorption. [126, 127] The second, the Local Surface Plasmon Resonance (LSPR) effect, manifests due to enhancement of the electric field strength next to the nanoparticle due to the collective oscillation of the electron cloud in response to impinging light. [128, 129, 130] This allows the absorption cross-section of the photoactive material within the immediate vicinity to increase. [131] In some reports, they are also able to contribute towards charge transport, [132] exciton dissociation, [133] and stability [134]. Due to exponential decay of the enhanced field within tens of nanometres from the particle, nanoparticles would ideally be situated in the active layer, in intimate contact with the polymer. This would be the case if nanoparticles were added to electrospun P3HT fibres. This encapsulation may provide optimal LSPR enhancement given that metal-associated charge trapping and recombination mechanisms can be avoided (a major focus of Chapter 6). [134] Within optimised devices, Ag and AuNPs have enabled efficiency improvements, generally owing to increased J_{sc} and FF. [135]

3.3 Selection and Synthesis of Nanoparticles

Within this chapter, three different nanoparticle types were incorporated into electrospun nanofibres: PEO-reduced AgNPs, OA-capped AgNPs and OA-capped AuNPs. Nanoparticles were selected based upon criteria, aimed at producing thinner, more functional nanofibres for PV applications.

Selection Criteria

- i. The nanoparticle synthesis should be straight-forward, cheap and reproducible.
- ii. The particles should be sufficiently small so as to be entirely encapsulated within the electrospun fibres. If too large, they may cause an increase in viscosity as theorised by Einstein. [136, 137]
- iii. The nanoparticles should be easily dispersed and possess long term stability within chloroform-based spinning solutions, and tolerate additions of DMF.
- iv. Selected nanoparticles should enhance light-harvesting by the photoactive polymer. Unlike the co-solvent approach, the nanoparticles remain inside the electrospun nanofibres after solvent evaporation, meaning it is important that they provide functionality. Due to the small size imposed by prerequisite (ii), the particles should possess a strong plasmonic resonance to harness the LSPR effect rather than light scattering as a particles' scattering cross-section reduces with diameter. [131, 138]

3.3.1 In Situ Reduction of AgNO_3 by PEO

PEO-reduced AgNPs are produced simply through the addition of AgNO_3 to the spinning solution which is reduced to AgNPs by PEO chains (experimental details in Section 2.1.1.1). It is proposed that the silver ions are first chelated by the polymer chain into a pseudo-crown ether prior to reduction, assumed to be through interaction with the electronegative ether oxygen atoms in the backbone. [139] The reduction of the now bound silver ion proceeds by oxidation of the PEO backbone by the metal. [140] DMF, the solvent used to solubilise the silver salt into solution, also contributes towards the formation of the AgNPs. [141, 142]

Previous reports show that these particles satisfy selection criterion (ii) when formed in aqueous solutions, measuring a few nanometres in diameter. [80, 81] Indeed, in Figure 3.3 a - b, TEM analysis (described in Section 2.2.1.2) reveals that the approximately spherical particles possess diameters of 3.7 ± 1.4 nm when produced within chloroform, determined from 100 unbiased counts measured using ImageJ - a likely suitable size for incorporation into nanofibres. Due to the lack/weak binding of a capping agent, the nanoparticles could not be isolated from the spinning solution without significant aggregation. TEM imaging was therefore conducted within the PEO matrix, masking the diffraction and preventing high-resolution imaging.

To ensure particle stability, absorption spectrophotometry was employed to track the absorbance of the nanoparticle-containing spinning solution over time. The evolution of the plasmonic response is determined by a number of competing variables, such as the formation of, changing nature of, and subsequent stability of PEO-reduced AgNPs. The surface plasmon resonance (SPR) peak of the PEO-reduced AgNPs dispersed within the chloroform-based PEO solution (refractive index of ~ 1.45 [143, 144]) appears at 420 – 450 nm determined by UV-Visible spectroscopy (described in Section 2.2.2.1, presented in Figure 3.3c). FDTD simulations (described in Section 2.2.2.5) suggest that a 3 nm Ag sphere dispersed within chloroform will possess SPR at ~ 405 nm, which suggests that the PEO-reduced AgNPs are not perfectly spherical, which has a marked effect on the energy of the electron oscillations. [131] However, this SPR energy is not atypical of small AgNPs produced by PEO [80], DMF [145] or enzymes [146].

The intensity and position of the nanoparticle's resonance is determined by, but not limited to, its composition, size, shape, and aspect ratio. [147] It is also dependent upon the refractive index of the surrounding medium, proximity to other nanostructures, and presence of aggregates. [148, 149] However, the greatest effect on intensity is the loading of the dispersed nanoparticles, meaning concentration may also be estimated from the intensity of the plasmonic absorption. The reduction of AgNO_3 to nanoparticles increases the intensity, while aggregation and precipitation of the AgNPs will act to decrease the intensity, all else considered equal. In Figure 3.3d, the plasmonic intensity develops rapidly over the first 24 h following salt addition, indicating AgNP formation.

At this point, the absorbance is 0.82 wrt the maximum absorbance (1.0) reached after 96 h. The plateauing intensity beyond 24 h is an indication of the depletion of silver ions and slowing nanoparticle generation rate. By 168 h, the plasmonic intensity reduces to 0.91. This intensity reduction beyond 96 h could be due to a size increase from Ostwald ripening or aggregation out-competing new particle formation towards the end of the reaction. The observation is a manifestation of a number of responses to complex changes and is therefore difficult to deconvolute.

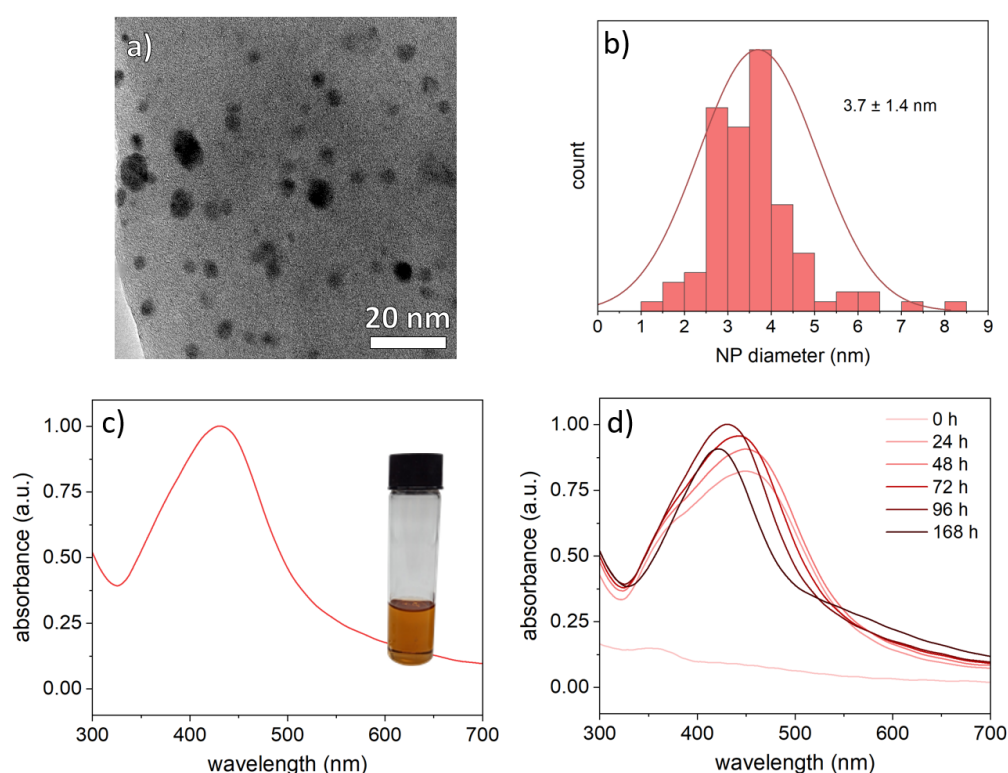


Figure 3.3: (a) TEM micrograph of the PEO-reduced AgNPs dispersed within a PEO matrix (collected by Dr Barbara Maciejewska) and (b) histogram of the diameter distribution, revealing a number-average diameter of 3.7 ± 1.4 nm. (c) UV-Visible absorbance spectra of PEO-reduced AgNPs dispersed in chloroform. (Inset: Digital photograph of PEO-reduced AgNPs dispersed in a PEO spinning solution.) (d) Absorbance spectra of the PEO-reduced AgNP-containing PEO spinning solution over time, showing NP formation and long-term stability.

Typically, an increase in particle size results in a red-shifted, broader and less intense plasmonic resonance for the same volume of material. However, a concomitant blue-shift is seen in the peak position from 449 nm at 24 h to 421 nm at 168 h, suggesting the particles do not increase in size. Instead, it is proposed that blue-shift can be explained by the particles becoming more spherical, or by a decreasing concentration of Ag^+ ions

adsorbed at the nanoparticle surface. This in turn, increases the electron density of the nanoparticles, resulting in the apparent blue-shift. [150]

As PEO-reduced AgNP-containing spinning solutions still possess a strong plasmonic intensity when stored for several months, the stability of the dispersion is considered high, and the reduction in plasmonic intensity between 96 and 168 h is not due to significant aggregation, satisfying criterion (iii).

Importantly, PEO-reduced AgNPs have previously demonstrated the ability to reduce the diameter of fibres electrospun from an aqueous PEO solution by 30%. [80] The simultaneous improvement in fibre morphology is also advantageous to producing ultra-thin fibres at the cusp of the beading onset.

3.3.2 Thermal Reduction of Inorganic Precursors by Oleylamine

3.3.2.1 Oleylamine-Capped Silver Nanoparticles

Almost monodisperse AgNPs were obtained by the reduction of Ag^+ ions by the weak reducing agent, oleylamine (experimental details in Section 2.1.1.2). The synthesis used within this work was adapted from the protocol outlined by Hiramatsu and Osterloh [83] by removing the additional solvent, using AgNO_3 and oleylamine as the only reagents. With this approach, oleylamine acts as the sole solvent, reducing agent and stabilising surfactant, [151] previously reported for the synthesis of Fe_2O_4 and CoFeO_4 nanoparticles. [152, 153] The greater concentration of reducing agent means the reaction time decreases to just 10 minutes rather than several hours quoted in literature. After precipitation in methanol, the nanoparticles are isolated and redispersed easily in chloroform.

The proposed mechanism, reproduced in Figure 3.4, involves the coordination of the nitrogen lone pair (or π -system of the imine in secondary reactions) to the Ag^+ ion. An electron is then transferred to the Ag^+ forming an amino radical, and subsequently the creation of an imine (or nitrile). Eventually, the oleylamine (or oleyl-imine/nitrile) caps the forming AgNPs, stabilising the dispersion. [154]

The primary reason for the selection of these nanoparticles was their simple and rapid synthesis (criterion (i)), and that OA-capped AgNPs have previously been shown to deliver

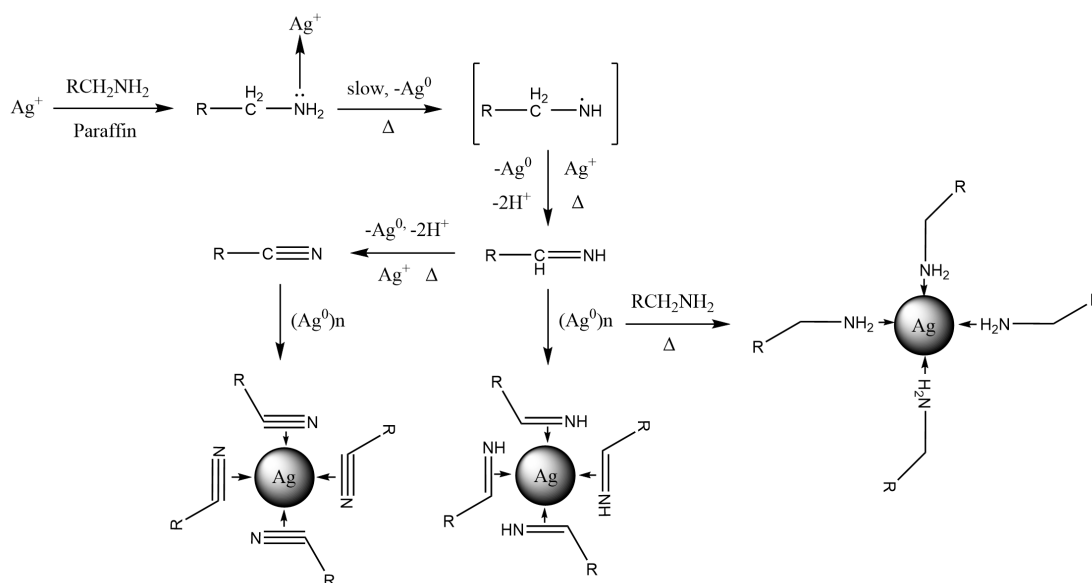


Figure 3.4: Schematic illustration of the mechanism of silver nitrate reduction by oleylamine to form OA-capped AgNPs. Adapted from reference [81].

greater light-harvesting and exciton generation upon incorporation into P3HT:PCBM active layers, ascribed to both LSPR and scattering effects. [155]

In Figure 3.5a - c, TEM analysis reveals a narrow size dispersion of the metal cores, measuring 9.6 ± 2.8 nm in diameter - later shown to be a suitable size for encapsulation. Analysis of the interplanar distances imaged by TEM confirm that the nanoparticles contain a highly crystalline lattice with the (110), (111), and (211) d-spacings identified at 0.278, 0.246, and 0.173 nm, respectively, as in Figure 3.5d - i. These correlate well with theoretical spacings of 0.289, 0.236 and 0.167 nm, respectively, obtained using a lattice constant of 0.409 nm (JCPDS card no.04-0783).

The oleylamine ligand allows for dispersion of the AgNPs within organic solvents, including chloroform, due to the non-polar alkyl chain of the surfactant. The UV-Visible absorbance spectra of the OA-capped AgNPs in Figure 3.6 presents a plasmonic peak centred at 409 nm, which correlates well with the LSPR position predicted by FDTD simulation. Although easily dispersed within the spinning solution, a steady reduction in the plasmonic intensity over time is observed in Figure 3.6b. By 96 h, the intensity drops to 0.82 of the maximum intensity delivered immediately upon OA-capped AgNP addition, at 0 h. As these particles are synthesised prior to spinning solution preparation, this intensity

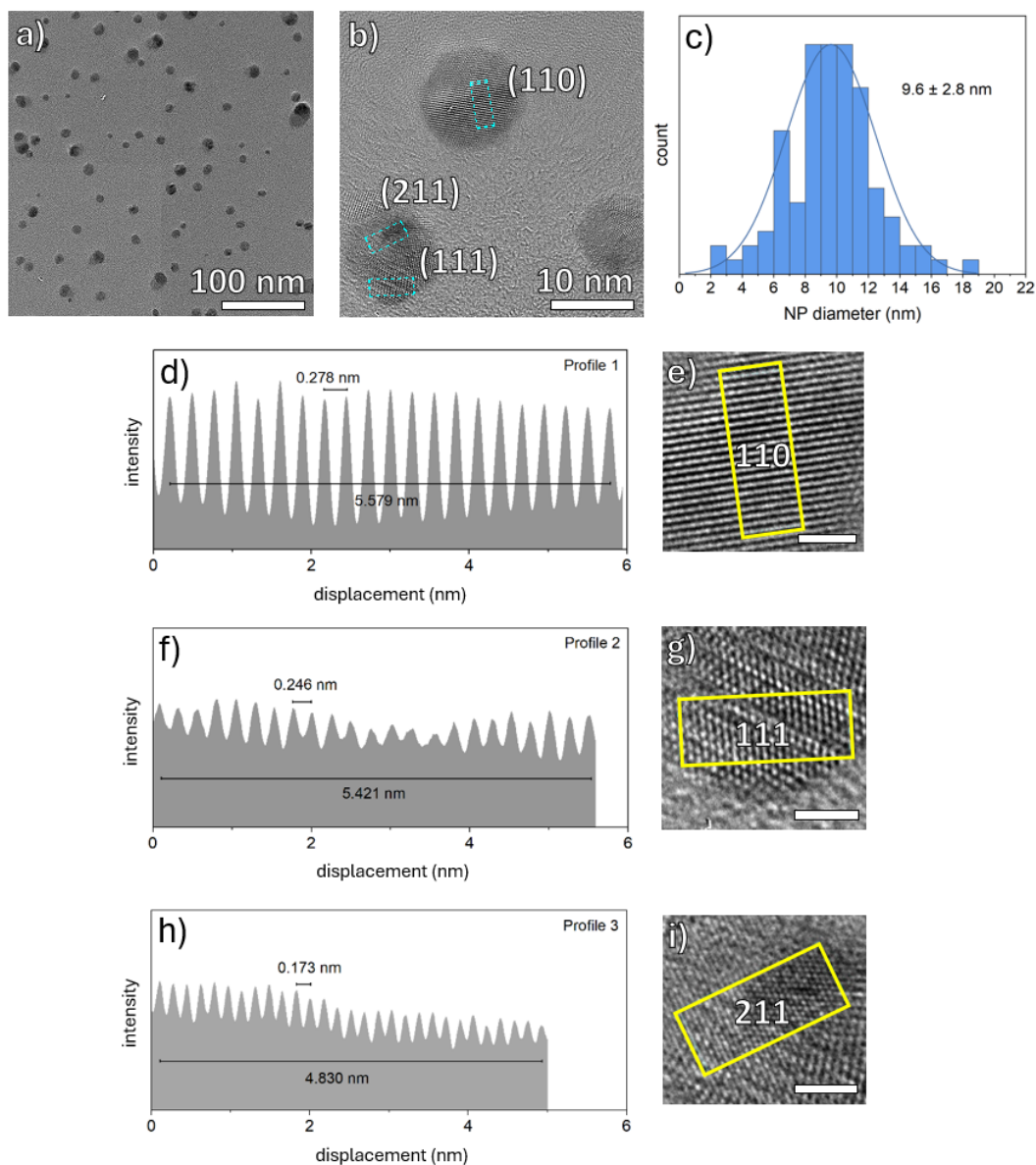


Figure 3.5: (a) Low and (b) high magnification TEM micrographs of OA-capped AgNPs (collected by Dr Dillon McGurty) and the (c) distribution of NP diameters from 100 counts extracted from these images. (d - i) d-spacings of the (d, e) 110, (f, g) 111 and (h, i) 211 lattice planes extracted from the profiles shown in (c). (d, f, h) Brightfield intensity and (e, g, i) close-up micrograph of the respective profiles and assigned miller indices (Scale Bar: 2 nm)

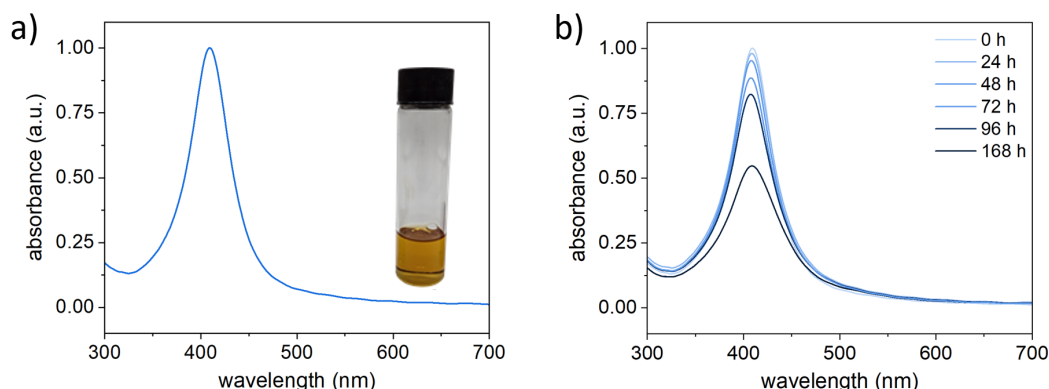


Figure 3.6: (a) UV-Visible absorbance spectrum and digital photograph (inset) of OA-capped AgNPs dispersed within chloroform, presenting a strong plasmonic response centred at 409 nm, and (b) the evolution of the plasmonic response of the OA-capped AgNP-containing PEO spinning solution, indicating gradual aggregation over time.

reduction is attributed to the formation of larger precipitates. By 168 h, the intensity decreased significantly to just 0.55 of its initial level. After several months of storage, the spinning solutions are colourless, indicating complete aggregation and precipitation. Overall, OA-capped AgNPs possess temporary stability in the spinning solution, which was considered acceptable for incorporation into fibres electrospun within 96 h of addition.

3.3.2.2 Oleylamine-Capped Gold Nanoparticles

OA-capped AuNPs were synthesised using the equivalent approach with chloroauric acid (HAuCl_4) in place of AgNO_3 . TEM analysis reveals that the nanoparticles are 9.9 ± 2.4 nm in diameter and apparently spherical in shape (Figure 3.7a-b, and g).

The composition was confirmed by the crystallinity displayed in the AuNP's TEM micrograph. Here, in Figure 3.7c-f, one observes the (110) and (111) Miller indices with spacings of 0.278 and 0.242 nm, respectively. Theoretically, these interplanar distances are 0.288 and 0.236 nm (lattice parameter of 0.408 nm, JCPDS card no. 04-0784). Higher order planes were observed in the electron diffraction pattern (Figure 3.7h and Table 3.1), successfully confirming the synthesis of AuNPs.

The OA-capped AuNPs possess impressive stability in both chloroform and the spinning solution. Figure 3.8 presents an intense plasmonic response to incident light centred at 523 nm. Upon addition of the AuNPs to the PEO spinning solution, the plasmonic intensity increased over the first 24 h as residual agglomerates are separated

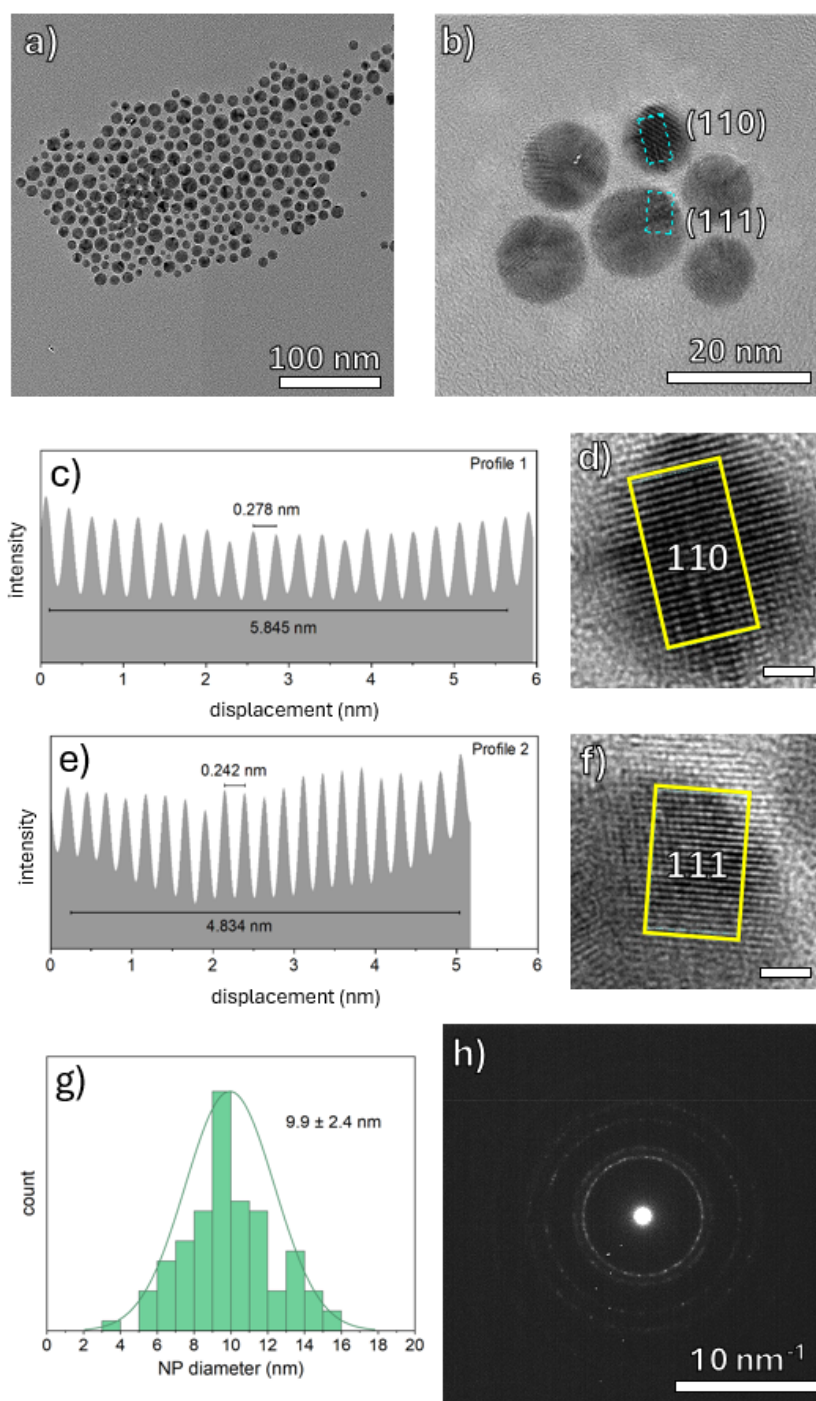


Figure 3.7: (a) Low and (b) high magnification TEM micrographs of OA-capped AuNPs collected by Dr Dillon McGurty. (c, d) 110 and (e, f) 111 d-spacings extracted from (b). (c, e) Brightfield (BF) image brightness/intensity profiles and (d, f) close-up micrographs of the respective profiles (scale bar: 2 nm). (g) Distribution of OA-capped AuNP diameters from 100 counts extracted from TEM micrographs. (h) Electron diffraction pattern produced by several OA-capped AuNPs.

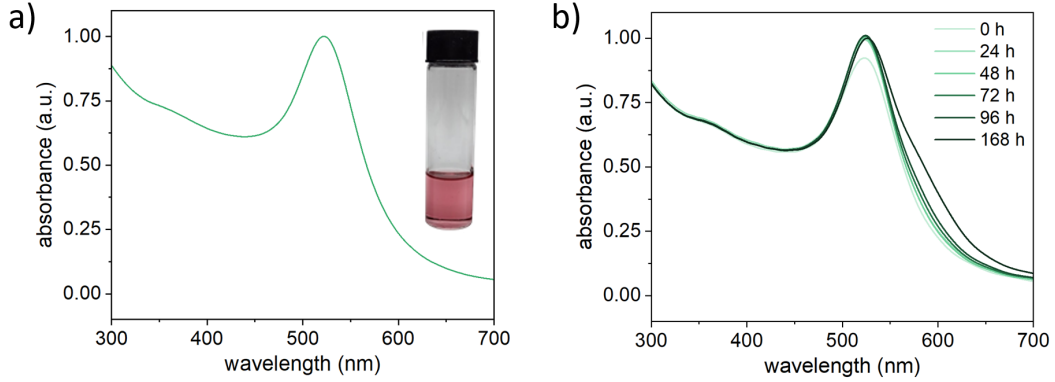


Figure 3.8: (a) Absorption spectrum and digital photograph (inset) of OA-capped AuNPs dispersed within chloroform presenting a strong plasmonic response centred at 523 nm, and (b) the evolution of the plasmonic response of the OA-capped AgNP-containing PEO spinning solution, indicating impressive long-term stability.

into primary particles. Over the following 168 h, the OA-capped AuNPs were impressively stable, retaining a plasmonic intensity of 0.99 of the maximum level.

Ring	Diameter (nm^{-1})	D-spacing (nm)	(hkl)	Theoretical D-spacing (nm)
1	8.583	0.233	111	0.236
2	9.973	0.201	200	0.204
3	14.179	0.141	220	0.144
4	16.770	0.119	311	0.123
5	22.15	0.090	331	0.094

Table 3.1: Lattice d-spacing and assigned Miller indices extracted from the electron diffraction pattern obtained from OA-capped AuNPs in Figure 3.7h.

3.3.3 Metallic Content of Nanoparticles

Throughout this thesis, nanoparticle addition rates are quoted in wt % wrt the PEO concentration in the spinning solution. This value refers to the total mass of AgNO_3 added in the case of PEO-reduced AgNPs, or to the mass of OA-capped NPs including the capping layer. Therefore, the metal addition varies by nanoparticle type.

TGA analysis in Figure 3.9 confirms that AgNO_3 possesses a residual silver content of 63.2 % (expected value of 63.9 %). Therefore, a 10 wt% (wrt PEO) addition of AgNO_3 corresponds to a ~ 6.32 wt% (wrt PEO) addition of PEO-reduced Ag. As oleylamine completely degrades by 900 °C under nitrogen (0.1 % mass residual), the metallic content of the OA-capped NPs can also be evaluated from the residual mass. Therefore, TGA suggests

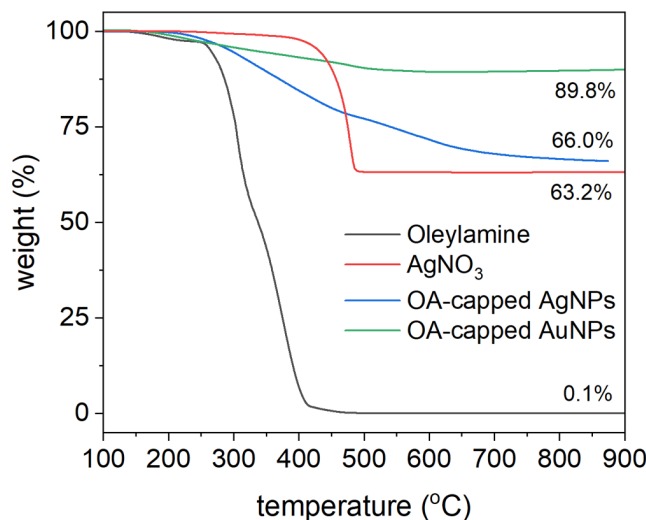


Figure 3.9: TGA analysis of OA-capped NPs and AgNO₃ used to evaluate the metallic content of nanoparticle addition.

the silver and gold content of the OA-capped NPs to be 66.0% and 89.8%, respectively. This difference is logical as the OA-capped NPs are of similar diameter, and the density of gold is nearly twice that of silver. Binding of the oleylamine ligands to the metal core in Figure 3.10 delays its degradation until higher temperatures, see Figure 3.10c-d.

3.4 Synthesis of PEO Nanofibres by Electrospinning

3.4.1 Inconsistencies in the Co-solvent Approach

Achieving low diameters of organic semiconductor nanofibres is integral in allowing effective dissociation of excitons produced within the fibres. In greater diameter fibres, an increasing proportion of absorption events forming an exciton occur further than one exciton diffusion length from the surface, or heterojunction upon acceptor infiltration, leading to recombination.

As described in Section 3.2, the previous state-of-the-art approach to producing thin fibres of this polymer class involves the addition of DMF and acetic acid co-solvent to the chloroform-based spinning solution. Without co-solvent, the lowest spinnable concentration of 900 kDa PEO is 0.50 wt%, needed to retain a uniform morphology without beading. Within this work, SEM studies in conjunction with statistical analyses (procedure described in Section 2.2.1.1) reveals that this concentration produces ~350

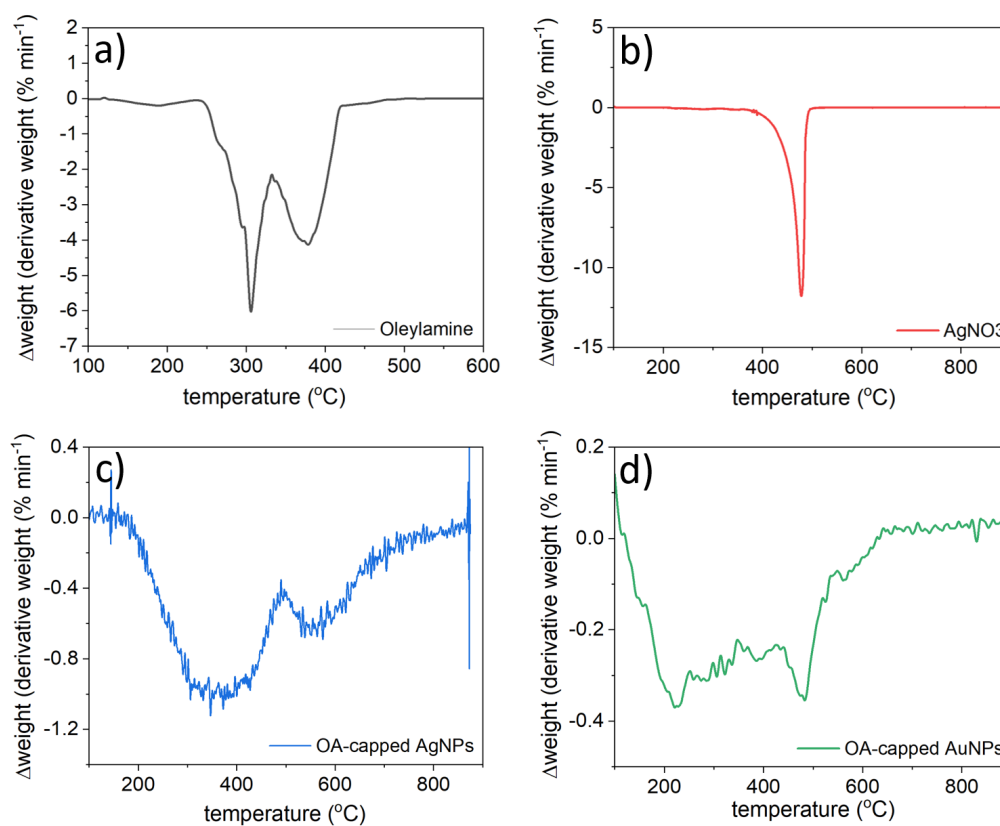


Figure 3.10: First derivative of the TGA traces of (a) oleylamine, (b) AgNO₃, (c) OA-capped AgNPs and (d) OA-capped AuNPs showing the rate of weight loss. (see also Table A.3.1.)

nm fibres, 30% thinner than the 500 nm diameter quoted by Kim et al. [67] When the PEO concentration is reduced to 0.35 wt% or 0.25 wt% PEO, heavy beading can be easily observed on the fibres. (Figure 3.11 and 3.12) The reduced entanglement at these concentrations cannot resist the surface tension which favours the adoption of a ‘bead-on-a-string’ fibre to minimise free surface energy. [99]

Upon the addition of 13.3 wt% DMF:acetic acid co-solvent, Kim et al. reported the spinnable concentration of PEO was reduced to 0.35 wt% before beading was observed, yielding 100 nm PEO fibres. The lower concentration, and therefore viscosity, generates less resistance to stretching, [156] leading to a finer fibre, whilst the higher dielectric constant and conductivity of the solution helps retain a uniform morphology. [157, 158]

During replication studies with PEO, an analogous reduction in the spinnable PEO concentration to 0.35 wt% is reported. In Figure 3.13, co-solvent addition sets up a narrow ‘electrospinnable’ window for the 0.35 wt% PEO solution between 4 and 8 wt%

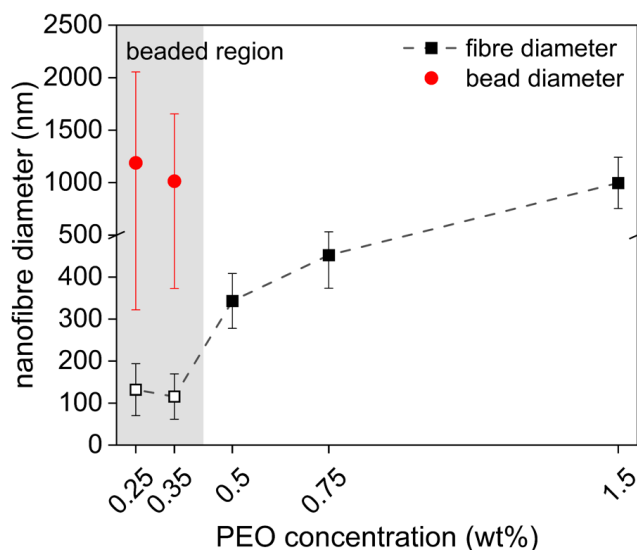


Figure 3.11: The diameters of beads and linear fibre sections of the PEO nanofibres spun from dilute spinning solutions. In the absence of a polar co-solvent, the lowest spinnable polymer concentration yielding uniform fibres is 0.50 wt%, producing mats of 350 nm fibres.

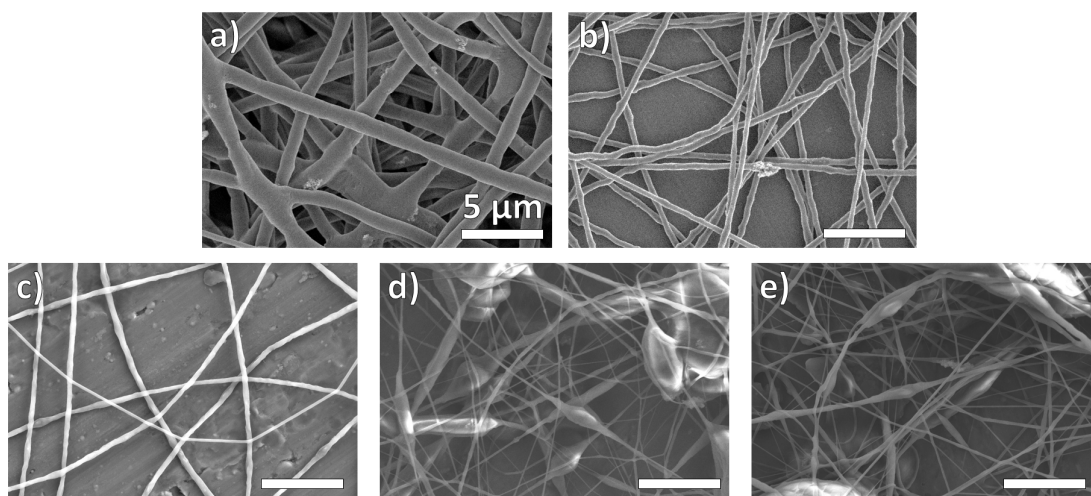


Figure 3.12: SEM micrographs of PEO nanofibres collected from the electrospinning of a (a) 1.5 wt%, (b) 0.75 wt%, (c) 0.50 wt%, (d) 0.35 wt% and (e) 0.25 wt% 900 kDa PEO spinning solution in chloroform.

DMF addition. Without DMF addition, conductivity of the solution is too low to inhibit beading, leading to micron size beads connected by thin linear sections. At 2 wt% DMF addition, the bead diameters have halved in size to 500 nm while concurrently the linear sections became thicker, until the two values converge at 4 wt% DMF, producing 150 nm homogeneous fibres without beads.

However, the diameter reduction with co-solvent addition within the 4 - 8 wt% DMF

processing window was not clear cut. The lowest diameter of PEO fibres were spun from a 92:8 w/w chloroform:DMF solvent mixture, measuring 141 ± 35 nm. Essentially, co-solvent addition to PEO fibres delivers a diameter reduction only by enabling the electrospinning of more dilute polymer solutions, rather than presenting a steady diameter reduction with respect to the addition concentration.

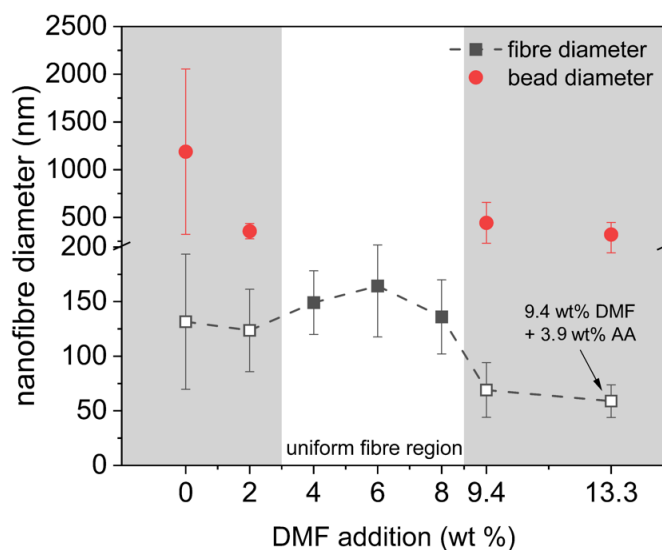


Figure 3.13: The narrow electrospinning window of 0.35 wt% 900 kDa PEO in chloroform determined by DMF addition. Within this processing window, uniform fibres were collected but a progressive diameter reduction was not observed.

Additionally, the beading onset was found to occur at DMF additions of > 8 wt%, lower than previous reports. Beyond this point, additions of 9.4 wt% DMF and 3.9 wt% acetic acid produced detrimental effects upon the fibre structure with heavy beading reoccurring. In short, the lowest attainable diameter of uniform PEO nanofibres electrospun in the absence of nanoparticles within this work was ~ 140 nm, due to the greater limitation of co-solvent addition. This prevented replication of the 100 nm fibres produced by Kim et al. utilising 13.3 wt% co-solvent. [67] This may be due to differences in the starting material and solvents, but also discrepancies in the electrospinning set-up, in particular the uniformity of the electric field.

After verification of the co-solvent approach, despite achieving lesser diameter reductions, the strategy was applied to P3HT fibres. The well-studied polythiophene, P3HT, has been thoroughly documented, and the P3HT:PCBM BHJ architecture is well-understood, making it the logical choice to use as a platform to develop an approach

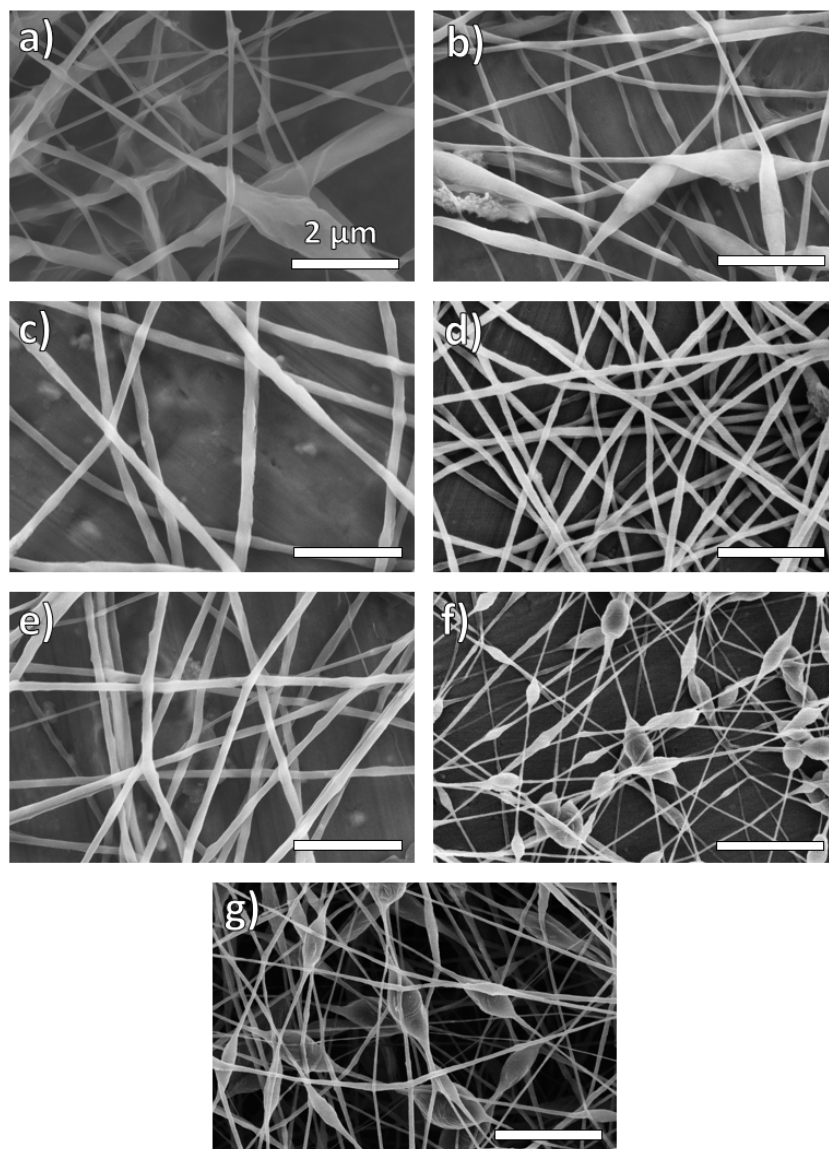


Figure 3.14: SEM micrographs of PEO nanofibres electrospun from 0.35 wt% 900 kDa PEO spinning solutions dissolved in chloroform:DMF with a ratio of (a) 100:0, (b) 98:2, (c) 96:4, (d) 94:6, (e) 92:8, (f) 90.6:9.4 w/w and (g) 86.7:9.4:3.9 w/w/w chloroform:DMF:acetic acid, revealing the spinnable window and earlier beading onset beyond 8 wt% DMF addition, meaning 100 nm PEO fibres could not be obtained.

to reducing electrospun fibre diameters, or more largely, to develop alternative device architectures such as the nanofibrous heterojunction.

Upon the addition of 0.25 wt% P3HT to the spinning solution, there is an increase in viscosity allowing uniform fibres to be electrospun from solutions containing 0.35 wt% PEO without the need for DMF. DMF additions between 0 and 5 wt% in Figure 3.15 and 3.16 were observed to induce incremental reductions in P3HT/PEO fibre diameter

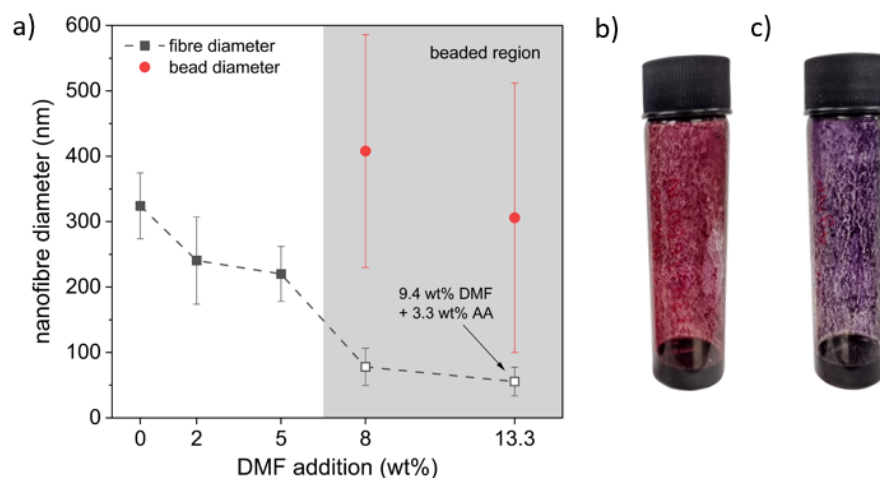


Figure 3.15: (a) Diameter reductions of P3HT/PEO nanofibres electrospun from solutions containing increasing proportions of DMF. Above 5 wt% DMF, beading prevented further diameter reductions, limiting P3HT/PEO fibre diameters to 220 - 230 nm without nanoparticle introduction. Digital photographs of P3HT/PEO spinning solutions containing 8 wt% DMF addition, (b) without and (c) with PEO-reduced AgNPs. The photographs were captured immediately after vials were upturned to show the precipitation of P3HT.

from 325 nm to 220 nm, a 33% decrease.

DMF additions above 5 wt% had adverse effects at both the macro and nano scale. Firstly, it induced significant P3HT precipitation from the spinning solution, captured in Figure 3.15b-c, meaning the electrospun P3HT/PEO nanofibres contained an unknown polymer ratio. Secondly, at the nanoscale, DMF additions above this level or any addition of acetic acid induced significant beading (Figure 3.15a and 3.16d-e). These beads present shorting risks being several times larger than typical active layers (100 – 200 nm). [36, 65] Ultimately, the 5 wt% limitation meant that the thinnest achievable P3HT/PEO fibre without nanoparticles was 230 ± 42 nm in diameter, whereas Kim et al. obtained fibres of 110 nm – a more significant difference than observed with the PEO system. [67]

Both this work and Kim and coworker's research used P3HT sourced from Rieke Metals, therefore the difference in tolerance to the anti-solvent was surprising, limiting co-solvent addition to 38% of the reported value. [67] The 5 wt% limit was demonstrated by both the 4002E and RMI-001E P3HT products sold by Rieke Metals, synthesised through oxidative addition and 'Rieke' chemistry, respectively - therefore, even with similarly sourced polymer, the polar co-solvent approach delivers significantly varying diameter

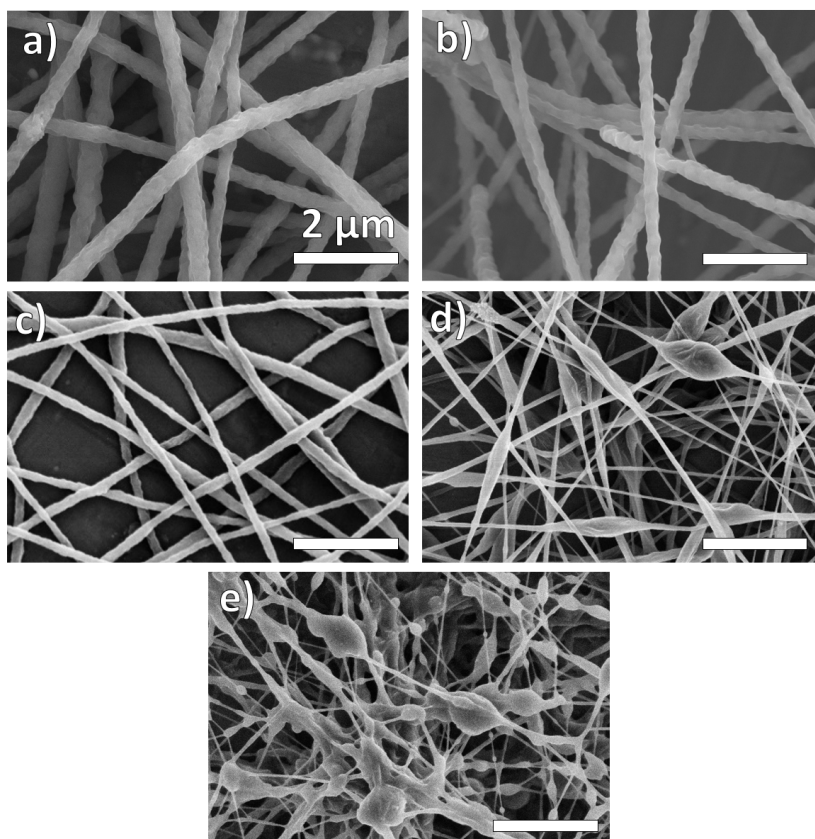


Figure 3.16: SEM micrographs of P3HT/PEO nanofibres electrospun from spinning solutions containing 0.35 wt% PEO and 0.25 wt% P3HT in (a) chloroform, (b) 98:2 w/w chloroform:DMF, (c) 95:5 w/w chloroform:DMF, (d) 92:8 w/w chloroform:DMF and (e) 86.7:9.4:3.9 w/w/w chloroform:DMF:acetic acid. Resultantly, DMF addition had to be further limited to 5 wt% upon P3HT addition.

reductions. However, this strategy does retain the benefit that the final nanofibres are pristine P3HT as the additive evaporates during electrospinning.

Therefore, although co-solvent introduction presents the most promising approach to electrospinning ultra-thin nanofibres of photoactive polymers to date, it provides an inconsistent degree of success and is fundamentally limited in its application to other polymer donors which may be further intolerant. To produce fibre diameters near the scale of exciton diffusion lengths, they must be highly tolerant of the anti-solvent addition.

Nagata et al. found P3HT to be the most tolerant of non-solvent addition (84:16 w/w chloroform:ethanol) out of a pool of tested polymers including poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV), poly[[4,8-bis[(2-ethylhexyl)oxy] benzo[1,2-b:4,5-b] dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl) carbonyl] thieno[3,4-b]thiophenediyl]] (PTB7), poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophene-2-yl)-benzo[1,2-

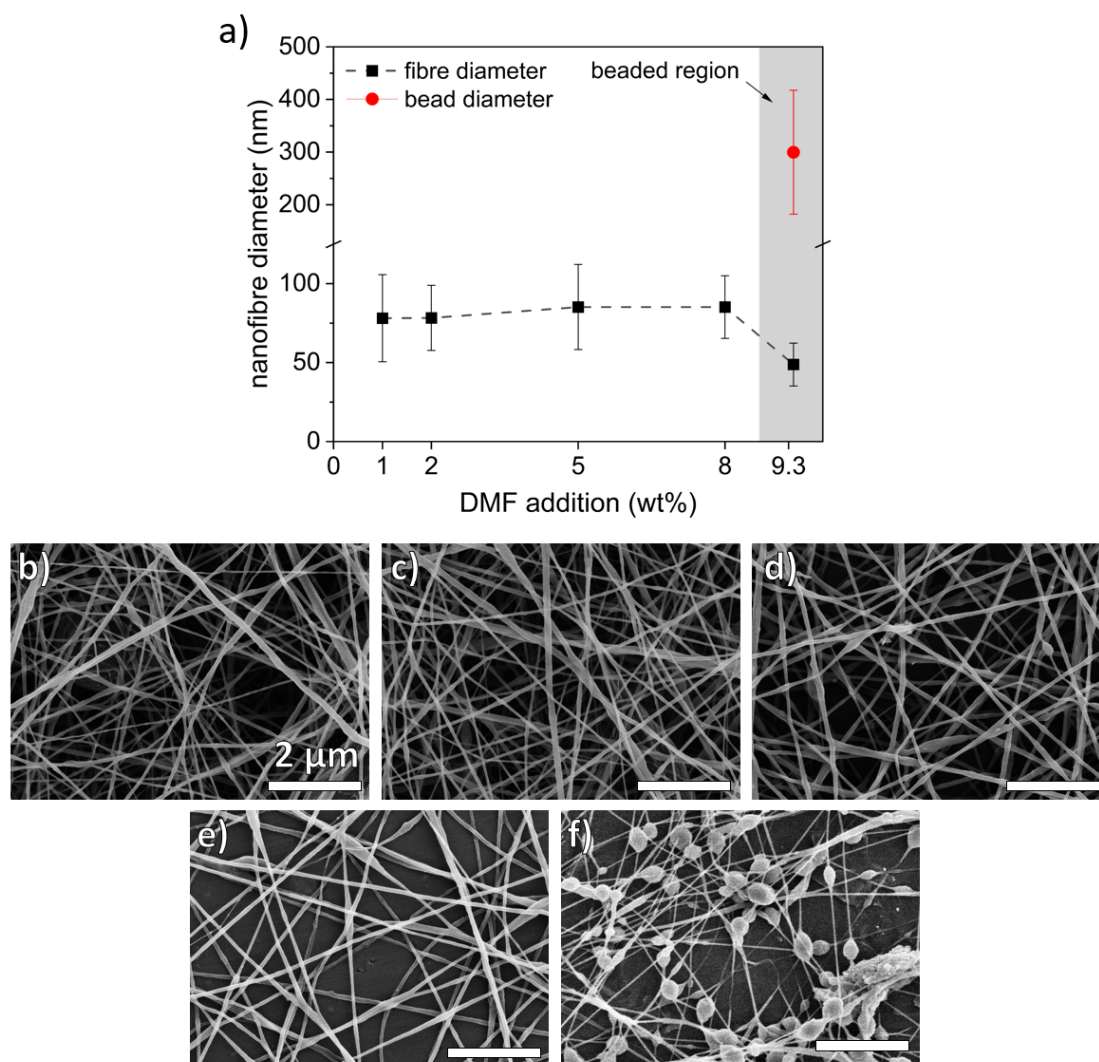


Figure 3.17: (a) Diameters of PEO-reduced AgNP-containing PEO nanofibres electrospun from spinning solutions containing varying DMF additions, aged for 48 h. The fibre diameter is independent of DMF content. SEM micrographs of PEO-reduced AgNP-containing PEO nanofibres spun from 0.35 wt% PEO solutions dissolved in (b) 99:1 w/w, (c) 98:2 w/w, (d) 95:5 w/w, (e) 92:8 w/w, and (f) 90.6:9.4 w/w chloroform:DMF.

b:4,5-b]dithiophene))-alt-(5,5-(1,3-di-2-thienyl-5,7-bis(2-ethylhexyl)benzo[1,2-c:4,5-c]-dithiophene-4,8-dion)] (PCE12) and poly[2,2-bis([(2-butyloctyl)oxy] carbonyl) [2,2:5,2:5,2- quaterthiophene] -5,5-diyl] (PDCBT) [159]. P3HT produced a stable <100 nm nano-dispersion, whereas the other polymers produced micron-sized particles, and PDCBT coagulated. With other polymers presenting greater susceptibility to non-solvents, one would expect a lesser extent of diameter reduction to be achievable via the co-solvent strategy.

When AgNO₃/PEO-reduced AgNPs were introduced to the spinning solution 48 h prior to spinning, the onset of beading occurred above the same DMF weight addition

of 8 wt%, as in Figure 3.17. A minimum addition of 1 wt% DMF was required to solubilise the silver salt, but between 1 and 8 wt% DMF addition, the diameter of the PEO fibres were stable around 80 nm. In the presence of nanoparticles, co-solvent did not produce a measurable effect, with the diameter reductions dominated by nanoparticle addition, introduced in Section 3.4.2.

The advantage of producing nanofibres of this class of polymers by electrospinning is that the diameter and morphology is controlled by the behaviour of the auxiliary polymer and its interplay with other additives such as polar solvents or nanoparticles; The photoactive polymer plays a minor role within the electrospinning process, only displaying morphological differences after washing (Section 4.3.1). This allows one to switch the semiconductor polymer for another. The approach described hereafter relies on minimal additions of DMF to solubilise AgNO_3 , but this can be omitted entirely when using OA-capped Ag and AuNPs to equal success. One may expect the nanoparticle mechanism to be compatible with a greater variety of organic semiconducting polymers than the co-solvent strategy.

3.4.2 Influence of Nanoparticle Addition

3.4.2.1 Nanoparticle-induced Nanofibre Diameter Reductions

In order to describe and explain the mechanism of fibre diameter reductions caused by the presence of nanoparticles, the influence of their addition upon the properties of the spinning solution, the electrospinning process, and the resultant nanofibres were studied. The strategy was primarily developed with PEO fibres containing PEO-reduced AgNPs, and subsequently tested with OA-capped Ag and AuNPs. Ultimately, the concept was then applied to P3HT fibres containing each nanoparticle type.

Stable additions of 10 wt% AgNO_3 wrt the PEO concentration (0.35 wt%), or 0.035 wt% of the total spinning solution weight, could be made before precipitation of the nanoparticles or polymeric material was observed. In Figure 3.18a, the addition allowed for a reduction in the diameter of PEO nanofibres electrospun after 48 h of solution ageing. The observed fibre diameter was found to be closely linked to the concentration of the nanoparticles added to the spinning solution at a fixed ageing time. Even at very low

additions, PEO-reduced AgNPs were able to deliver significant reductions to diameter. Above 0.1 wt% AgNO_3 , the decrease in diameter slowed and eventually plateaued at around 80 nm, up to 40% thinner than pristine fibres (without nanoparticles) spun herein. At 5 wt% addition, the lowest diameter of a PEO nanoweb generated within this work was produced at 75 ± 17 nm. (Figure 3.18c) This champion nanoweb was achieved through the optimisation of the electrospinning parameters including the applied voltage, tip-collector separation, feed rate and needle size. To my knowledge, this is the smallest reported diameter of a PEO nanofibre, in particular from spinning solutions based upon chloroform. Generally, aqueous or polar solutions of PEO produce lower diameter fibres due to the greater conductivity and dielectric constant. [80, 160, 161] These PEO-reduced AgNP-containing PEO nanofibres are 20% thinner than the 100 nm fibres spun by Kim et al. [67]

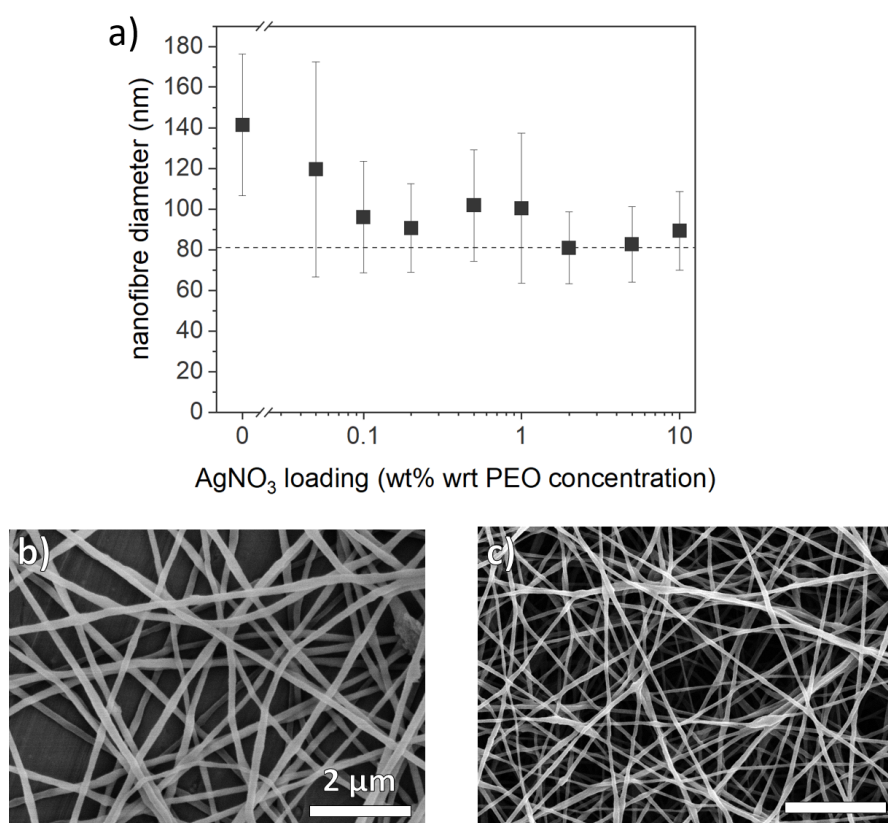


Figure 3.18: (a) Diameter reduction of PEO nanofibres upon the introduction of varying AgNO_3 concentrations to 0.35% PEO solutions, and after 48h of ageing, PEO-reduced AgNPs. (b) SEM micrographs of pristine PEO nanofibres electrospun from a 0.35 wt% PEO spinning solution dissolved in 92:8 w/w chloroform:DMF. (c) SEM of the 75 nm champion PEO-reduced AgNP-containing PEO nanofibre web electrospun 48 h after the addition of 10 wt% AgNO_3 wrt PEO.

3.4.2.2 Surface Tension

To elucidate the reasoning behind the observed diameter reduction, nanoparticle influence upon the physical properties of the spinning solution including surface tension, electrical conductivity and viscosity were investigated as described in Sections 2.2.3.1 - 2.2.3.3. These factors are often quoted as the most influential parameters within electrospinning. [56, 99] First, the influence of nanoparticle introduction to the surface tension of PEO solutions was investigated using the pendant drop technique.

Surface tension plays a critical role in the formation of the Taylor cone when the voltage is applied during electrospinning. It also has significant interplay with the favoured morphology of spun fibres. In short, a higher surface tension spinning solution will favour a beaded morphology over uniform fibre architectures as they possess a lower surface area to volume ratio, to minimise the total free energy of the system. Thus, lower surface tension solution is considered favourable to achieving ultra-thin nanofibres. [162, 163] Surface tension has been previously described as a determining factor for the electrospinnable window, in particular for attaining a uniform fibre morphology, while its effect on the fibre diameter is less understood or defined. [164, 165, 166]

Within Figure 3.19a, neither PEO-reduced AgNPs, OA-capped AgNPs, or OA-capped AuNPs produced any measurable change in the surface tension of the solution regardless of loading, up to 5 wt% wrt PEO (0.0175 wt% of the total spinning solution). In Figure 3.19b - e, the dimensions and shape of representative pendant droplets are visually similar regardless of nanoparticle presence.

Due to the low concentration of polymer and nanoparticles, the solution's surface tension is largely determined by the solvent mixture, resulting in no or negligible influence by the nanoparticles. Chloroform-air and DMF-air interfaces possess surface tensions of 26.7 mN m^{-1} [167] and 35.8 mN m^{-1} [168], respectively. As the measurements in Figure 3.19 were made on 92:8 w/w chloroform:DMF-based spinning solutions, an intermediate value of $\sim 30 \text{ mN m}^{-1}$ was measured. Additionally, the dissolution of PEO into chloroform can provide an increase in surface tension to $\sim 31 \text{ mN m}^{-1}$. [169]

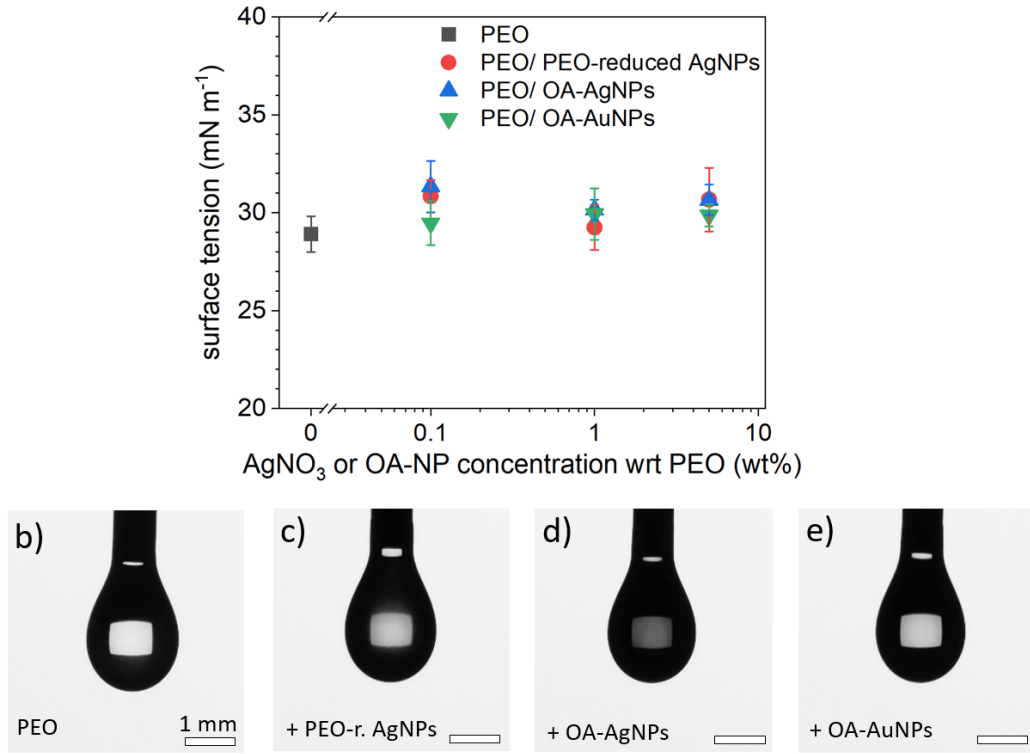


Figure 3.19: (a) Surface tension of PEO-based spinning solutions showing negligible influence upon nanoparticle addition up to 5 wt% wrt PEO. (b - e) Representative examples of the pendant droplets formed from the pristine and nanoparticle-containing solutions. (Scale bars: 1 mm)

Spinning Solution	$D_s(mm)$	$D_e(mm)$	$\gamma(mNm^{-1})$
PEO	1.361	1.779	30.2
PEO-reduced AgNPs	1.374	1.800	31.1
OA-capped AgNPs	1.389	1.785	29.2
OA-capped AuNPs	1.400	1.804	30.0

Table 3.2: Extracted dimensions from the example pendant drops shown in Figure 3.19 b-e and independence of surface tension.

3.4.2.3 Electrical Conductivity

Under the external electric field, ions in solution move in opposing directions and electrons are transferred from solution to the metallic needle, leading to a net positive charge at the surface of the fluid. These regions of excess charges are essential for electrospinning, as an entirely non-conductive solution cannot generate sufficient electrical forces to overcome the surface tension of the Taylor cone and generate an electrospinning jet.

Upon AgNO₃/PEO-reduced AgNP addition to the spinning solution, strong enhancements in the conductivity of solution were measured. Pristine PEO solutions were

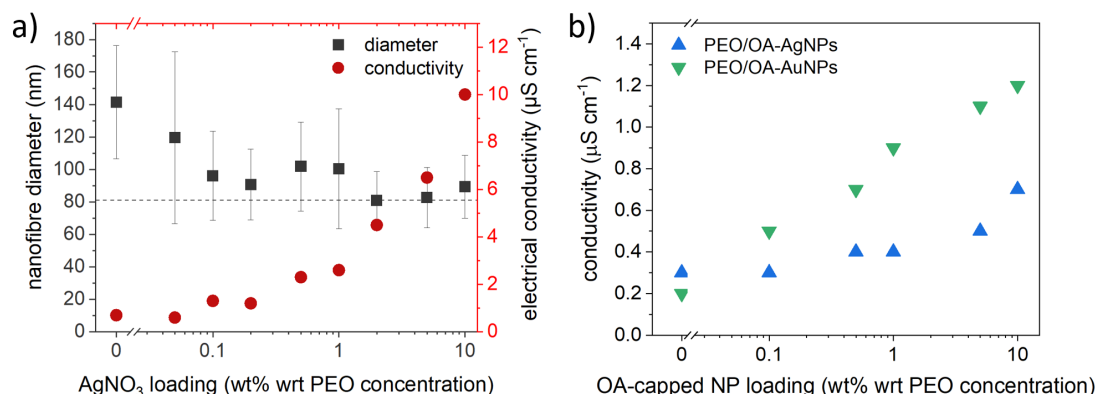


Figure 3.20: (a) Enhanced solution conductivity and reduction in the fibre diameter upon AgNO_3 / PEO-reduced AgNP infusion to 0.35 wt% PEO spinning solutions. (b) Analogous but lesser influences to conductivity were measured upon the introduction of OA-capped NPs.

found to possess a solution conductivity of $0.7 \mu\text{S cm}^{-1}$, which increased linearly with salt/nanoparticle concentration to $10 \mu\text{S cm}^{-1}$. (Figure 3.20a) Higher conductivity was attributed largely to ions, rather than surface-charged particles, as they possess higher charge mobility and charge density.

In Figure 3.20b, a similar yet considerably lower conductivity enhancement is seen upon the introduction of OA-capped Ag and AuNPs at the same weight loading. Due to the precipitation and purification of these nanoparticles with methanol, they contain a lower concentration of residual ions. The nanoparticles themselves present a lesser contribution due to the insulating capping layer which reduces surface charge, and their larger nanoparticle size lowers mobility.

Increasing conductivity means the elongational forces experienced by the electrospinning jet under the same applied voltage are increased. Repulsion between like charges distributed along the jet can further promote uni-axial elongation, ultimately providing additional stretching and a thinner fibre. [170, 171] This also leads to an improvement in the morphology of the fibres spun from the same PEO concentration upon the introduction of 5 wt% PEO-reduced AgNPs, aged for 48 h. The coulombic repulsion at higher charge density favours a uniform morphology with increased surface area per unit mass. This has been previously demonstrated using corona discharge to provide counter ions to those at the jet surface during electrospinning of PEO nanofibres. As the concentration of neutralising ions was increased, so did the number of beads per unit length of the fibre. [172]

The addition of AgNO_3 coincides with the diameter reduction of fibres spun after 48 h of solution ageing. However, the relationship between conductivity and diameter is non-linear, suggesting that conductivity is not the sole or primary reason for the diameter reduction. Later in Section 3.4.2.5, it is shown that without ageing the solution, allowing time for nanoparticles to form and influence the spinning solution, diameter reductions are not seen despite the conductivity enhancement. In short, the diameter reductions are determined by more complex behaviours than can be explained by conductivity alone.

3.4.2.4 Viscosity

Viscosity is proportional to the degree of molecular entanglement within a liquid and is the most dominant factor defining the spinnability of a polymeric solution. Viscosity is dictated by the molecular weight and nature of the polymer, its concentration, and the solvent. [173, 174, 175]

Viscosity provides resistance to the elongational forces, preventing jet break up or electrospaying, and resists the formation of beaded structures favoured by surface tension. [99] More concentrated, higher viscosity solutions provide greater resistance to stretching producing nanofibres with a greater diameter. [56, 176] Therefore, to obtain the thinnest possible fibre, one must use the lowest possible polymer concentration sufficient to prevent beading as demonstrated by Figure 3.11.

In Einstein's effective viscosity formula, it was theorised that the addition of spherical particles to a liquid must increase its viscosity, [136, 137] however in Figure 3.21, the introduction of nanoparticles reduces viscosity. These viscosity reductions were measured using 1.5 wt% PEO spinning solutions as a higher polymer concentration was necessary to generate the minimum of 10% torque upon the viscometer spring. [94] At this concentration, a maximum addition rate of 5 wt% AgNO_3 wrt the PEO concentration before material precipitation.

72 h after the addition of 1 - 5 wt% PEO-reduced AgNPs, the viscosity had reduced to just 20 - 30% of its initial level. The relationship between viscosity and as-spun fibre diameter is more linear in Figure 3.22 steadily reducing from 1000 nm to 300 nm with increasing addition. Similarly, in Figure 3.23, a 2 wt% infusion of OA-capped

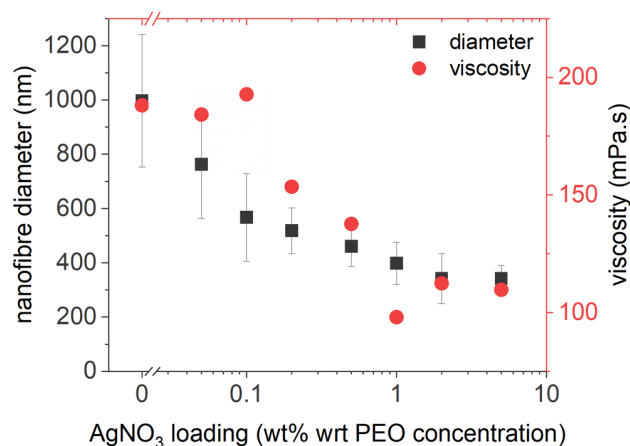


Figure 3.21: Decrease in solution viscosity and reduction in the fibre diameter upon AgNO₃/PEO-reduced AgNP introduction to 1.5 wt% PEO spinning solutions, aged for 72 h.

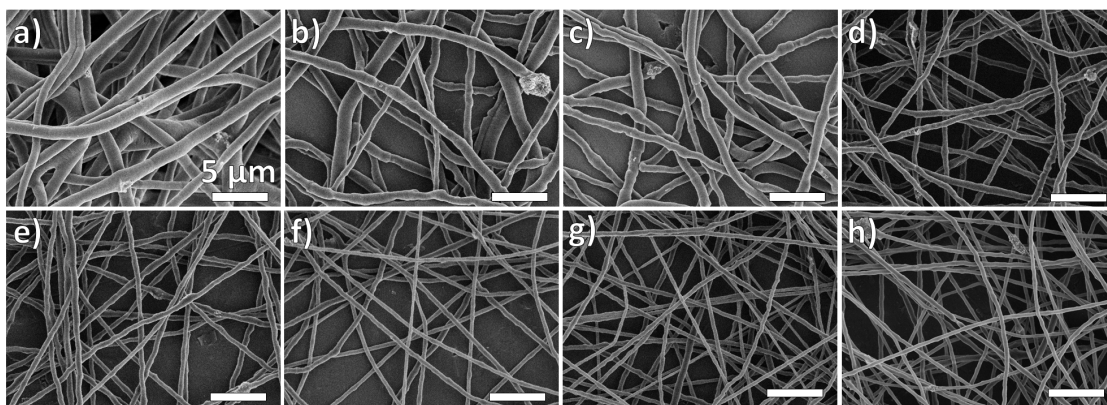


Figure 3.22: SEM micrographs of nanofibres electrospun from 1.5 wt% PEO solutions in 92:8 w/w chloroform:DMF with PEO-reduced AgNP doping levels of (a) 0, (b) 0.05, (c) 0.1, (d) 0.2, (e) 0.5, (f) 1, (g) 2 and (h) 5 wt% AgNO₃ wrt PEO aged for 72 h.

Ag and AuNPs delivered 45% and 75% viscosity reductions, respectively, coinciding with 35% and 70% reductions in the PEO fibre diameter. Again, strong correlation between the nanoparticle loading, resultant solution viscosity and fibre diameter was seen. These findings provide initial indications that the diameter reductions may be induced by a nanoparticle-driven viscosity reduction.

Initially, it is considered whether the viscosity had reduced due to capping of the nanoparticles by the PEO chains, which reduces the number of chains entangled within the solution contributing to the overall viscosity. However, unlike PEO-reduced AgNPs which may interact with the PEO chains, the same reductions were observed using OA-capped NPs which possess a dense ligand layer isolating them from interactions

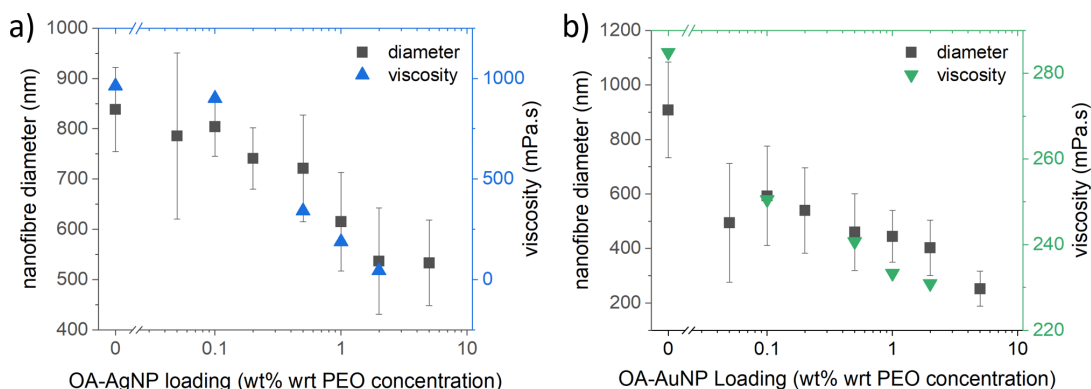


Figure 3.23: Decrease in solution viscosity and reduction in the fibre diameter upon 5 wt% (wrt PEO) (a) OA-capped AgNP and (b) OA-capped AuNP introduction to 1.5 wt% PEO spinning solutions aged for 72 h. Corresponding SEM micrographs are displayed in Appendix Figure A.3.1 and A.3.2.

with PEO. If PEO capping was the rationale for the viscosity reductions, this would suggest that the oleylamine ligands are substituted following addition of the particles to the spinning solution.

Therefore, FT-IR analysis (Section 2.2.2.6) was used to determine the ligand content prior to addition and after isolation. 72 h after infusion to the spinning solution, OA-capped AgNPs were separated by means of high speed centrifugation (10 000 rpm). They were then washed with chloroform to remove unbound material and recollected by centrifugation once again. In Figure 3.24, there is no evidence that oleylamine is replaced by PEO in the capping layer. The metal-nitrogen interactions formed with oleylamine are relatively labile, however, the electron-donating effect of oxygen in PEO is not as strong as amine moieties. [177] Literature on PEO/OA-capped NP blends has also corroborated that ligand exchange does not occur, as composites displayed changes to T_g reliant upon the oleylamine ligand remaining bound. [178]

The FT-IR absorption intensities of nanoparticles which had been exposed to the spinning solution were weaker, suggesting some loss of the oleylamine ligand content. However, the particles retained closer matching characteristics to oleylamine than PEO. The asymmetric CH_2 and CH_3 vibration modes of oleylamine at 2853 and 2924 cm^{-1} appear in consistent relative intensities before and after introduction to the spinning solution. [179, 180] In contrast, PEO possesses similar vibrational modes but in different relative intensities.

Furthermore, the lack of PEO C-O and C-C stretching modes at 840, 1059, 1097, and 1145 cm^{-1} in the spectra of the isolated particles, suggests negligible ligand displacement occurs. [181, 182] PEO absorption in the fingerprint region is much more intense than the C-H asymmetric vibration modes, therefore, if capping of the nanoparticles by PEO was occurring at levels needed to produce the bulk rheological changes to the spinning solution, one would expect to see evidence of this.

Instead, literature suggests that AuNPs smaller than the entanglement mesh size (~ 5 nm) can reduce the bulk viscosity of PEO melts. [183, 184] Particles greater than this critical size (20 nm) did not change viscosity. The reduction was attributed to an increase in the polymer reptation tube diameter, yet the study did not speculate the rationale for the change. [183] Reptation was first introduced by de Gennes [185] and explains how a polymer chain can be considered as confined to an imaginary tube by its entanglement with surrounding polymer. [186] This restricts the flow of chains in the melt, and therefore by increasing the diameter of this tube, the viscosity may be reduced. A similar phenomenon may be occurring within semi-dilute PEO solutions upon the addition of nanoparticles of ≤ 10 nm.

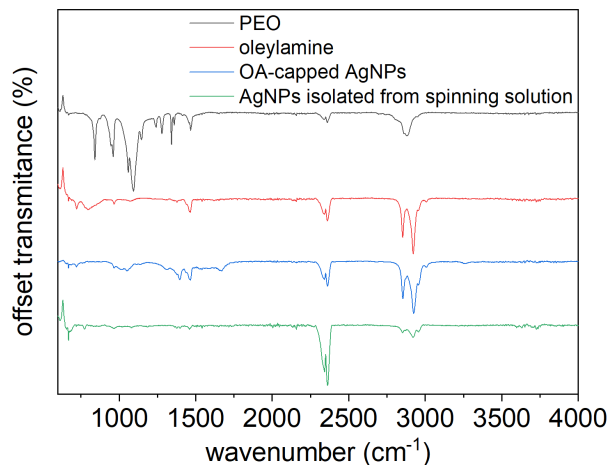


Figure 3.24: FTIR spectra of OA-capped AgNPs as-synthesised and after isolation from the spinning solution following 72 h ageing. Both the before and after spectra reveal oleylamine content in the capping layer, and no evidence of PEO adsorption.

3.4.2.5 Time-dependent Modulation of Spinning Solution Properties

The influence of particle presence upon the electrical conductivity and viscosity of the solution, and resulting fibre diameter, is a dynamic process changing with the ageing

time of the solution following nanoparticle addition.

Solution viscosity was found to decrease over time for all three nanoparticle types. AgNPs were found to provide the greatest changes with $> 90\%$ reductions (value taken at a shear rate of 60 s^{-1}) with respect to the initial level prior to addition (Figure 3.25b and 3.26). However, the time taken for this drop varied dependent on the type. PEO-reduced AgNPs only produced a change beyond 24 h of ageing, presumably due to the time taken for the PEO to reduce the added AgNO_3 into nanoparticles. When using OA-capped AgNPs, synthesised separately, the viscosity had already undergone a $> 80\%$ decrease by 24 h. Reductions within 24 h were also observed with the Au analogue, however interestingly, the viscosity plateaued beyond 48 h at $\sim 55\%$ of the initial level.

In Figure 3.26, the shape of the viscosity-shear rate curves suggest non-Newtonian shear thinning behaviour. [187] This behaviour is considered typical of polymeric solutions, as the polymer chains become partially disentangled during flow in the shear direction. [188, 189] Figure 3.26 and 3.27 reveal that different loadings of nanoparticles can produce the same degree of disentanglement at different ageing times. This suggests that the same diameter fibres may be obtained from solutions with lower silver content simply by waiting longer to achieve equivalent viscosity reductions prior to electrospinning. Therefore, in applications where nanoparticle presence is undesirable, ultra-thin PEO (or P3HT) nanofibres can be obtained with minimal salt/particle additions followed by an extended solution ageing period.

Over the same time period, electrical conductivity also rose (Figure 3.25a). This is probably a direct result of the decreasing viscosity which allows the mobility of ions and charged nanoparticles to increase as there is now less resistance to their transport. [190] The PEO-reduced AgNP-containing PEO solution's conductivity rose by $0.8 \text{ } \mu\text{S cm}^{-1}$, or 27% over 96 h. Similar increases were observed for OA-capped NP addition, however due to the lower initial conductivity, these represent a relative increase of 120% and 50% for the Ag and Au particles, respectively. It should be noted that the pristine PEO solution also increased by $0.2 \text{ } \mu\text{S cm}^{-1}$ or 100% , despite the absence of particles perhaps due to better solvation or cross-contamination.

Concomitantly, the diameters of the as-spun PEO-based nanofibres presented a continuous and dynamic decrease, with thinner fibres being produced from nanoparticle-containing spinning solutions of increased age. After a critical period, the solution possesses very low entanglement which provides insufficient resistance to stretching to maintain uniform fibre morphologies, inducing beading. The beading onset age was dependent upon the type and loading of the nanoparticle, and the initial viscosity or polymer concentration in the original solution. For 5 wt% (wrt PEO) PEO-reduced AgNPs or OA-capped AuNPs, bead-on-a-string structures were collected after 72 h of ageing. (Figure 3.25c) However, beading was observed after just 48 h when using OA-capped AgNPs, which was consistent with the faster drop in viscosity seen in Figure 3.25b. In comparison, pristine PEO solutions yield stable fibre diameters over the entire ageing period at ~ 140 nm.

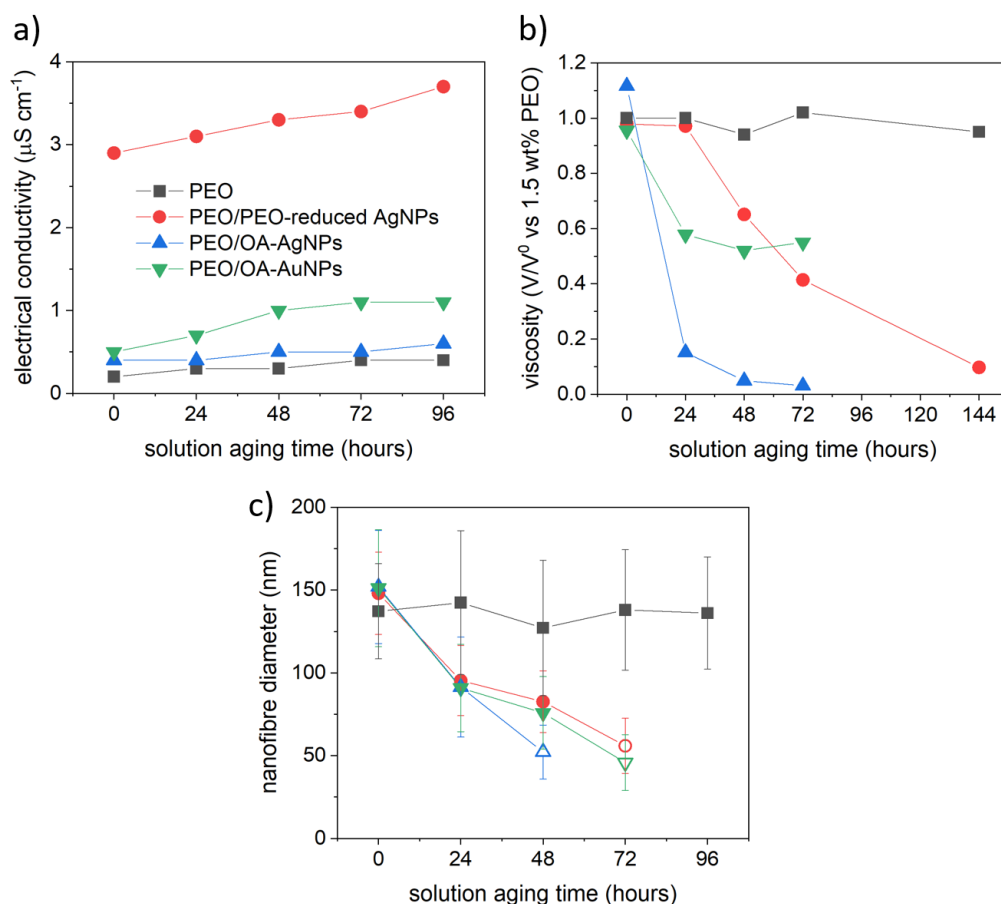


Figure 3.25: (a) Increase in electrical conductivity with ageing time of 5 wt% (wrt PEO) nanoparticle-containing 0.35 wt% PEO solutions and (b) ageing time-dependent viscosity (at 60 s^{-1}) reductions of 2 wt% (wrt PEO) nanoparticle-containing 1.5 wt% PEO solutions. (c) Reducing diameters of 5 wt% nanoparticle-containing PEO nanofibres spun from 0.35 wt% solutions after variable ageing time. Symbols without fill represent beaded fibre morphologies.

By identifying the optimal ageing time for the spinning solution, the thinnest possible PEO nanofibres were collected measuring 75 ± 16 , 91 ± 19 and 83 ± 21 nm for PEO-reduced AgNPs, OA-capped AgNPs and OA-capped AuNPs, respectively. In order to elucidate the primary mechanism for the diameter reductions, the required ageing time to induce these reductions is considered. If the enhanced electrical conductivity was the major factor, one would expect to spin thinner fibres at 0 h, as conductivity increases by the greatest degree at the instant of salt/particle addition. However, negligible difference between pristine PEO solutions and those containing particles at 0 h are reported. This therefore suggests that viscosity is the main factor controlling the fibre width. The picture becomes more complex as a 40% diameter decrease is found for fibres spun after 24 h ageing, however in Figure 3.25b, this coincides with the delay before the viscosity begins to drop in PEO-reduced AgNP-containing solutions. Whilst, this could be due to the difference in nanoparticle influence upon viscosity within 0.35 wt% (used for spinning) and 1.5 wt% (required to meet viscometer torque requirements) PEO solutions, it does suggest that the two factors may act cooperatively, with viscosity as the primary mechanism.

However, a PEO spinning solution prepared using a polymer concentration to yield equal viscosity to that of an aged nanoparticle-containing solution, would result in heavily beaded fibres. Therefore, while electrical conductivity acts as a secondary factor, it may be necessary to achieve a uniform fibre structure. Greater repulsion between neighbouring like-charged ions and particles at higher charge density, promotes the formation of higher surface area uniform fibres to minimise net repulsion. Beads present bulk-like regions with a lower surface area to volume ratio. Here, most charges are completely surrounded by like-charges from all directions. Within uniform fibres, an increased proportion of these species are located at the surface, and so are surrounded by fewer repulsive forces. This concept is communicated in Figure 3.28a.

Overall, reduced viscosity lessens the resistance to stretching and concurrently, greater conductivity enhances the elongational forces for a given voltage. Simultaneously, it is shown that the charges provide a greater jet pathlength between the needle and ground plate. This may provide more time for elongation to occur before the fibre solidifies or is collected. Electrical charges are largely responsible for generating the whipping or

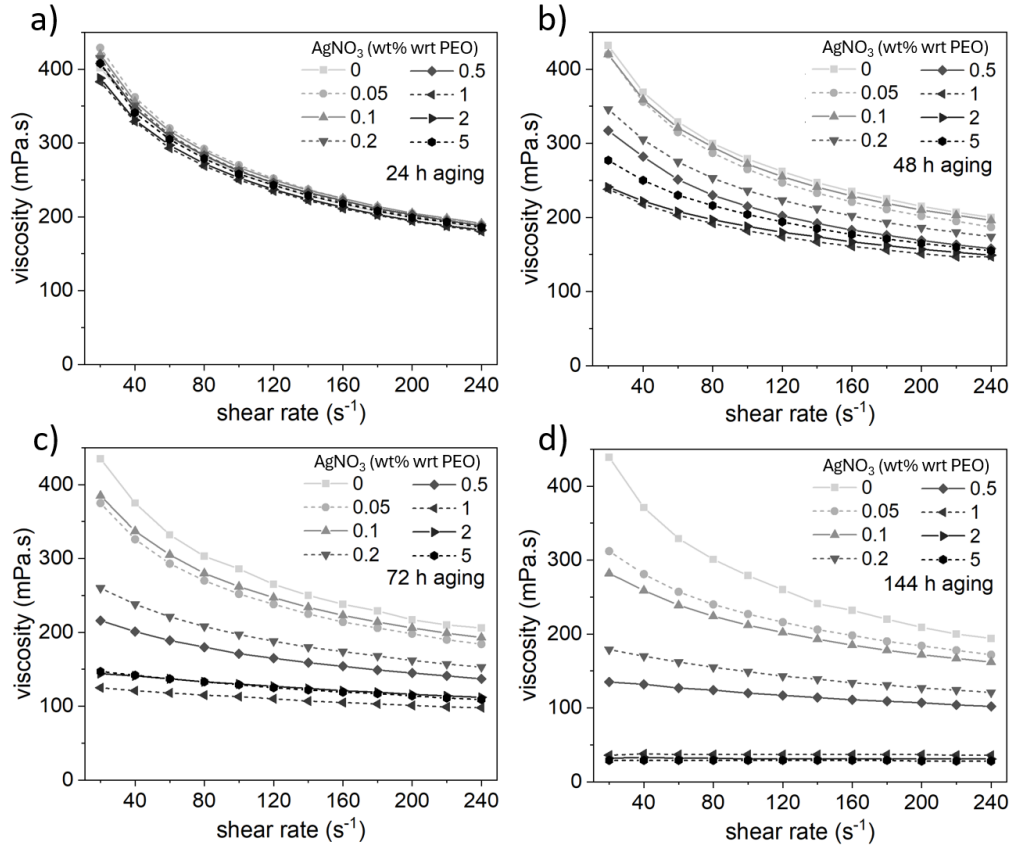


Figure 3.26: Reducing viscosities of PEO-reduced AgNP-containing PEO nanofibres as a function of shear rate with variable silver loadings measured after (a) 24, (b) 48, (c) 72, and (d) 144 h of solution ageing.

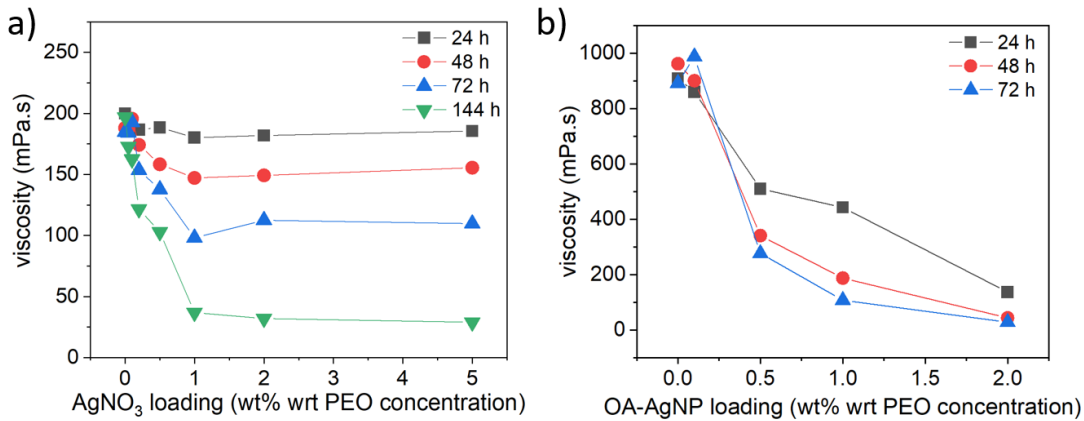


Figure 3.27: The viscosity of PEO solutions (at 60 s⁻¹) with variable loadings of (a) PEO-reduced AgNPs and (b) OA-capped AgNPs as a function of solution ageing time.

bending instabilities of the jet, therefore an increased density of these surface charges can lead to earlier and more frequent whipping instabilities. [99, 191] Lower viscosity solutions will also typically produce a shorter linear jet section prior to whipping. [192] This is

observed, by eye, in this system as the length of the linear jet section reduces from > 5 cm to < 3 cm for 48 h-aged 5 wt% (wrt PEO) nanoparticle-containing solutions (Figure 3.28b - f). As a result, the collected fibres are generally distributed over a greater area.

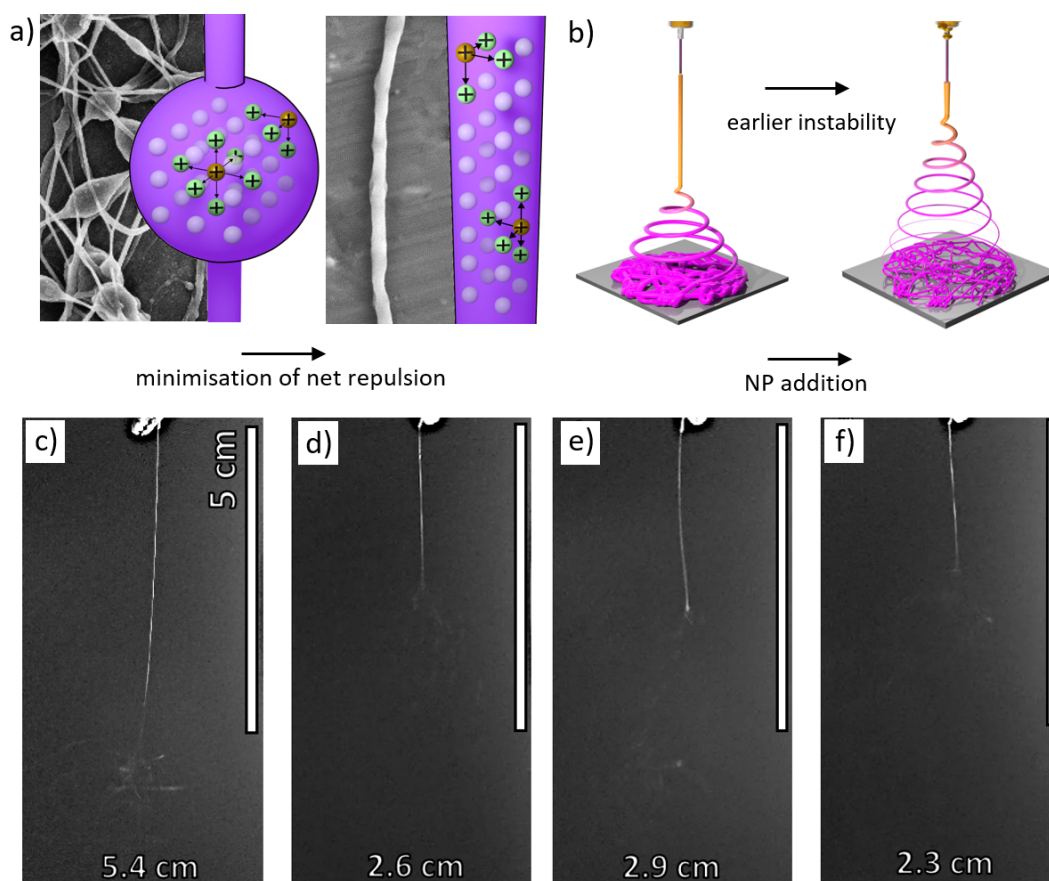


Figure 3.28: (a) Mechanism of how high charge density may promote the formation of high surface area, uniform morphologies which minimises the repulsion between neighbouring charges. (b) Schematic demonstration of increased fibre flight pathlength upon earlier whipping onset. Digital photographs of the linear section of (c) PEO electrospinning jets showing a shorter distance before the first bending instability upon (d) PEO-reduced AgNP, (e) OA-capped AgNP or (f) OA-capped AuNP addition leading to greater thinning.

Each subsequent bending instability leads to a significant thinning of the jet compared to the previous section, and increases the overall pathlength of the fibre during flight exponentially. Therefore, nanoparticle addition offers greater pathlengths promoting further reduction in the fibre diameter.

3.5 Application to and Synthesis of Ultra-Thin P3HT Nanofibres

3.5.1 Time-dependant Diameter Reductions in P3HT/PEO Nanofibres

Following the investigation of nanoparticles within PEO fibres, the time-dependent diameter reductions were translated to photoactive fibres via the addition of 0.25 wt% P3HT. PEO dominates the viscosity of the spinning solution and therefore, analogous time-dependent diameter reductions are observed for nanoparticle-containing P3HT/PEO nanofibres. As mentioned in Section 3.4.1, DMF was limited to 5% of the total solvent weight with PEO-reduced AgNPs, or omitted in the case of OA-capped NPs.

Over 96 h ageing, the diameter of as-spun P3HT/PEO nanofibres reduced from 240 nm to < 100 nm (Figure 3.29a - g). By 120 h, the fibre diameter rose again to ~ 150 nm due to the onset of fibre inhomogeneity and beading. Over the same period, pristine P3HT/PEO solutions yielded stable diameters at 220 - 240 nm. In Figure 3.29i, equal diameter reductions were produced by the addition of OA-capped NPs, regardless of DMF presence.

BET analysis (details given in Section 2.2.4.4) reveals that after PEO-reduced AgNP addition and 96 h solution ageing prior to spinning, the P3HT/PEO fibre surface area effectively doubled from $5.55 \pm 0.08 \text{ m}^2 \text{ g}^{-1}$ to $11.79 \pm 0.13 \text{ m}^2 \text{ g}^{-1}$. (Figure 3.29h) This suggests potential for increased heterojunction area for exciton dissociation following PEO removal and PCBM infiltration.

Upon 0.25 wt% P3HT addition, the optimal ageing time to yield the thinnest possible fibres was extended from 24 - 48 h to 96 h, due to the higher initial viscosity with the additional polymer content of solution. In Figure 3.30, the optimal ageing time and diameter of the P3HT/PEO fibres reduce with lower P3HT concentration until they align with figures observed for the PEO fibres.

3.5.2 Dimensions of P3HT Nanofibres following PEO removal

As-spun P3HT/PEO nanofibres were submerged in IPA heated at 70 °C (above the T_g of PEO) to promote melting and selective dissolution of the PEO to yield virgin P3HT-based nanofibres. The efficacy of this procedure is discussed further within section 4.3.2.

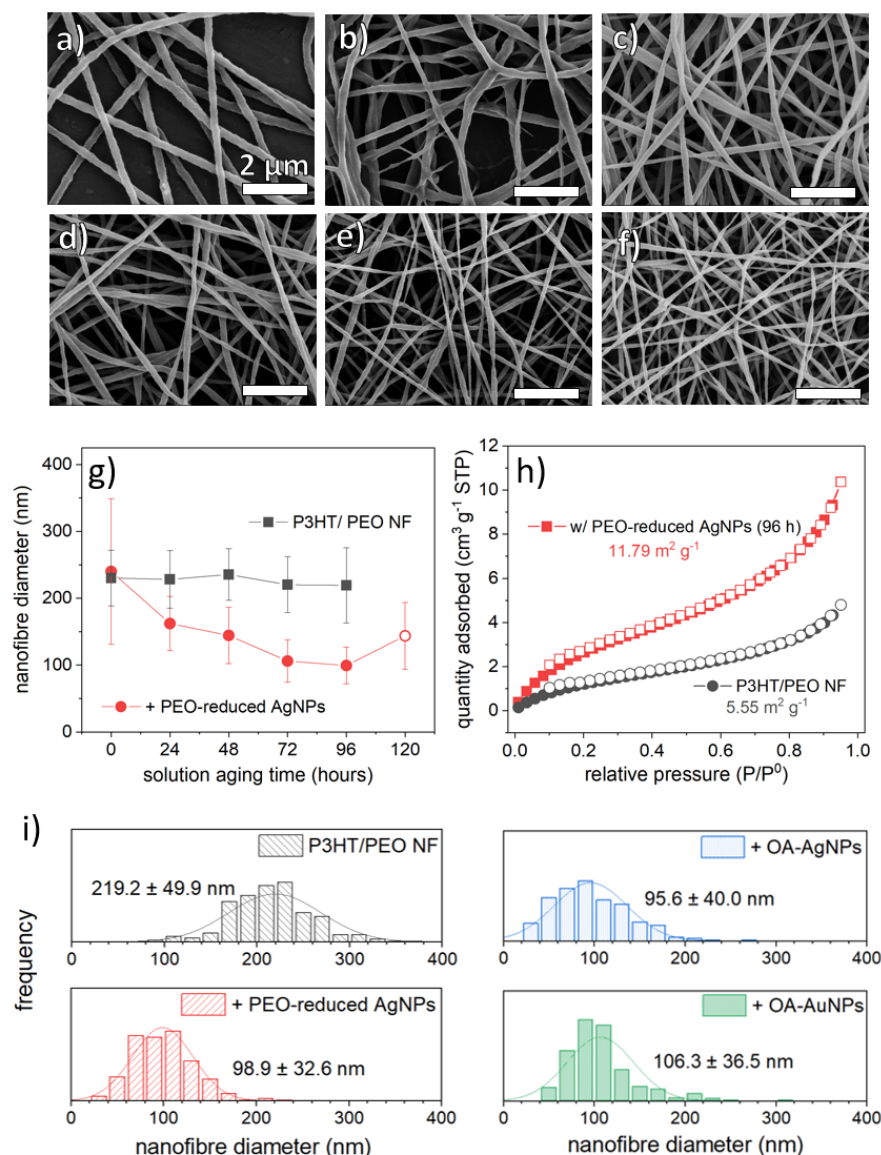


Figure 3.29: SEM micrographs of (a) pristine P3HT/PEO nanofibres and (b - f) PEO-reduced AgNP-containing P3HT/PEO nanofibres spun after (b) 0 h, (c) 24 h, (d) 48 h, (e) 72 h and (f) 96 h of solution ageing time. (g) Diameters of P3HT/PEO fibres with and without PEO-reduced AgNP addition, showing ageing-time dependent diameter reductions. Symbols without fill represent beaded fibre morphologies. (h) BET analysis of the fibres presenting increased surface area induced by the presence of PEO-reduced AgNPs. Solid symbols indicate the absorption curve and unfilled symbols the desorption profile. (i) Fibre diameter histograms of pristine and NP-containing P3HT/PEO solutions, revealing a step-change in fibre diameter distribution. OA-capped NP-containing fibres were spun from solutions based only on chloroform, i.e. DMF addition could be omitted.

SEM and AFM were combined to determine that as-spun blend fibres were cylindrical, with a width of $99 \pm 33 \text{ nm}$ (diameter of the fibre parallel to the substrate) and height of $98 \pm 25 \text{ nm}$ (diameter normal to the substrate) as determined by SEM and AFM,

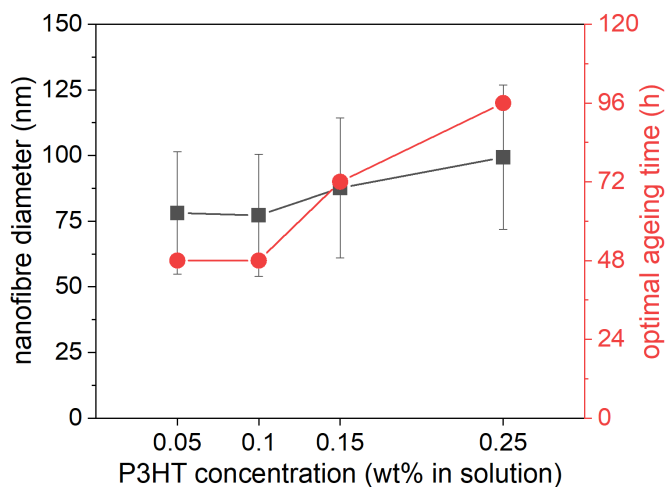


Figure 3.30: Reducing as-spun P3HT/PEO nanofibre diameters and optimal ageing time before beading with variable concentrations of P3HT added to the spinning solution.

respectively (Figure 3.31a - c and Section 2.2.1.5 for procedure details). This suggests that the solvent had entirely evaporated and the fibres solidify before collection to prevent relaxation of labile polymer chains to form oval or ribbon-like fibre cross-sections. [193]

During the washing procedure for PEO removal, the fibres ‘slump’ or flatten on the substrate to form fibres which are wider than they are tall. For charge dissociation, the formation of a minor axis diameter is advantageous as it offers shorter diffusion pathways for excitons formed at the fibre core to reach the heterojunction with infiltrated PCBM. In Figure 3.31d-f, pristine P3HT nanofibres were measured to possess a vertical diameter of 101 ± 40 nm and horizontal diameter of 330 ± 91 nm. In comparison, the nanoparticle-induced diameter reductions delivered vertical and horizontal diameters of 73 ± 25 nm and 116 ± 33 nm, respectively.

Reducing the P3HT content from 0.25 wt% to 0.15 wt% offers the thinnest, continuous fibres presented within this work at 96 ± 27 nm wide and 55 ± 13 nm high as in Figure 3.31j - l. At P3HT concentrations of < 0.15 wt%, the fibres after washing became largely discontinuous. To the best of my knowledge, the 55 nm minor diameter presents the thinnest instance of P3HT fibres reported in literature to date. This figure represents a 45% reduction in diameter within this work, and is 30% thinner than any prior report, [67] offering the next step towards reported P3HT fibres and the ideal photoactive nanofibre for solar applications. Ignoring inter-diffusion of P3HT and PCBM upon backfill, these fibres

provide exciton diffusion pathways of ≤ 28 nm, or around 3x the exciton diffusion length of the material - meaningfully shorter than the 50 nm fibre radius without nanoparticle addition, or the lowest reported length of 40 nm in prior reports. [67]

Ignoring diffusion, just 25% of excitons are produced ~ 10 nm from the fibre surface in pristine P3HT nanofibres (or 44% of excitons within the thinnest P3HT fibres in literature [67]). Here, the dimensions of nanoparticle-containing fibres allow over 50% of excitons to be formed within one exciton diffusion length of the surface. In reality, significant diffusion of PCBM into the fibres is expected, irrespective of the use of an orthogonal solvent, [120, 121] which enables a substantially larger exciton population to be separated. The actual ability of these fibres to dissociate excitons is evaluated in Chapter 5.

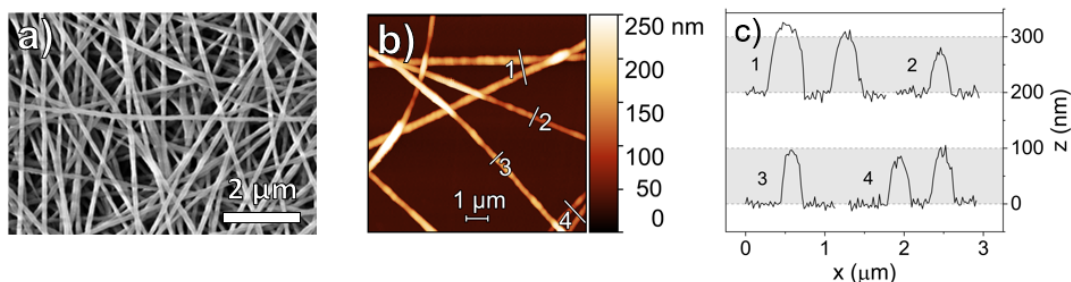
Fibre	As-spun diameter (nm)	Washed vertical diameter (nm)	Washed horizontal diameter (nm)	Excitons within 10 nm of surface (%)
P3HT NF (Literature)	110	80	80	43.8
P3HT NF	219.2 ± 49.9	101.0 ± 39.8	329.4 ± 90.7	24.6
P3HT/PEO-red. AgNP NF (0.25% solution)	98.9 ± 32.6	73.1 ± 24.6	115.9 ± 33.2	40.0
P3HT/PEO-red. AgNP NF (0.15% solution)	87.7 ± 26.7	55.1 ± 13.2	96.4 ± 14.1	50.4

Table 3.3: The final major and minor diameters of P3HT-based nanofibres.

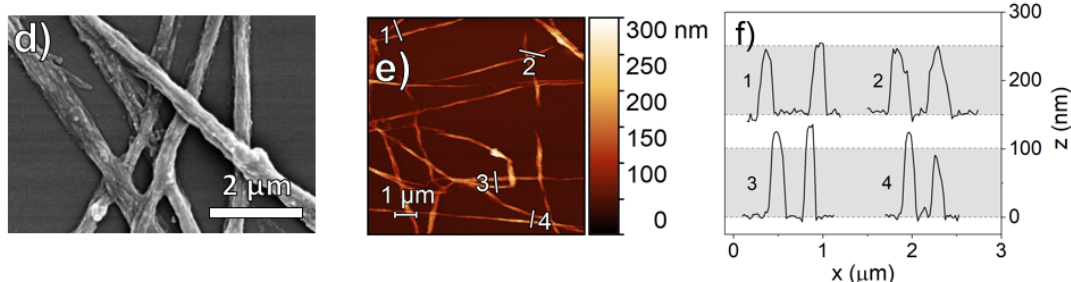
3.6 Investigating Universality of Mechanism: PCE12/PM6 Donor Polymers

To demonstrate the adaptability of this strategy in producing ultra-thin fibres with a variety of photoactive polymers, P3HT is replaced with 0.25 wt% PCE12 and poly[(2,6-(4,8-bis(5-(2-ethylhexyl-3-fluoro) thiophen-2-yl)-benzo[1,2-b:4,5-b'] dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)] (PM6). The P3HT:PCBM BHJ exhibits device efficiencies of $\leq 4\%$ [79], while contemporary systems featuring these donor polymers are capable of delivering far greater PCEs of 11% [194] and 19% respectively, when used in conjunction with NFAs. [13] PCE12 or PM6 nanofibres were

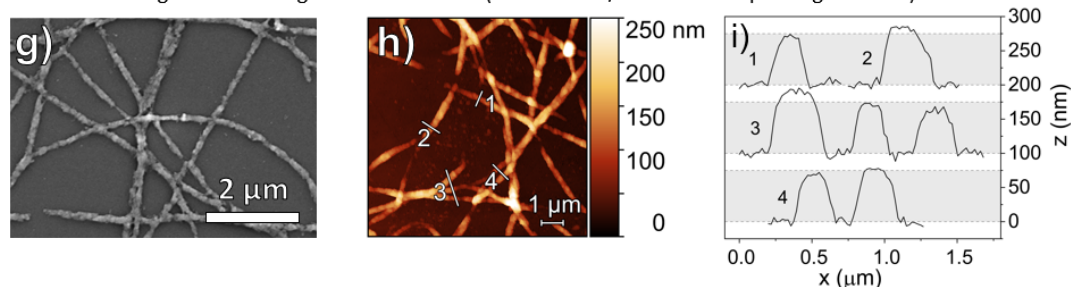
PEO-reduced AgNP-containing P3HT/PEO Nanofibres



P3HT Nanofibres



PEO-reduced AgNP-containing P3HT Nanofibres (0.35% P3HT/0.25% P3HT spinning solution)



PEO-reduced AgNP-containing P3HT Nanofibres (0.35% P3HT/0.15% P3HT spinning solution)

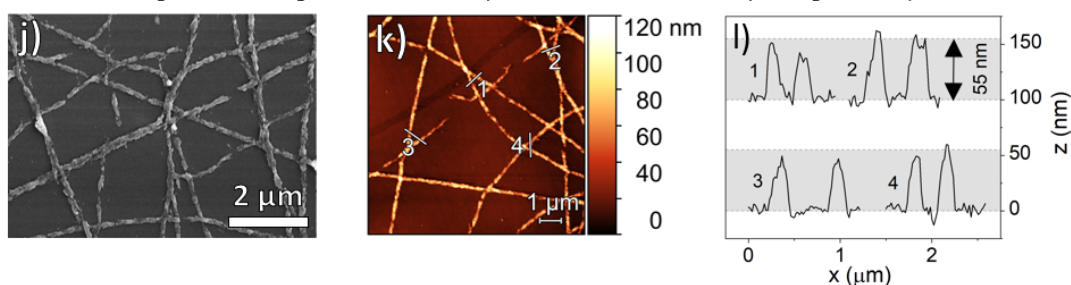


Figure 3.31: (a,d,g,j) SEM micrographs, (b,e,h,k) AFM images and (c,f,i,l) extracted height profiles of (a - c) as-spun PEO-reduced AgNP-containing P3HT/PEO NFs, and washed (d - f) P3HT NFs, (g - i) PEO-reduced AgNP-containing P3HT NFs from a spinning solution containing 0.25% P3HT and (j - l) 0.15 wt% P3HT.

successfully spun under otherwise identical solution and spinning conditions. Delaminated dark blue/purple nanofibre mats are shown in Figure 3.32.

As hypothesised, nanoparticle addition produced a 40% diameter reduction for PCE12/PEO and PM6/PEO fibres after 96 h ageing. The pristine fibre diameters

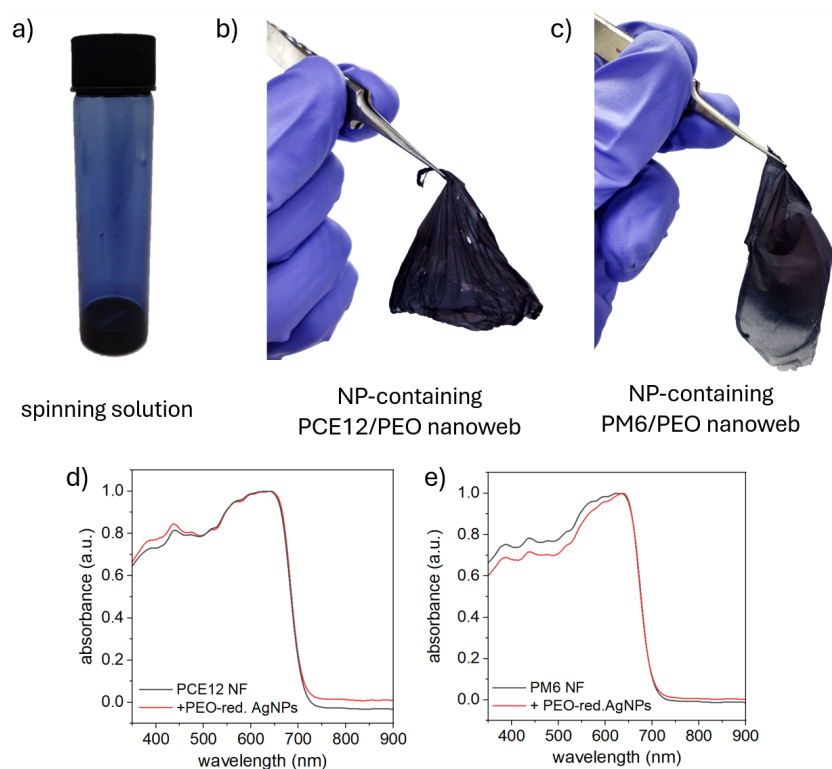


Figure 3.32: Digital photograph of (a) PCE12/PEO/OA-AuNP spinning solution and delaminated as-spun webs of (b) PCE12/PEO/OA-AuNP and (c) PM6/PEO/OA-AuNP electrospun nanofibres. Normalized absorbance spectra of washed OA-AuNP (d) PCE12/OA-AuNP and (e) PM6/OA-AuNP nanofibres deposited onto ITO-coated glass (collected using an integrating sphere).

(determined by SEM) reduce by 28% (PCE12) and 19% (PM6) during PEO removal in Figure 3.33a-d and Table 3.5. Resultantly, the horizontal diameter of the washed fibre drops by 50% (PCE12) and 46% (PM6). With optimisation, it is expected that sub-100 nm fibres could be achieved.

Fibre	As-spun diameter (nm)	Washed horizontal diameter (nm)
PCE12 NF	267.4 ± 100.4	193.8 ± 46.1
PCE12/OA-AgNP NF	158.8 ± 38.9	131.2 ± 54.6
PM6 NF	291.7 ± 50.4	235.3 ± 97.8
PM6/OA-AgNP NF	174.7 ± 44.0	127.9 ± 48.1

Table 3.4: (Horizontal) diameters of PCE12 and PM6-based nanofibres before and after washing determined from SEM micrographs in Figure 3.33.

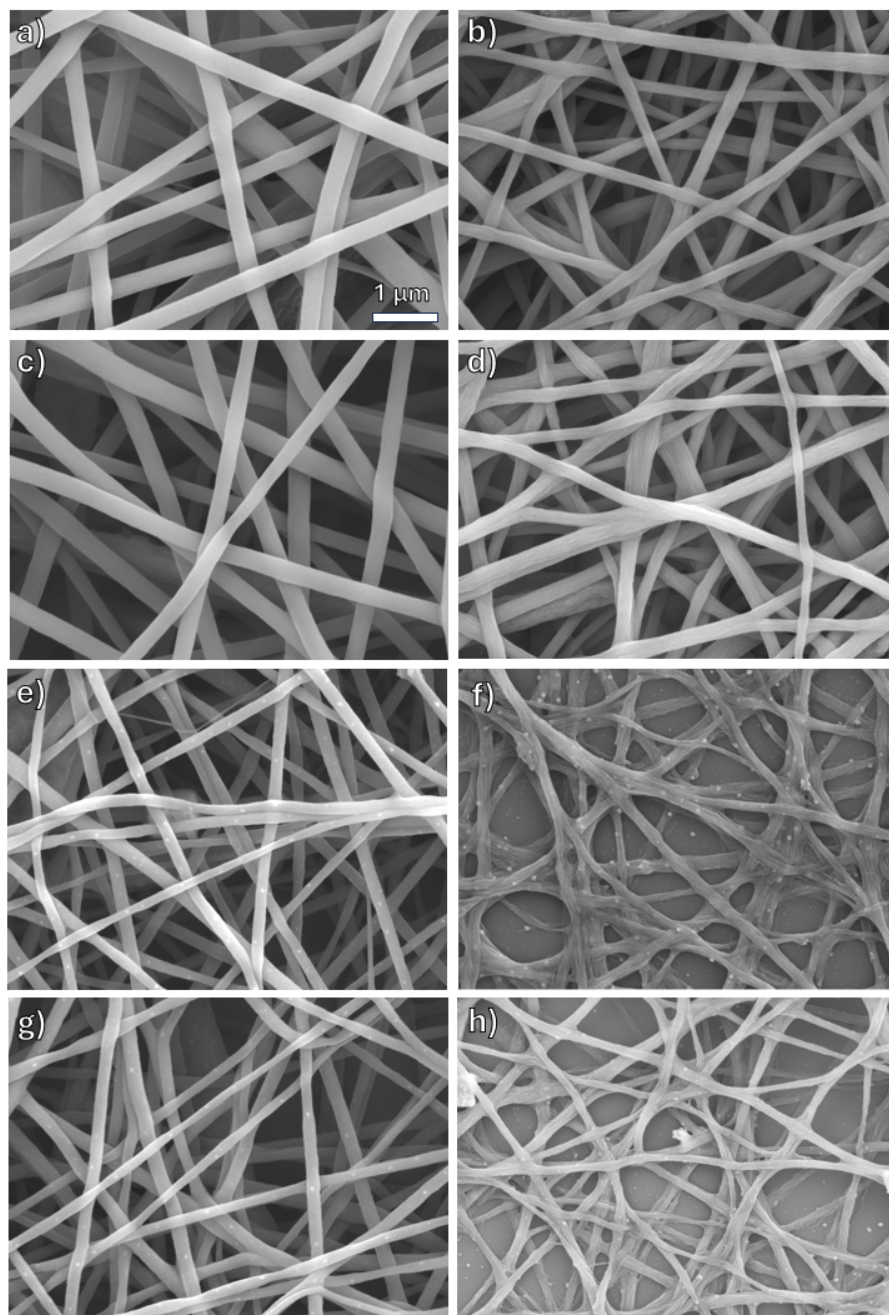


Figure 3.33: SEM micrographs of pristine (a) as-spun PCE12/PEO, (b) washed PCE12, (c) as-spun PM6/PEO and (d) washed PM6 NFs. Micrographs of NP-containing (e) as-spun PCE12/PEO, (f) washed PCE12, (g) as-spun PM6/PEO and (h) washed PCE12 NFs, presenting analogous diameter reductions under equivalent spinning conditions to P3HT. The OA-AuNP batch contained a population of larger diameter particles observable in the micrographs.

3.7 Conclusions

In this chapter, a method of synthesising ultra-thin diameter electrospun nanofibres of both PEO and P3HT, through the addition of gold or silver plasmonic nanoparticles

measuring ≤ 10 nm, has been demonstrated.

First, the limitations of the state-of-the-art co-solvent approach to producing thin photoactive nanofibres is explored. It is identified that the addition limit of anti-solvent, and therefore the success of this approach, can vary substantially using similarly-sourced P3HT. In short, the addition of DMF was limited to just 5 wt%, around half of previously reported values [67]. This meant that the thinnest attained P3HT/PEO nanofibres in the absence of nanoparticles was 220 nm, rather than 110 nm quoted in literature.

SEM revealed that through the addition of PEO-reduced AgNPs, the diameters of PEO fibres reduces to 75 nm and P3HT/PEO fibres to 100 nm - reductions of 46% and 55% versus their pristine counterparts, respectively. In the presence of PEO-reduced AgNPs, PEO diameters were independent of DMF addition, with 75 - 80 nm fibres being obtained from solutions containing 1 - 8 wt% DMF. BET analysis of the pristine and nanoparticle-containing P3HT/PEO nanofibres corroborates the reduced diameter with a doubling of the surface area.

With OA-capped Ag and AuNPs, DMF addition was not required and comparative diameters were electrospun. No longer linked to the tolerable levels of DMF, analogous results can be expected with a vast range of polymers perhaps with the only requirement being that the polymer is soluble in chloroform. As the PEO and nanoparticles control electrospinning, and have negligible interaction with the photoactive polymer, this mechanism was successfully applied to the contemporary polymers, PM6 and PCE12, spun under identical conditions.

To determine the mechanism of the diameter reduction, the effect of nanoparticle addition upon important measurands of the spinning solution is elucidated. Firstly, it is recognised that the nanoparticles do not affect the surface tension of the spinning solution. However, the nanoparticles do increase the solution conductivity and reduce the viscosity. Enhanced conductivity increases the elongation forces for a given applied voltage while reduced viscosity offers less resistance to stretching at constant elongation forces, promoting further fibre thinning. The length of the linear jet section portion prior to the bending instability was found to almost halve upon nanoparticle introduction, increasing the flight pathlength of the fibre and hence providing additional time for stretching. The

charge density from the added particles/ions may help retain the uniform morphology, as a pristine PEO solution with equal viscosity to the aged nanoparticle-containing PEO solutions would produce heavily beaded fibres. Like-charged nanoparticles and ions repel each other during fibre flight, and uniform fibres are favoured to minimise overall repulsion.

Whilst it is unconfirmed why viscosity reduces upon nanoparticle addition, FT-IR analysis did not show any change in the composition of the capping ligands after introduction of OA-capped AgNPs to the spinning solution for 48 h. Instead, literature provides an explanation in an increase in the reptation tube diameter of PEO. The nanoparticles' influence on the spinning solution is time-dependent with the conductivity increasing and the viscosity reducing with ageing. Simultaneously, the diameters of the fibres also reduce with this ageing time. Therefore, the thinnest fibres are collected at the critical ageing time beyond which the viscosity drops further and the fibres begin to break up and bead. Without ageing, nanoparticle-containing fibre diameters are similar to those spun without nanoparticles, when conductivity has already risen, and so viscosity appears to be the primary reason for the fibre diameter changes.

These learnings are then applied to P3HT by first producing P3HT/PEO blend fibres. By optimising the P3HT content and ageing time of the solution, P3HT/PEO fibres down to 80 nm may be obtained. In conjunction with AFM, SEM studies revealed that the fibres, which were cylindrical upon collection, flatten during the washing procedure leading to an anisotropic cross-section with major and minor diameters. AFM was used to determine the minor diameters of the final P3HT nanofibres. In the absence of nanoparticles, pristine P3HT nanofibres have a vertical diameter of 116 nm, reducing to 55 nm after adding nanoparticles and 0.15 wt% P3HT to the spinning solution.

Consequently, excitons produced at the fibre core have a 50% shorter diffusion pathway to the surface, and over 50% of excitons are produced within one exciton diffusion length of the surface. When considering the non-negligible P3HT:PCBM inter-diffusion, a vast majority of excitons will be dissociated in nanoparticle-containing fibrous active layers. These fibres, achieved by this novel, unparalleled and adaptable diameter reduction method, present a significant step-change to how photoactive fibres are electrospun.

4

Electrospinning and Diameter-Influence Upon P3HT Nanostructure

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4.1 Highlights

The processing conditions by which photoactive layer architectures are generated imparts a unique nano-structure upon the resultant features of the film or fibre. In turn, the relative molecular orientations, degree of crystallinity, nature of the heterojunction, and morphology of the percolation pathways following electron acceptor infiltration, directly determine

its photoelectric performance. Initially, the overall morphology and polymer/nanoparticle composition of washed P3HT nanofibres is explored. Subsequently, the process-structure relationship within electrospun P3HT and the effect of any subsequent washing or annealing processes are probed by polarized spectroscopy, and X-ray and electron diffraction studies.

Greater absorption of light polarized parallel to the fibre reveals that polymer chains involved in amorphous P3HT regions are planarized and aligned along the fibre axis due to the uni-axial fibre elongation. Upon diameter reduction, the perpendicular to parallel polarized-light absorption ratio reduces from 0.88 for pristine P3HT fibres, to 0.62 for sub-100 nm PEO-reduced AgNP-containing fibres. Enhanced in-plane polymer alignment provides a more optimal orientation for light harvesting. Conversely, diffraction characteristics reveal that the $[0k0]$ crystallite axis is oriented along the fibre with polymer backbones orthogonal to the axis. Hermans' orientation parameters calculated from azimuthal scans demonstrate that whilst the initial addition of AgNO_3 initially degrades the extent of crystallite alignment, following the formation of PEO-reduced AgNPs over 96 h, the ultra-thin fibres contain equivalent or greater along-fibre alignment versus their pristine counterparts. UV-Vis absorption measurements of the spinning solution and 4D-STEM analysis reveals that the fibres contain anisotropic (10 nm wide and up to 80 nm long) crystals which were formed prior to spinning. These are then aligned along the fibres under the same elongational driving forces. This nano-structure offers a promising platform for lateral charge transport through long-range $\pi - \pi$ stacking, whilst the increased prevalence of end-on crystallites may enhance vertical transport versus edge-on rich films ($(h00)$ normal to the substrate).

4.2 Background

4.2.1 Preferential Crystallite Orientation of P3HT

Preferential orientations of P3HT polymer chains and crystallites deliver unique and sometimes advantageous photovoltaic performance. Epitaxial films of semiconducting polymers may be generated through manipulation of the solution or substrate, via deposition techniques or post-processing steps. [195]

Depending upon the host solvent [196] or speed of drying, [197] spin-coating can create isotropic, edge-on, face-on ($(0k0)$ normal to the substrate) or bimodal orientations of P3HT. The idealised P3HT unit cell, orientations and terminology used within this chapter are defined in Figure 4.1. Slower drying films favour the thermodynamically stable edge-on orientations, whereas fast-dried solutions form kinetically-trapped metastable face-on states or even an isotropically oriented film. [198, 199] Perturbation of or a change in configuration may be induced by the introduction of electron acceptors or other components to solution. [200, 201] The crystallite orientation found within these films can be manipulated further by pre-processing such as mechanical rubbing of the substrate, which increases the prevalence of face-on orientations [202] or post-processing such as thermal [198] or solvent [203] annealing, promoting the transition of face-on to edge-on orientations. Rubbing of thin-film itself has also been shown to improve the polymer backbone alignment with respect to the substrate [204, 205].

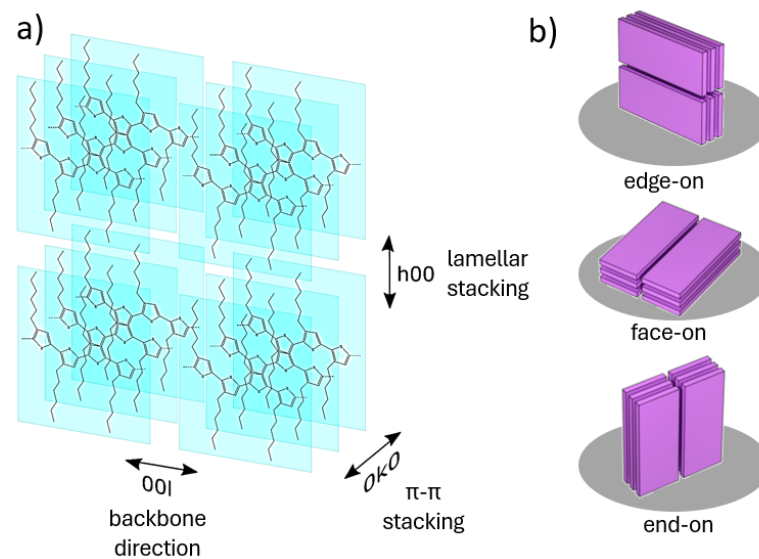


Figure 4.1: (a) Depiction of an idealised P3HT crystalline unit cell with annotated stacking/direction terminology, and (b) schematic of the edge-on (the same orientation as in (a)), face-on and end-on P3HT configurations, defined by the unit cell's orientation with respect to the substrate interface (shown in grey).

To induce alignment or common orientation in a lateral direction, films may be vapour annealed or the solutions aged, [112] slowly cooled, or a non-solvent added, to induce the controlled formation of fibrillar nano-crystallites in solution. Self-assembled P3HT crystals generally grow preferentially in the $\pi - \pi$ (020) direction, forming high-aspect nanowires

which produce favoured long-range orientations once cast. [112, 206, 207] Resultantly, films produced from these fibres, generate edge-on [208] and even end-on (00l normal to the substrate) [209, 210] configurations wrt the substrate. Films of oriented nanowires have even be fabricated via off-centre spin-coating [211], solution-floating methods [212] or directional solidification under a temperature gradient. [213]

The shear and stretching forces that electrospinning jets experience during flight have been extensively reported to generate preferential alignment of polymer chains along the length of electrospun fibres. This has been demonstrated with a variety of techniques using polarized radiation, including UV-Visible, [66, 113, 214, 215] PL, [216, 217, 218] FT-IR, [219, 220] and Raman [221, 222] spectroscopy. These spectroscopic techniques operate under the principle that the probability of radiation being absorbed is greater when the electric field vector of the incident radiation and the transition dipole moment of the molecule are oriented in a common direction. By carefully selecting transitions which possess a dipole moment along the polymer backbone, such as the $\pi - \pi^*$ electronic transition in the UV-Visible spectrum (Figure 4.2a - b) or the antisymmetric C=C stretching mode within the IR region (Figure 4.2c), backbone orientation preference may be elucidated using directionally polarized radiation. Resultantly, in Figure 4.2a, Yoon et al. demonstrated that light absorption was greater with light polarized parallel to (along) the fibre axis as opposed to perpendicular to (across) the fibre axis. [66] Likewise, greater PL intensity is recorded with either a parallel-polarized excitation source or selective detection of parallel-polarized light emission. (see Figure 4.2b) Thinner diameter fibres are often shown to contain a greater degree of polymer alignment and extent of crystallinity, however this has not been applied to photoactive polymers such as P3HT. [223, 224, 225].

These techniques provide data averaged over both the amorphous and crystalline material. Alternatively, diffraction studies using X-rays [61, 112, 227, 228, 229, 230, 231] or electrons [61, 208, 232, 233, 234] can be used to elucidate the alignment of polymer exclusively in crystallites wrt to the fibre length. Grazing-incidence wide angle X-ray scattering (GI-WAXS) studies take advantage of different diffraction behaviour when an aligned fibre bundle is positioned so that the X-ray beam is incident down the fibre axes versus across the axes to reveal alignment. [112, 229] Under the condition of crystallite

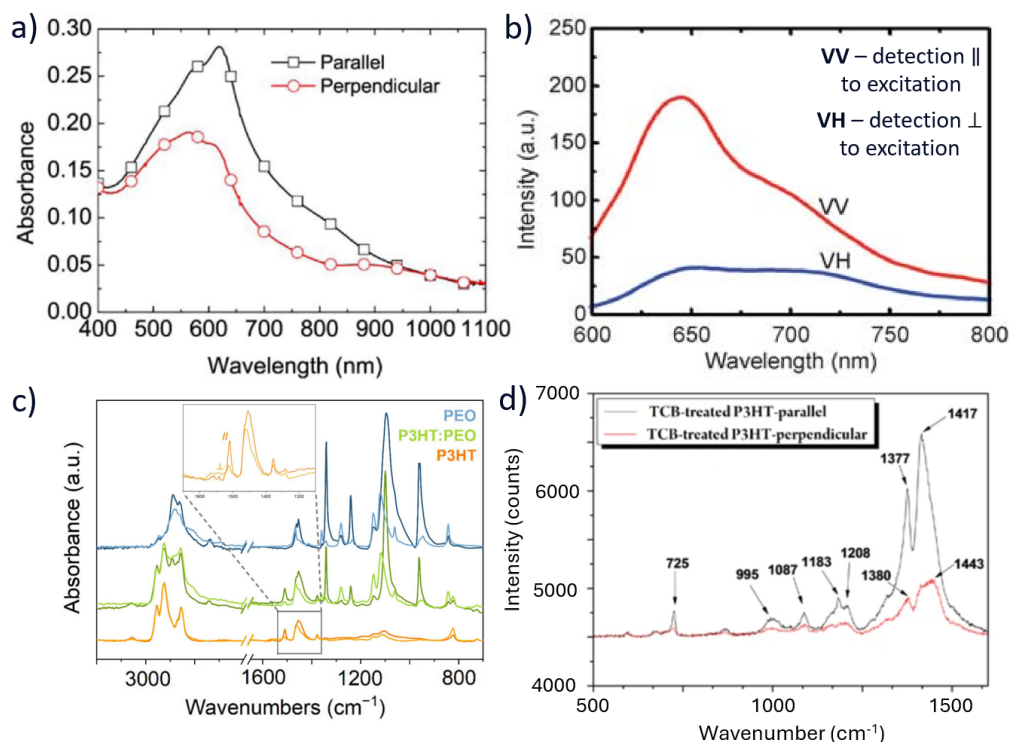


Figure 4.2: Spectroscopic strategies to elucidating the preferential alignment of polymer backbones within electrospun P3HT nanofibres using (a) UV-Visible, (b) PL, (c) FT-IR and (d) Raman spectroscopy with parallel and perpendicularly polarized light. Reprinted (adapted) with permission from references [66, 218, 114, 226], respectively. Copyright 2017 KIM, Springer, Copyright 2011 The Royal Society of Chemistry, Copyright 2022 The Authors, CC BY 4.0., Copyright 2016 The Authors, CC BY 4.0.

alignment, with the backbone directed along the fibre axis, the fibre will not give rise to IP (100) and (020) diffraction when the X-ray beam is perpendicular to its axis, as in Figure 4.3a-b. This analysis has also been applied to mechanically-strained or directionally-crystallised P3HT films (see Figure 4.3c-e).

Bulk techniques provide excellent representative datasets of the nanoweb, however to record the X-ray characteristics produced with different beam-to-fibre orientations, alignment of the fibres in a common direction is essential. To make comparisons between samples, one must produce a consistent degree of fibre-to-fibre alignment as this will heavily influence the measurements. As reproducible fibre-to-fibre orientation is difficult to achieve with electrospun fibres using rotating collectors (or producing any common alignment of other nanomaterials), analysis of individual fibres is also powerful.

There are few characterisation options for single-fibres, and fewer still for nanoscale fibres, however successful implementations of micro-Raman, [237], nanoscale AFM-IR

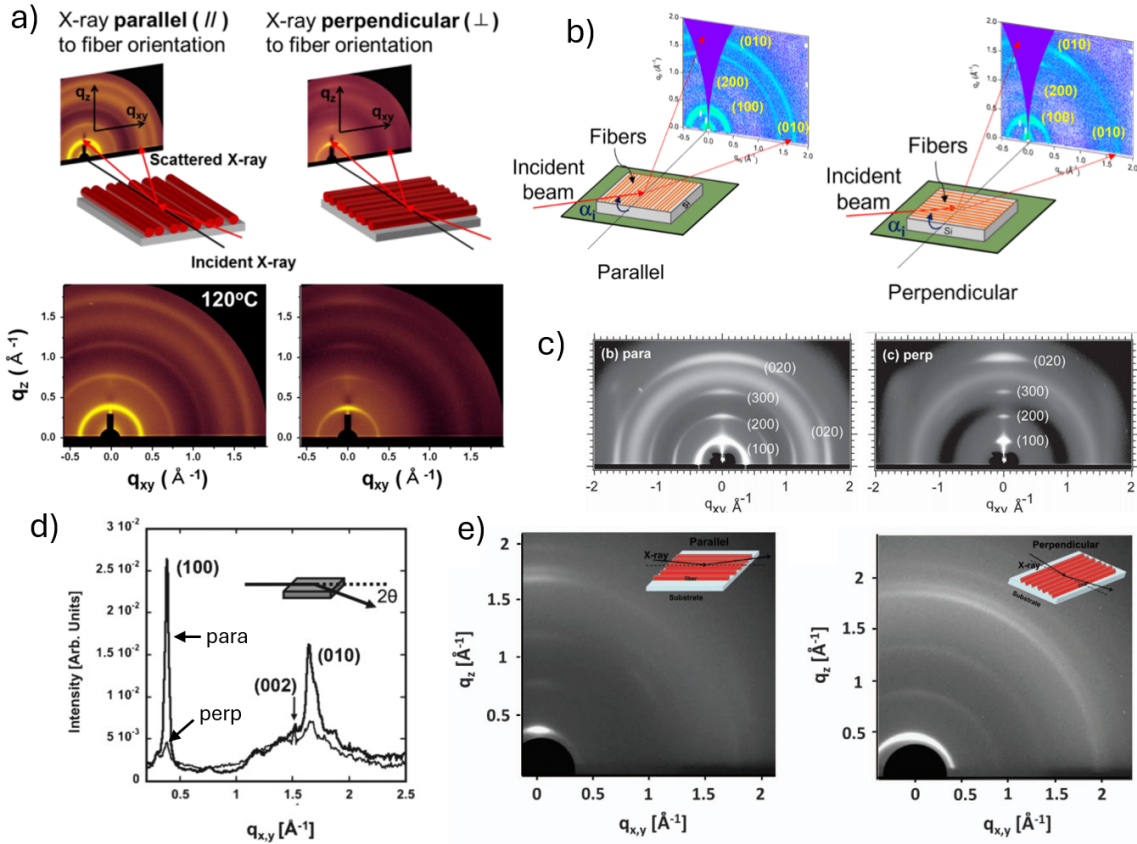


Figure 4.3: GI-WAXS spectra of (a - b) electrospun P3HT nanofibres, (c) mechanically strained thin-films, and (d - e) directionally solidified fibrous films. Different scattering behaviour is observed when the X-ray beam is oriented parallel and perpendicular to the fibre axis or strain direction. Alignment of P3HT crystallites along the fibre axis is generally indicated by the absence of in-plane (100) and (020) scattering. Reprinted (adapted) with permission from references [229, 112, 235, 236, 226], respectively. Copyright 2015 Elsevier Ltd, Copyright 2022 American Chemical Society, Copyright 2021 The Authors, CC BY 4.0., Copyright 2009 WILEY-VCH Verlag GmbH Co. KGaA, Weinheim, Copyright 2016 The Authors, CC BY 4.0.

polarimetry [238, 239] or transmission-mode XRD [240] have been reported. At fibre diameters below < 200 nm, under the diffracting limit, Raman spectromicroscopy produces inaccurate order/alignment parameters due to the birefringence and surface curvature. [222, 241] If one wishes to elucidate the orientation of individual crystallites within nanoscale fibres, there is limited choice. Advances in nanoprobe XRD may unlock the potential for nanoscale spatial resolution in the future (~ 40 nm) [242] but to my knowledge has not yet been applied to electrospun fibres. Instead, this has only been applied to thicker melt-spun or natural fibre specimens, as nanoscale electrospun fibres offer low SNR.

Alternatively, individual electrospun fibres may be probed by select area electron diffraction (SAED), producing similar data to bulk X-ray studies upon single fibres.

[243, 244] Via this technique, preferential P3HT crystallite alignment has been revealed in fibrous materials. In Figure 4.4a, the presence of (020) and (100) diffraction spots perpendicular to the electrospun fibre suggests the backbone direction (001) lies along the fibre. Self-assembled P3HT fibres assemble most effectively along in the $\pi - \pi$ stacking direction. Therefore these fibres commonly show the opposite preferential orientation to typical electrospun fibres, with the polymer backbones orthogonal to the fibre [209, 232, 208, 245] (see Figure 4.4c - d), however there are exceptions to this rule (see Figure 4.4b). [246]

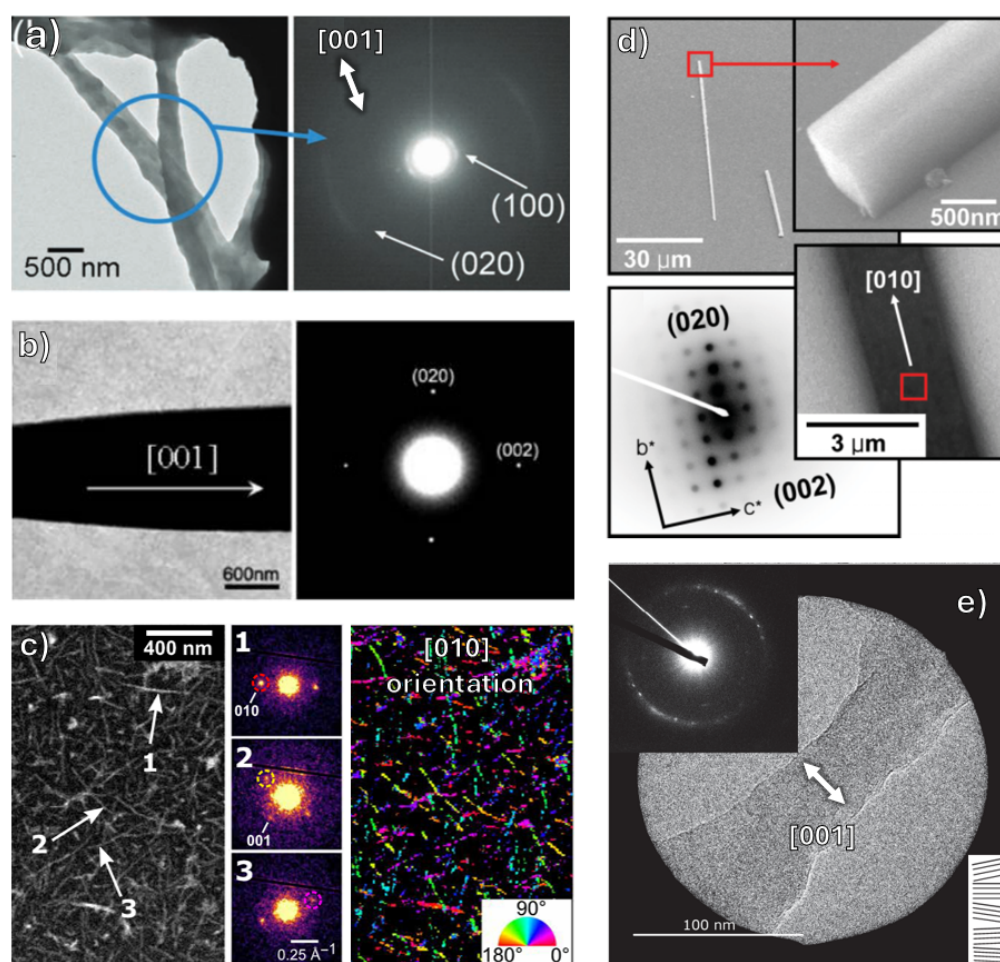


Figure 4.4: Electron diffraction patterns and accompanying TEM/STEM images of (a) electrospun P3HT:PCBM fibres and (b - e) self-assembled nanofibres grown via various protocols, revealing preferential polymer backbone orientation either along or across the fibre axis. Reprinted (adapted) with permission from references [61, 246, 245, 208, 232], respectively. Copyright 2012 WILEY-VCH Verlag GmbH Co. KGaA, Weinheim, Copyright 2010 American Chemical Society, Copyright 2021 The Authors, CC BY 4.0., Copyright 2006 WILEY-VCH Verlag GmbH Co. KGaA, Weinheim, Copyright 2012 The Royal Society of Chemistry.

In electron diffraction experiments, $\pi - \pi$ stacking is typically observed, whilst the (100) lamellar spacing can often be eclipsed by the central direct-beam disc due to its large inter-spacing of ~ 1.6 nm unless a highly-focussed beam and long camera length are used, despite its strong diffraction. Pristine crystals produce a well-defined series of diffraction spots, (Figure 4.4d [208]) whereas other materials generate several or a continuum of Bragg spots at various azimuthal angles, indicating the presence of several misaligned crystallites or an amorphous phase (Figure 4.4e [232]). This is the expected case with electrospun P3HT-containing fibres (Figure 4.4a [61])

The use of a nanobeam under STEM conditions allows researchers to provide high spatial resolution, where a diffraction pattern is collected at each scanned position - offering the potential to locate and determine the orientation of individual crystals within polycrystalline samples, as demonstrated with seed-grown P3HT nanowires. [247] This technique when applied to the investigation of polymeric material is not trivial due to their beam sensitive nature. [247] Radiolysis of polymeric materials causes scission and cross-linking, resulting in a loss of crystallinity. [248] Even so, combining low beam dosages of a few $e^- \text{ \AA}^{-2}$ with cryogenic conditions and ‘blind selection’ procedures, researchers have been able to collect 4D-STEM measurements of crystalline polymers, [249] including P3HT [245, 250] (see Figure 4.4c). The structure of amorphous P3HT films may then be probed by the pairs distribution function (PDF), or an orientation map of the crystallites in self-assembled nanofibres can be produced from the angle between the (020) Bragg spot and the fibre axis.

4.2.2 H-/J-Aggregation

The optical properties of supramolecular assemblies (aggregates) are distinct from the isolated chromophore due to intermolecular interactions; spectral shape cannot be explained by a standard Franck-Condon progression. Molecular packing influences the interaction between neighbouring chromophores as transition dipoles may interact either side-by-side or head-to-tail to form H-aggregates or J-aggregates, respectively. [20]

In H-aggregates, the molecules are generally oriented side-by-side due to $\pi - \pi$ stacking. [251] This allows for parallel transition dipole coupling between adjacent molecules,

and the exciton can delocalise over the interacting molecules. This interaction may be constructive or destructive, leading to energy splitting in Figure 4.5. [33] In the lower energy state, the dipoles cancel out (the transition is forbidden). Meanwhile, in the higher energy state, the vector sum of the dipoles is non-zero. [33] Therefore, the optically allowed transition involves the higher energy state, resulting in a blue-shift in the absorption spectrum. [252] Additionally, as fluorescence occurs primarily from the lowest excited state, and emission from this state is optically forbidden, radiative decay of the excited state is attenuated. In vibronic systems, Spano explained that vibronic coupling partially allows transitions involving the higher vibronic states e.g. (0-1) and (0-2), whilst (0-0) remains forbidden. [33, 252]

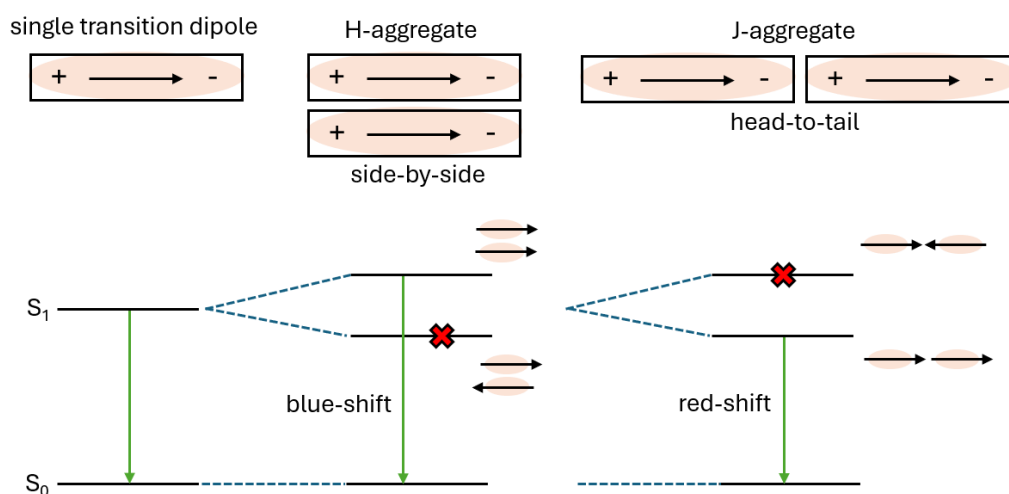


Figure 4.5: Energy diagram schematic of the ground and excited energy states of two electronically coupled chromophores oriented in a side-by-side(head-to-tail) manner, producing a H(J)-aggregate. The in-phase and out-of-phase interactions of the transition dipoles (which lie along the axis of the conjugated segment) cause energy splitting, and transitions involving the lower energy state are optically forbidden (allowed) in H(J)-aggregates.

Alternatively, in J-aggregates, the chromophores and transition dipole interactions are arranged in a head-to-tail orientation. [251] In this regime, the selection rules are now inverted - the dipoles cancel out for the higher energy interaction, whilst the net transition dipole moment is enhanced for the lower energy state, leading to a red-shift in absorption (Figure 4.5). Furthermore, the (0-0) transition is allowed, meaning J-aggregates possess faster radiative decay rates. [33] Faster charge generation has also been reported for J-aggregates, resulting in improved PCE. [253]

Organic semiconductor polymer chains have been previously described as unconventional J-aggregates, being a series of bonded chromophores (repeat units or conjugated segments) arranged in a head-to-tail-like fashion. [252] However, P3HT thin-films typically present H-aggregate behaviour. This arises from dominant intermolecular interactions due to close π - π stacking, and weak intrachain coupling due to disorder along the backbone arising from rapid solvent evaporation and disruption by amorphous chains. [254] Hence, the (0-0) vibronic transition is optically forbidden, yet in reality, the intensity of the (0-0) transition is 0.5 - 0.9 relative to (0-1) due to thermal excitation and defects. [254]

However, in self-assembled [254] or electrospun P3HT nanofibres, improved order/planarization in the backbone direction (induced by the elongation of the forming fibre in the case of electrospinning) may enhance the head-to-tail coupling of chromophores along the chain. [254] As a result, the intensity ratio of the (0-0)/(0-1) transition can exceed 2. [254]

Hence, Spano and co-workers developed the HJ-aggregate model to describe the behaviour of conjugated polymers, which possess intrachain (J-like) and interchain (H-type) interactions. [255] P3HT aggregates may exhibit either H-type (dominant interchain coupling) or J-type (dominant intrachain coupling) behaviour depending on the molecular packing. Therefore, the processing method of organic semiconductors can heavily influence its spectral shape.

4.3 Morphology and Composition of Electrospun P3HT Nanofibres

4.3.1 Phase Separation and Selective Dissolution of PEO

Sulfur atoms in the thiophene ring of P3HT and the oxygen-rich backbone of PEO provide means of determining their spatial distribution within the blend fibres. In Figure 4.6b - c, the EDX line scan across the PEO-reduced AgNP-containing P3HT/PEO nanofibre reveals that the lower viscosity P3HT and higher viscosity PEO polymers phase separate during electrospinning to produce an enriched P3HT core and PEO sheath, depicted in Figure 4.6a. This phenomenon was first reported by Kim et al. who determined this core-shell structure was energetically favourable. [67] Figure A.4.1 presents the EDX

spectra collected in STEM from which linescans were generated, alongside the carbon and silver linescans and elemental mapping (Figure A.4.2) of the as-spun fibre in Figure 4.6b. Procedural details of collection are presented in Sections 2.2.1.3 - 2.2.1.4.

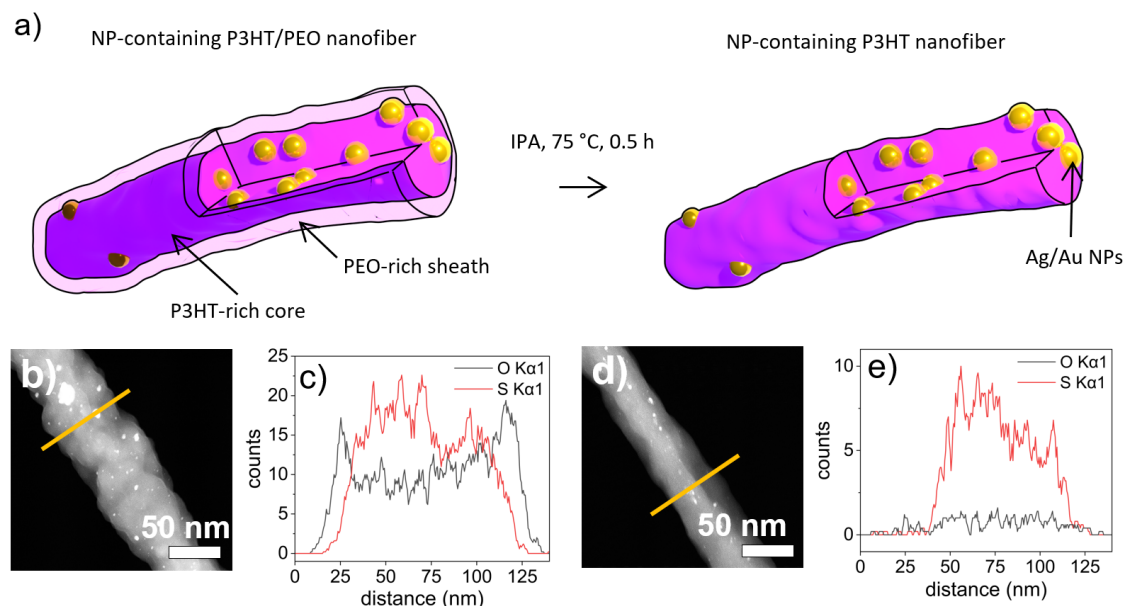


Figure 4.6: (a) Schematic of as-spun and washed PEO-reduced AgNP-containing P3HT nanofibres. (b – c) EDX line scan of an as-spun NP-containing P3HT/PEO nanofibre showing phase separation of the two constituent polymers into a P3HT-enriched core and PEO-enriched sheath. (d – e) EDX line scan of nanofibre after PEO removal revealing reduced oxygen content.

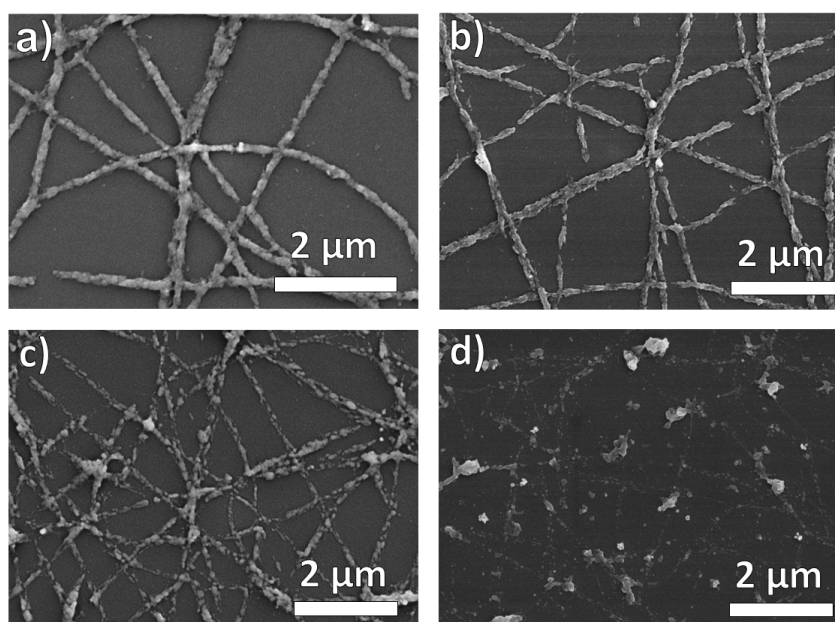


Figure 4.7: SEM micrographs of NP-containing P3HT nanofibres after selective removal of PEO spun from solutions containing (a) 0.25 wt%, (b) 0.15 wt%, (c) 0.10 wt% and (d) 0.05 wt% P3HT, presenting increasing discontinuity upon reduced the P3HT content.

A greater proportion of X-rays with the characteristic wavelength for oxygen were collected when the probe samples at the outer 20 nm of the fibre than were measured at the centre, in line with the expected profile shape for a PEO sheath. Concurrently, sulfur was entirely undetected within the outermost 10 nm of the material, inside of which it increased steadily to a maximum count close to the centre of the fibre as anticipated. These findings confirm that nanoparticle presence does not interfere with or reduce the ability of the polymers to separate from each other to form a preferable core-shell structure for PEO removal.

As the auxiliary polymer, PEO, is insulating, it is vital that it is removed to restore the charge transport properties of P3HT. To this end, the formation of a sheath is advantageous as it reduces the chance of isolated PEO domains forming within the fibre core which would prove difficult to remove. Equally, it is essential for long-range charge transport that the core is uninterrupted to form continuous P3HT nanofibres after washing. In Figure 4.7, increasingly discontinuous fibres are obtained when the P3HT solution content is reduced to ≤ 0.10 wt%, likely because the core becomes disconnected. With the blend fibre containing $\leq 22\%$ P3HT by weight, the original fibre morphology is lost after washing. Fibres spun from solutions containing 0.15 wt% P3HT were considered as the best compromise between fibre continuity and diameter - important contributors towards the fibres' exciton dissociation ability and charge transport.

Within this work, the efficacy of PEO removal was determined using a TGA isotherm held at 370 °C for 1 h under N₂ [65, 67, 63]. This determined that washing was effective at removing up to 98.5% of PEO (Figure 4.8b-c). This isothermal temperature completely degraded PEO, whilst the mass of P3HT was negligibly affected. Acetonitrile, used during device fabrication in Chapter 5, offered a lower effectiveness, leaving a 5% PEO residual, and without heat, the efficacy of IPA to leech out the auxiliary polymer was reduced with $>50\%$ of fibre still PEO, shown in Figure A.4.3. The dynamic temperature scan of the washed fibres in Figure 4.8a shows the washed fibres follow the thermal trace of pristine P3HT.

The near-complete removal of PEO was supported by EDX scans and the pXRD diffractogram in Figure 4.6d-e and Figure 4.8d. The oxygen count integration reduces

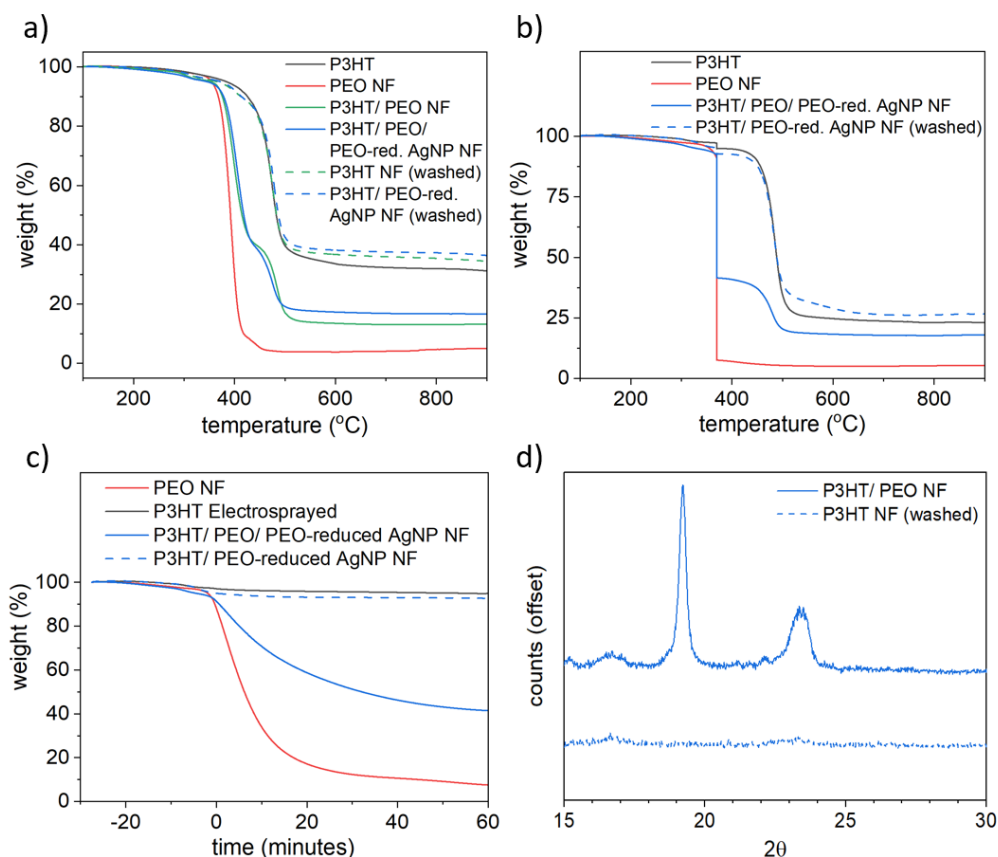


Figure 4.8: TGA thermograms of (a) a dynamic temperature scan of P3HT, PEO NFs, and P3HT-based NFs under nitrogen before and after PEO removal between 100 and 900 °C heated at 10 °C min⁻¹. (b,c) Dynamic temperature scan to 370 °C followed by a 1 h isotherm employed to determine the PEO residual after washing. (d) XRD traces of P3HT/PEO nanofibres and after washing.

from 1230 to 140, a relative loss of around 89%. A lesser oxygen count reduction was expected due to oxidation of P3HT in air during sample preparation. [256] XRD shows a complete loss of PEO's (120) and (112) reflections at 19.2° and 23.4° 2θ upon washing.

To avoid delamination of the nanoweb from the substrate once submerged in the hot solvent, nanowebs were heated to 70 °C (above the T_g of PEO) within a dry, nitrogen atmosphere for 2 minutes prior to washing. This pre-treatment was essential to partially melt the web and improve adhesion with the substrate. Alternatively, the nanoweb could be intentionally peeled off the substrate as a free-standing, robust material (Figure 4.9a-b) - a potential route to future solar fabrics. The P3HT/PEO web is strong, flexible and conforms to irregularly-shaped surfaces. After washing, the fibre morphology was largely retained with impressive continuity. (Figure 4.9c-d) However, the washed P3HT fibre

mats were fragile and brittle, and less suitable for photovoltaic cloths.

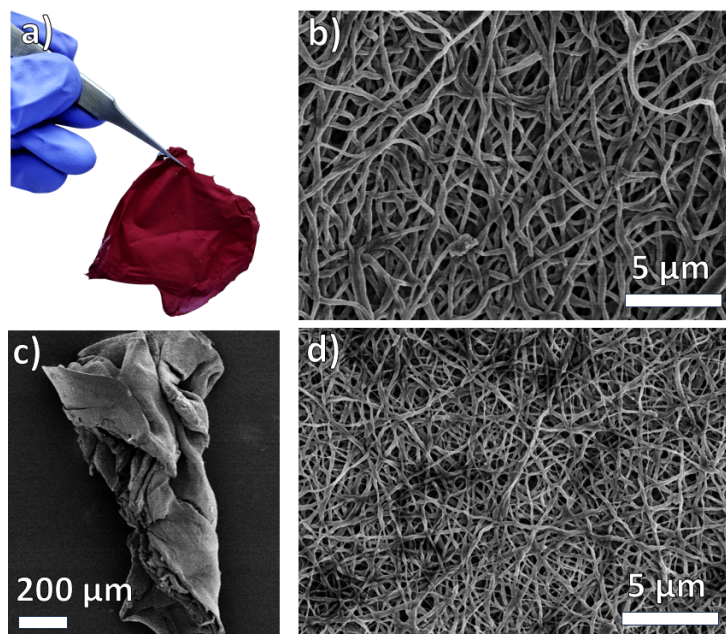


Figure 4.9: (a) Digital photograph and (b) SEM micrograph of P3HT/PEO free-standing nanoweb delaminated from the substrate. (c,d) SEM micrographs of the delaminated P3HT fibre mat following the washing procedure (solution contained 0.25 wt% P3HT).

4.3.2 Influence of P3HT Material upon Washed Fibre Morphology

The morphology of the final P3HT nanofibres was highly dependent upon the source of the P3HT polymer. Variance was observed in continuity, degree of slumping, surface texture and fusion at the junctions between fibres.

These studies explored three commercial polymers: two sourced from Rieke Metals, the first, RMI-001E (49 kDa, 2.0 polydispersity (PDI), 95% regioregularity (RR)), is produced by Rieke chemistry using a Zn/Ni catalyst, and the other, 4002-E, is prepared by oxidative addition (50 kDa, 2.8 PDI, 91% RR). The third was purchased from Ossila (M107, 24 kDa, 2.8 PDI, 94% RR). An exemplar P3HT/PEO fibre mat is shown in Figure 4.10a-b prior to washing. Each as-spun web was visually identical in morphology, texture and diameter, regardless of the starting material. However, after the washing step, the difference is apparent.

RMI-001E P3HT, used in Chapter 3, retains its fibre structure most effectively. The thicker mat in Figure 4.10c - d retained better continuity than the isolated fibres used for dimension measurements in Chapter 3. The fibre surface texture is rough and

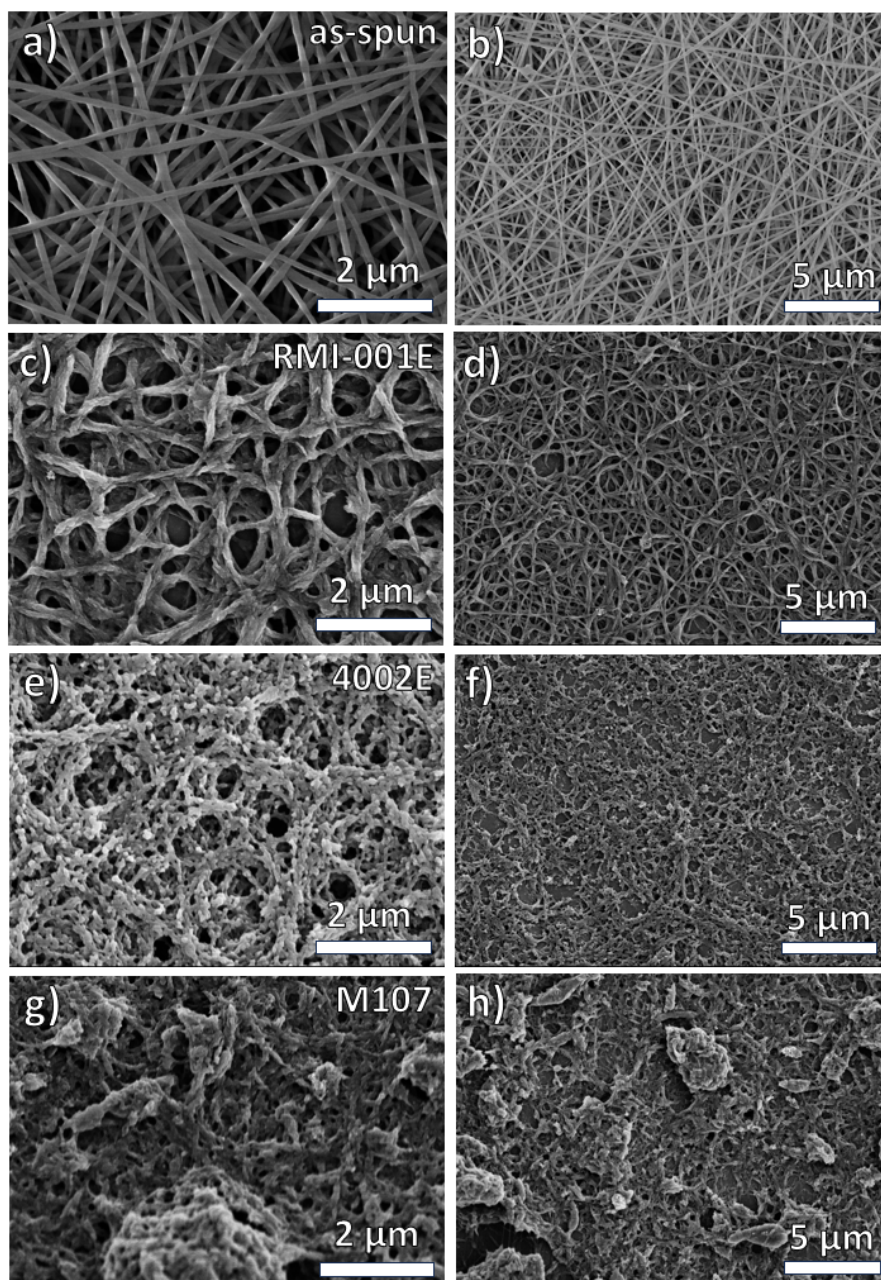


Figure 4.10: SEM micrographs of (a,b) as-spun P3HT/PEO nanoweb and (c - h) washed P3HT fibres prepared using Rieke Metals-sourced (c,d) RMI-001E P3HT and (e,f) 4002-E, and Ossila-sourced (g,h) M107, showing the variance in final structure with different starting materials.

comparatively, the fibre junctions possess low levels of fusion. The 4002-E materials present a distinctly different morphology. These fibres are thinner and shorter, possess smoother surfaces and contacting fibres are highly fused. Prospectively, RMI-001E-based fibres may be optimal for in-plane charge transport due their continuity, however for vertical transport, the fused junctions of 4002-E may be advantageous for fibre-to-fibre

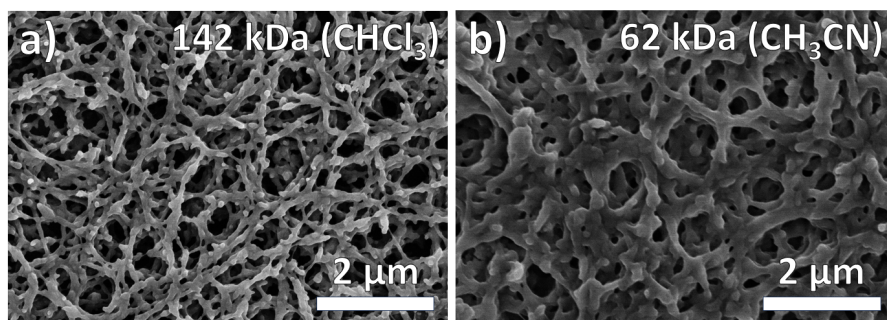


Figure 4.11: SEM micrographs of washed P3HT nanofibres electrospun using P3HT starting materials synthesised by oxidative addition with an FeCl_3 catalyst in (a) chloroform and (b) acetonitrile.

carrier transfer. M107 P3HT delivered a rough texture, however, the fibre structure was degraded and large fibre agglomerates were adhered to the surface. These micron-sized structures may present encapsulation issues if incorporated into devices.

Additionally, two polymers were prepared by the oxidative addition of 3-hexyl thiophene (3HT) in the presence of an FeCl_3 catalyst under an inert environment. The characterisation of these polymers may be found in Figure A.4.4. A 142 kDa and 62 kDa analogue were prepared in either chloroform or acetonitrile, respectively with a low RR of 66 - 68%. Again, the P3HT/PEO fibres were indistinguishable, but after washing produced a morphology similar to 4005-E, also prepared by oxidative addition. The higher Mw derivative produced thinner diameter fibres and underwent a lesser degree of spreading, as depicted in Figure 4.11. Therefore, the molecular weight, RR, and method of P3HT synthesis should be considered when selecting a starting material - the eventual choice will depend on the desired diameter, texture and fusion.

4.3.3 Nanoparticle Dispersion

Due to the stability of the nanoparticle dispersion over the duration of the spinning solution ageing time, and repulsion generated between nanoparticles when an electric field was applied, the dispersion within the final fibres is very effective. As a result, STEM and TEM analyses in Figure 4.12 and 4.13 reveal that the particles exist overwhelmingly as single, primary particles with low prevalence of aggregation. The higher atomic weight and crystallinity of Ag and Au NPs produces good contrast with the polymer matrix allowing them to be imaged. Therefore, the nanoparticles appear darker in the BF image

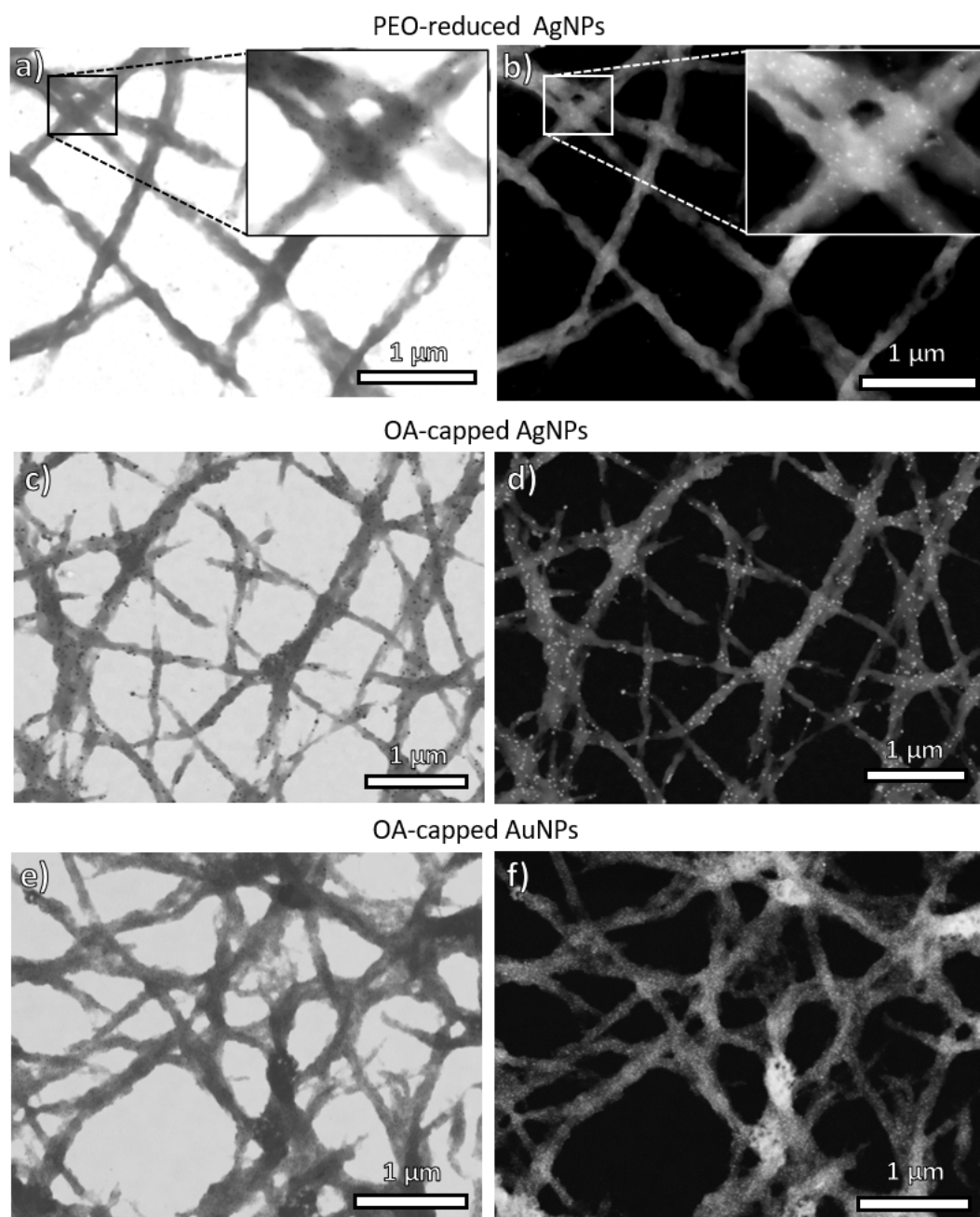


Figure 4.12: (a,c,e) BF and (b,d,f) ADF STEM-in-SEM micrographs of NP-containing P3HT fibres showing primary particle dispersions and low prevalence of aggregates with (a,b) PEO-reduced AgNPs, (c,d) OA-capped AgNPs and (e,f) OA-capped AuNPs.

and brighter in the ADF micrograph due to greater deflection of the direct beam. Good dispersion is advantageous as aggregation lowers the plasmonic intensity, and presents potential shorting pathways and charge trapping sites.

Material cost of the silver or gold is significant, therefore it is important to quantify the proportion of nanoparticles lost during the washing step. This suggests that In

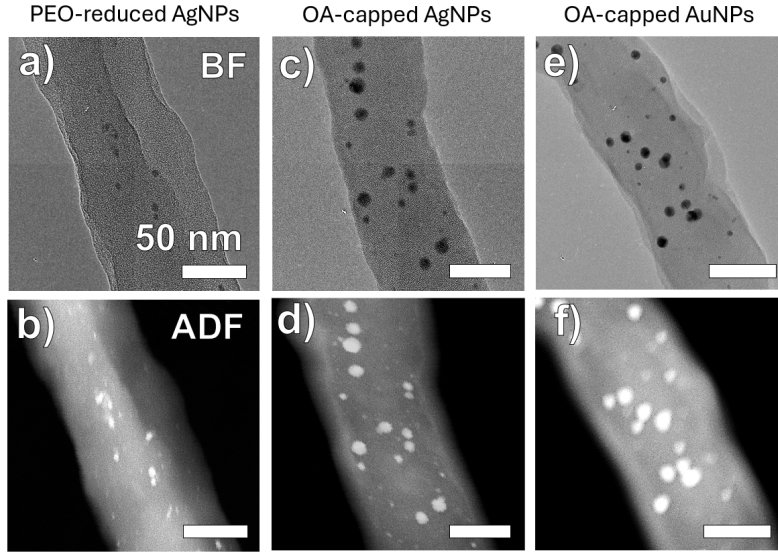


Figure 4.13: STEM (a,c,e) BF and (b,d,f) ADF micrographs of NP-containing P3HT nanofibres showing effective primary particle dispersions of (a,b) PEO-reduced AgNPs, (c,d) OA-capped AgNPs and (e,f) OA-capped AuNPs. The TEM microscope was operated by George Tebbutt.

Figure 4.14, the mass residual after heating washed pristine (4.48%) and washed PEO-reduced AgNP-containing fibres (11.18%) to 900 °C is shown. Comparing the residuals, it is estimated that ~85% of the nanoparticle mass can be retained, calculated from the 6.7% residual discrepancy. The estimated silver content displayed in Table 4.1 was determined by Equation 4.1 (methodology is outlined in Section 2.2.4.3). The washed P3HT/PEO-reduced AgNP fibre produces a greater weight residual than its as-spun counterpart, as after PEO removal, the silver content represents a larger mass percent suggesting significant NP retention.

$$R_{\text{NP-containing}} = X_{\text{Ag}} + R_{\text{pristine}} \left(1 - \frac{X_{\text{Ag}}}{100} \right) \quad (4.1)$$

Where R is the final TGA is residual of the washed pristine and nano particle-containing fibres and X_{Ag} is the final silver content in %.

Under air, the polymers are degraded further than is achieved under nitrogen. Under nitrogen, P3HT leaves a 25 wt% residual at 900 °C (Figure 4.8a), however in air, P3HT degrades via a two-step process leaving a residual of just 2 wt%. This produces smaller, consistent residuals allowing for more accurate estimations of the silver content.

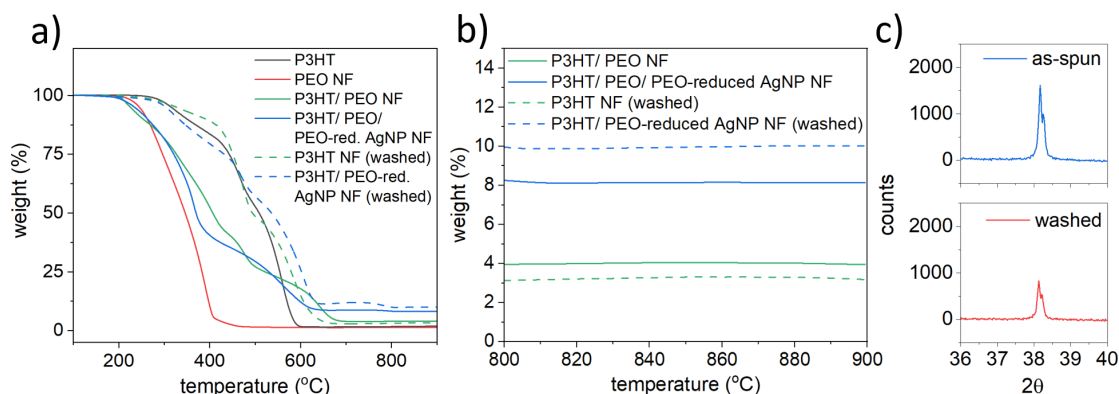


Figure 4.14: (a) TGA thermograms of NFs involving a 100 °C to 900 °C thermal scan at a ramp rate of 10 °C min⁻¹ in air. (b) Example ‘close-up’ of the weight residuals at 800 °C – 900 °C from which nanoparticle retention upon PEO removal is estimated. AgNO₃ concentration was 10 wt% wrt PEO and P3HT concentration was 0.25 wt% in the spinning solution. (c) XRD diffractograms of as-spun (top) and washed (bottom) PEO-reduced AgNP-containing P3HT fibres showing the (111) diffraction planes of PEO-reduced AgNPs at 38.1° 2θ. Nanoparticle retention could also be estimated from the count integration.

Sample	Residual at 900 °C (%)
Washed P3HT NF	4.48 ± 1.78
Washed P3HT/ PEO-red. AgNPs NF	11.18 ± 1.18
Residual difference	6.7
Estimated silver content	7.0
Silver content assuming full retention	8.2
Nanoparticle washing retention	85.3

Table 4.1: Thermogram residuals at 900 °C for washed P3HT and P3HT/PEO-reduced AgNP NFs from which nanoparticle retention upon washing. Estimated silver content calculated using Equation 4.1.

In Figure 4.14c, area integration of the Ag (111) X-ray scattering intensity in PEO-reduced AgNP-containing fibres before and after washing suggests a more modest retention of 50%, closer to the mass proportion of PEO removed. Due to the P3HT:PEO ratio of 0.25:0.35 wt% in solution, the washing step removes up to 55 wt% of the fibre mass (PEO), therefore 50 - 85% retention is considered reasonable. Whilst, OA-capped NP retention was not explored, it is expected to be in line with that of PEO-reduced AgNPs.

4.3.4 P3HT Crystallinity

Essential to OPV performance, pXRD was employed, as described in Section 2.2.4.1, to establish whether the electrospun fibres contain high-quality crystallites, vital for charge mobility, and ensure that nanoparticles do not have an adverse impact upon

P3HT crystallisation. First, the change in scattering behaviour of as-spun nanofibres as they are processed by washing and then annealing, was investigated to determine the influence of the heat-treatment processes.

Pristine P3HT nanofibres were used to establish a ‘baseline’ for electrospun crystallisation, shown in Figure 4.15a and Table 4.2. The (100) reflection of P3HT lamellar stacking in the as-spun fibres gives rise to a strong, broad peak centred at $5.51^\circ 2\theta$, corresponding to a d-spacing of 1.60 nm. The peak FWHM was $0.75^\circ 2\theta$. Assuming that crystallite size is the dominant source of peak broadening, this suggests the crystalline P3HT domains possess a coherence length of 10.6 nm in the alkyl-stacking direction, as estimated using the Scherrer equation (Equation 2.5). [232] Higher order (200) and (300) reflections were also observed at 11.06° and $17.67^\circ 2\theta$. The (020) reflection was contrastingly weak at $\sim 24^\circ 2\theta$. Periodicity in the (00l) backbone direction is not typically observed in semi-crystalline P3HT structures.

Upon washing, the polymer is exposed to an elevated temperature of 70°C for 1 h. Whilst this temperature is low compared to typical annealing temperatures of 120°C - 150°C [40], the crystallite d-spacing and coherence length rises to 1.63 nm and 12.3 nm, respectively. Conventional annealing at 120°C for 20 minutes under N_2 did not induce further changes to the inter-spacing and crystallite size.

To isolate the effect of electrospinning on crystallisation, the XRD characteristics of fibres are compared and contrasted with a spin-coated film. Annealed P3HT films gave rise to an identical (100) d-spacing of 1.64 nm and a lower crystallite size at 9.4 nm. In Figure 4.15c, the film’s (100) count integration was twice that of the nanofibre, however despite the equalisation of sample mass, it is not suitable to make comparisons about the extent of crystallinity. In pXRD, diffraction is collected exclusively in the OOP direction and therefore the detected X-rays are scattered from planes parallel to the substrate. As neither sample is expected to contain a random array of all possible crystallite orientations, one cannot make these comparisons.

As discussed in Section 4.2, thin-films of polyalkylthiophenes commonly possess favoured orientations wrt the substrate and air interfaces. On the other hand, there are numerous reports of crystallite alignment along the axis of various polymeric electrospun

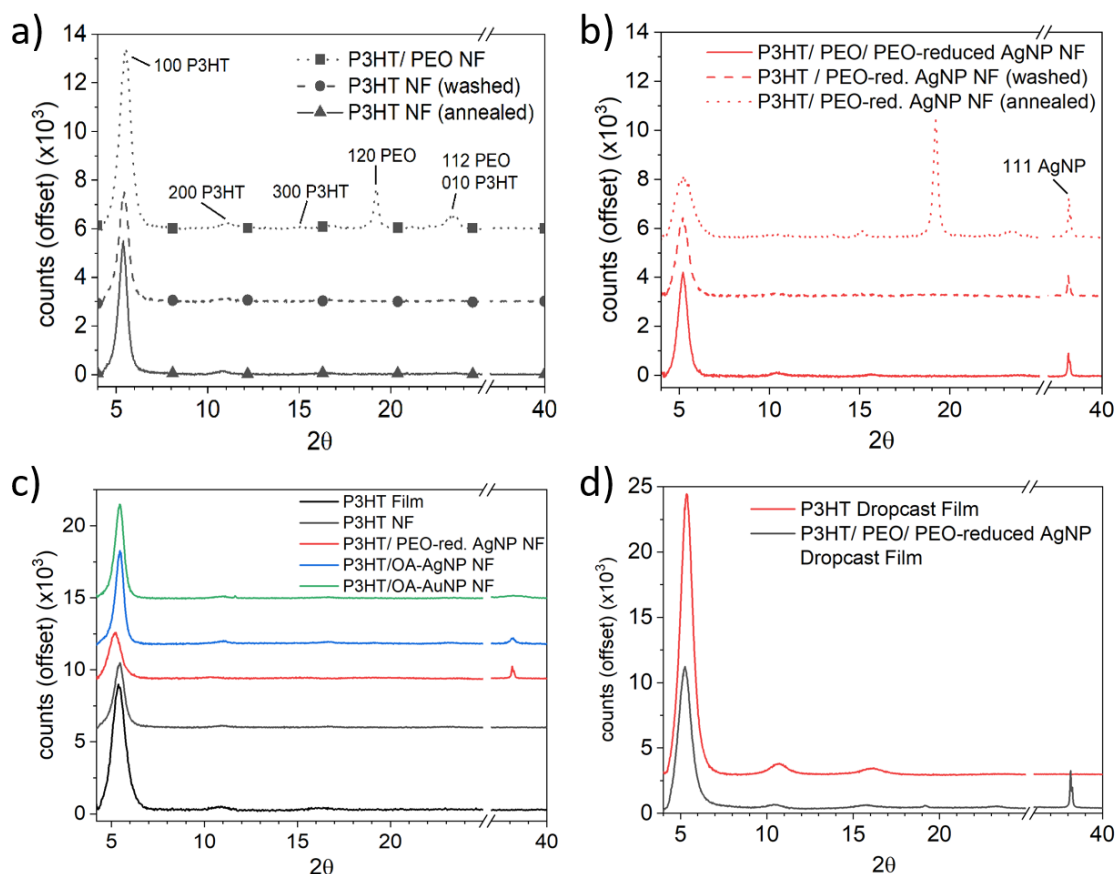


Figure 4.15: X-ray diffractograms of as-spun, washed, and annealed (a) pristine P3HT nanofibres and (b) PEO-reduced AgNP-containing nanofibres. (c) XRD traces of P3HT films, fibres and nanoparticle-containing fibres and (d) of the P3HT film compared to a film cast from the PEO-reduced AgNP-containing spinning solution. Samples were submitted to OMCS for characterisation and run by Dr Phillip Holdway.

fibres. One would also expect that fibres provide a lower preference for a single configuration due to the twisting of the jet in flight. Fibre crystallite alignment is investigated using a 2D detector in Section 4.5.2. Overall, the electrospun fibres contain well packed and larger crystallites versus the equivalent thin-film. In the remainder of this chapter, evidence is presented which suggests that minimal P3HT crystallisation occurs during electrospinning, but this is offset by crystals forming in the solution prior to spinning.

The addition of PEO-reduced AgNPs to P3HT nanofibres in Figure 4.15b saw a rise in the (100) inter-spacing to 1.70 nm (5.19° 2θ) and reduction in crystallite size to 7.1 nm. This adverse impact upon crystallisation suggests that nanoparticles perturb side chain interdigitation, the interlocking of the alkyl chains from two polymer backbones stacked in the (h00) direction, leading to a greater interlayer spacing. Akin to pristine

Sample	Peak Position (° 2 θ)	D-spacing (nm)	FWHM (° 2 θ)	Crystallite size (nm)
P3HT Film	5.38	1.64	0.85	9.4
P3HT/PEO-reduced AgNP NF				
as-spun	5.19	1.70	1.11	7.1
washed	5.18	1.70	0.78	10.2
annealed	5.12	1.72	0.66	12.1
film	5.24	1.69	0.85	9.4
P3HT NF				
as-spun	5.51	1.60	0.75	10.6
washed	5.43	1.63	0.64	12.3
annealed	5.39	1.64	0.64	12.3
P3HT/ OA-AgNP NF				
washed	5.46	1.62	0.53	14.9
P3HT/ OA-AuNP NF				
washed	5.45	1.62	0.61	13.0

Table 4.2: Crystallite characteristics extracted from the X-ray diffractograms of P3HT thin-films and nanofibres.

fibres, the thermal energy during washing led to an increase in the crystallite size by 30%, to 10.2 nm, which further rose to 12.1 nm upon annealing - now equal to the pristine fibres. Concurrently, the (100) d-spacing rose marginally - the thermal post-processing did not encourage interdigitation. There is no systematic disruption to crystallisation from nanoparticle addition, as more promising crystallite character was generated from electrospinning OA-capped NP-containing solutions. These fibres possess a lamellar spacing of 1.62 nm, and greater crystallite coherence lengths of 14.9 and 13.0 nm for the Ag and Au analogues, respectively.

Films cast from the PEO-reduced AgNP-containing P3HT/PEO solution also possess the expanded lamellar spacing of 1.69 nm, demonstrating that it is not an effect of spinning. The as-spun, un-annealed film had a crystallite coherence of 9.4 nm - equal to the annealed thin-film. In conclusion, the electrospun P3HT fibres contain crystallites with a greater size than films, however the addition of AgNO₃/PEO-reduced AgNPs created expanded spacings with potentially undesirable effects upon carrier mobility.

4.4 Optical Behaviour of Nanowebs: Absorption and Scattering

4.4.1 Increased J-Aggregate Character

Due to their curvature, roughness and high surface area, the electrospun fibres are efficient light scatterers, complicating their optical analysis. For thin-films, linear transmission/absorbance measurements are a good approximation for the light absorption. However, with fibres, linear transmission measurements are insufficient to determine absorption properties with significant ‘absorbance’ beyond 700 nm, where P3HT does not typically absorb (unless for pristine single crystals). [257] (Figure 4.16a) Fibre scattering means a linear transmission set-up provides an extinction measurement (scattered + absorbed). Deconvolution would be very difficult, therefore to compare absorption spectra, a combination of total transmittance and reflectance measurements using an integrating sphere were collected (described in Section 2.2.2.1). Once processed, the total fibre absorptance may be observed with a near-zero absorption above 700 nm, proving successful consideration of the scattering effects.

These measurements reveal that electrospinning P3HT produces two main spectral effects, a red-shift in absorption and a concomitant enhancement in the (0-0) vibronic transition. Comparison between the pristine P3HT thin-film and fibres shows a shift in the (0-0) transition from 607 nm to 613 nm, and the (0-1) transition shifts by 7 nm, to 563 nm. Red-shift arises from elongation of the polymer chains under the shear stress of the spinning process. The planarized polymer backbone leads to an increase in the conjugation length, reducing the energy gap of the $\pi - \pi^*$ transition. In thin-films, red-shifting may only be achieved via thermal annealing treatment.

Electrospinning appears to enhance the absorptance intensity ratio between the (0-0)/(0-1) vibronic transition from ~ 0.78 (film) to ~ 0.91 (fibres) in Figure 4.17a. This is indicative of increased J-aggregate character as described by *Spano et al.* [258, 252, 254] Films typically display H-aggregative behaviour as co-facial $\pi - \pi$ interactions are favoured, meaning that excitons are preferentially delocalised between neighbouring molecules due to dominant interchain interactions. H-aggregates possess a dipole-forbidden (0-0) transition,

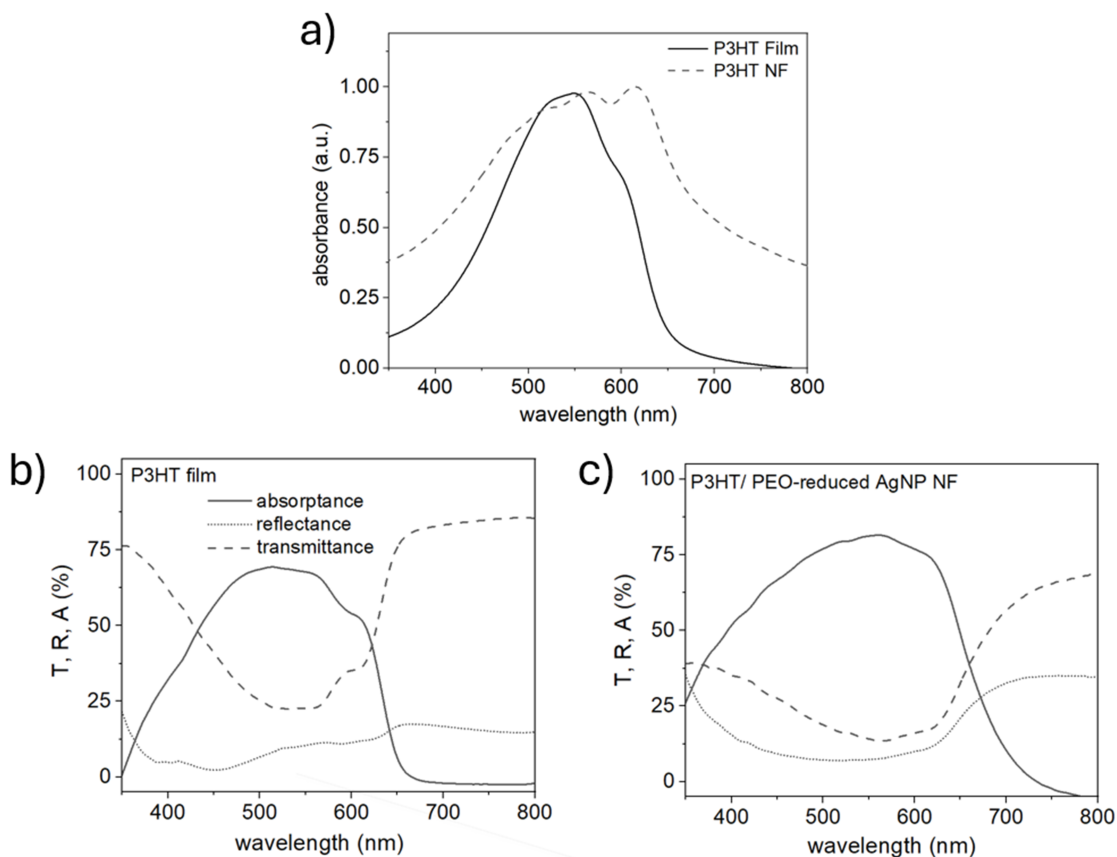


Figure 4.16: (a) Extinction spectra of P3HT film and PEO-reduced AgNP-containing P3HT NFs (absorbed + scattered radiation) obtained by classical linear transmission. Absorbance of the (b) P3HT film and (c) nanofibres as determined by combined total transmittance and reflectance measurements collected using an integrating sphere. Greater diffuse scattering is recorded for fibre specimens.

only enabled by thermal excitation or defects, which attenuates its absorbance intensity to ~ 0.5 to 0.8 of the second (0-1) transition.

J-aggregate character in electrospun fibres increases due to chain planarization and an increase in conjugation length, promoting coupling between conjugated segments oriented in a J-like, head-to-tail manner along the polymer chain backbone. Resultantly, the exciton is increasingly delocalised along the chain, rather than between chains. [252]

Upon nanoparticle introduction, J-type feature dominance increases very slightly with the ratio rising (0-0)/(0-1) to 0.92, 0.93 and 0.96 for PEO-reduced AgNPs, OA-capped AgNPs and OA-capped AuNPs, respectively. Instead of nanoparticles causing disruption, the diameter reduction following nanoparticle addition may create a greater extent of polymer chain alignment preventing this perturbation. PEO-reduced AgNP-containing

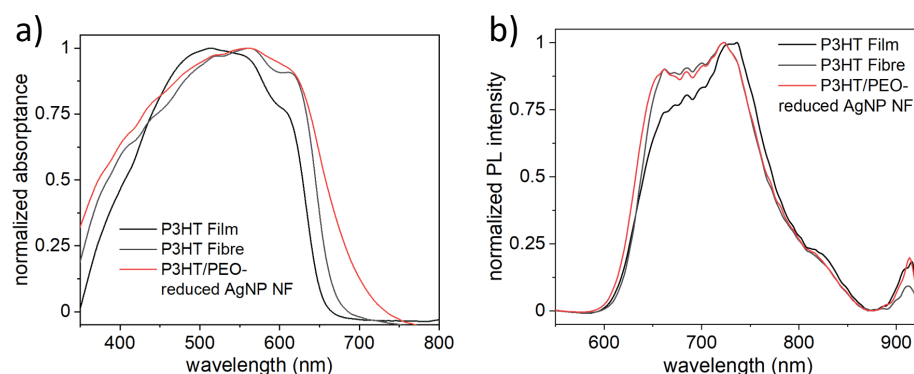


Figure 4.17: (a) Absorbance spectra determined by combined reflectance and transmittance measurements and (b) PL emission spectra of P3HT spin-coated films and electrospun fibres revealing increased J-aggregate character and red- and blue-shift, respectively. PL spectra were collected by Karim Elmostekawy. The artefact just beyond 900 nm represents second order Rayleigh scattering of the excitation laser, observed at twice the excitation wavelength.

fibres produced less resolved vibronic peaks versus the other spectra indicative of greater amorphous content in the matrix, which generate a continuum of absorption energy levels rather than the more discrete vibronic energies of P3HT crystallites. The higher absorption by fibres below 450 nm corroborates that fibres may contain greater amorphous content.

Both blue-shift and enhanced J-aggregate dominance are also observed in the PL emission spectra, shown in Figure 4.17b. The (0-1) transition shifts by around 8 nm, from 730 (film) to 722 nm (fibres). Simultaneously, the ratio between the (0-0) and (0-1) transition is enhanced from 0.73 to 0.90.

4.4.2 Nano-precipitation upon DMF Addition

Absorbance measurements of the spinning solution in Figure 4.18 reveals that DMF addition or ageing of the spinning solutions induces the formation of nano-precipitates as the orange, translucent solution, indicative of well-dissolved P3HT, becomes opaque, particularly upon cooling to room temperature prior to spinning. The pristine P3HT or OA-capped NP-containing solutions (with or without DMF addition) form a dark red-purple colour whilst the PEO-reduced AgNP-containing solutions become dark brown. This nano-precipitation was demonstrated through the addition of 5 wt% DMF to a P3HT solution in chloroform. The initially well-dissolved P3HT provides a $\pi - \pi^*$ transition absorption centred at 451 nm, however following non-solvent introduction, vibronic peaks associated with solid form P3HT appear. In fact, the use of orthogonal/poor

solvents is a well-reported strategy to producing self-assembled P3HT nanofibres. [232, 254, 259] However, based upon the ratio of the (0-0)/(0-1) transition in solution, these nanostructures display H-type character.

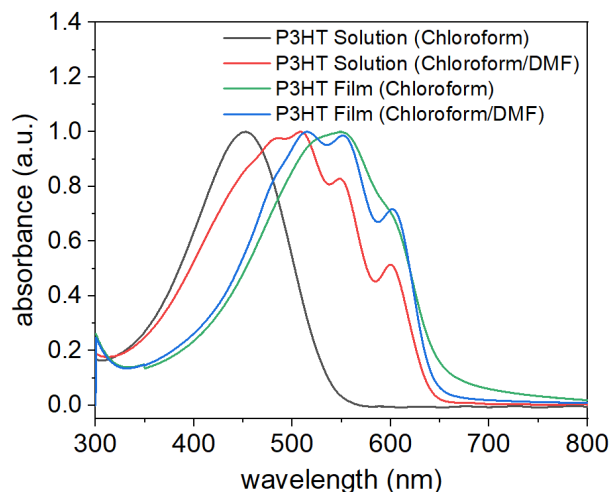


Figure 4.18: UV-Visible absorption spectra of P3HT solutions dissolved in chloroform and chloroform/DMF (non-solvent), and thin-films spin-coated from the each solvent system. The evolution of vibronic peaks suggest that crystallites are self-assembled in the spinning solution upon DMF addition.

The films spin-cast from chloroform and chloroform/DMF P3HT solutions display a similar H-type ratio, although dissimilarly, now the anti-solvent containing system has less contribution from amorphous chains, resulting in better resolved vibronic peaks. This suggests electrospinning is essential to introduce the J-type character detected in the fibres. However, one should note that J-aggregates can appear as H-type when in high concentrations in films or solutions due to disruption from adjacent crystallites which may be relieved in the spun fibre. [254] Overall, these findings suggest that even prior to electrospinning, nanoscale crystallites have already begun to form.

4.5 Electrospinning-Induced Polymer Chain Alignment

4.5.1 Polarized Absorbance Spectrophotometry

To investigate electrospinning-induced polymer alignment effects, polarized absorption spectroscopy is first employed by introducing a film polarizer to the total integrated reflectance/transmittance measurement set-up (Section 2.2.2.2). This technique pro-

vides evidence of any bulk-averaged orientation considering both crystalline and amorphous polymer regions.

To avoid confusion, I will define that within this section, orientation and alignment are used as terms to refer to the preferential directionality of polymer chains that compose the electrospun nanofibres. The nature of the polymer alignment is most often discussed in terms of its orientation wrt to the fibre axis, but following fibre collection, it may also be considered wrt to the substrate. In contrast, ‘fibre-to-fibre alignment’ refers to the directionality of the nanofibres with respect to each other. Additionally, in this thesis, regions of the P3HT fibre are discussed as being amorphous or crystalline. Herein, amorphous domains are defined as regions which do not produce coherent (h00) or (0k0) X-ray/electron diffraction, due to limited stacking order between adjacent chains, however the chain may still be relatively planarized/extended. Conversely, crystalline regions possess increased long-range order.

Macroscopic fibre-to-fibre alignment of P3HT/PEO nanofibres in a common direction was achieved using a rotating collector at $\sim 1\,000$ rpm, which was subsequently washed to yield aligned P3HT fibres. If a preferential orientation of polymer exists in the fibres, fibre-to-fibre alignment will allow measurement of the anisotropy over the bulk nanoweb. Akin to prior works, the absorption of light by these fibres is greater when the incumbent radiation is polarized parallel ($\parallel$) to the fibres versus perpendicularly ($\perp$) across. [66, 113] This occurs due to the greater absorption probability with common orientation between the electric field vector of the polarized light (normal to the propagation direction) and the $\pi - \pi^*$ transition dipole moment along the backbone. This suggests that, overall, the polymer chains were also oriented parallel to the fibre long-axis.

The aligned, P3HT fibre web with diameters of 230 ± 56 nm before washing, provide an absorbance (A) intensity ratio between the (0-1) transition at 560 nm with perpendicular and parallel polarization of $A_{\perp}/A_{\parallel} = 0.88$ in Figure 4.19b. Yoon et al. [113] measured greater anisotropy with parallel versus perpendicular light at 0.70 with fibres with >300 nm diameters. Whilst this seems to suggest a greater degree of alignment, these researchers measured extinction (absorption + scattered intensity) rather than absorbance by way of linear transmission. In Figure A.4.5, scattering is also shown to be more intense with

parallel polarized light. Linear transmission yields extinction anisotropy between the two polarizations of 0.81 for P3HT fibres in this work. It is important to remove this contribution to determine the degree of polymer alignment along the fibre axis. Therefore, this study was also conducted using an integrating sphere.

Two further nanofibre samples were prepared with fibre-to-fibre alignment, by electrospinning the same solution 24 and 96 h after the introduction of AgNO_3 /PEO-reduced AgNPs. This produced fibres with an average diameter of 162 ± 41 , and 99 ± 27 nm, respectively, prior to PEO removal. The anisotropy ($A_{\perp}/A_{\parallel}$) of the washed intermediate diameter (24 h aged) fibres increased to 0.79, rising again to 0.62 for the thinnest 96 h aged nanoweb in Figure 4.19c and d. In Figure A.4.5, the corresponding extinction anisotropy was found to be 0.68 and 0.53, respectively. Randomly oriented fibres produce no polarization dependency ($A_{\perp}/A_{\parallel} = 0.99$, Figure 4.19a).

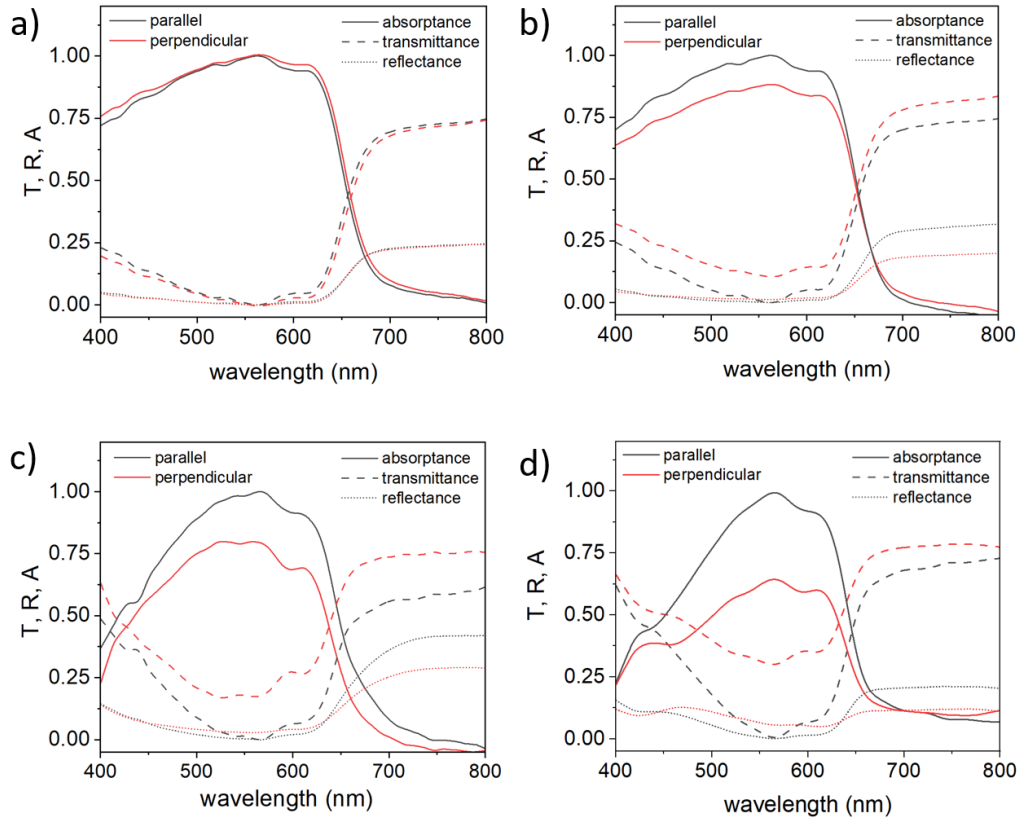


Figure 4.19: Polarized absorption spectra of (a) a randomly-oriented P3HT/PEO-reduced AgNP NF web collected using a static collector, and aligned fibre mats (collected on a rotating collector) containing (b) P3HT NFs and (c - d) P3HT/PEO-reduced AgNP NFs spun after (c) 24 h and (d) 96 h of ageing. The greater absorbance of light recorded using light polarized parallel to the fibre length versus perpendicular, indicates overall alignment of polymer chains along the fibre axis.

The first consideration is whether there is a change in the extent of fibre-to-fibre alignment between samples. For a fixed degree of along-fibre polymer alignment, worse fibre-to-fibre orientation would reduce the measured anisotropy for the bulk. Orientation analysis of SEM micrographs of pristine and 96 h particle-containing nanowebs spun for X-ray studies in Section 4.5.2 are displayed in Figure A.4.6 demonstrating a similar extent of fibre-to-fibre alignment. Logically, one would expect that thicker and therefore shorter pristine fibres would be more likely to be better aligned fibre-to-fibre under the rotation speed. Instead, this study reveals that the extent of chain alignment is affected by the diameter of the spun fibre, with thinner fibres possessing an increasingly aligned polymer. With greater confinement and having experienced greater stretching during flight, it is reasonable that the constituent polymer chains are also increasingly aligned in this direction, as communicated in Figure 4.20.

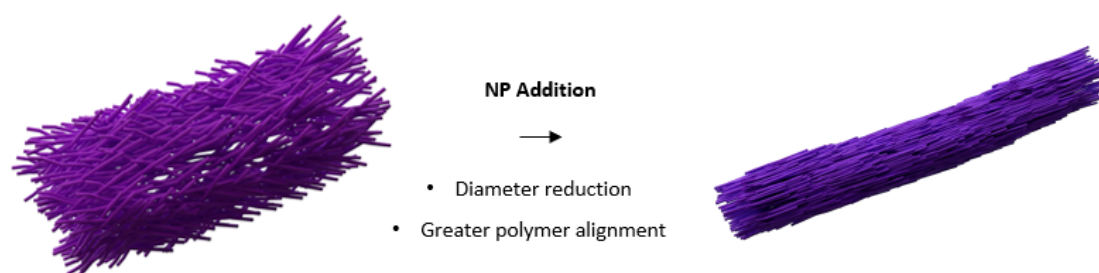


Figure 4.20: Schematic depicting the proposed orientation of amorphous polymer chains comprising a section of electrospun fibre, and the improvement in the extent of alignment upon nanoparticle-induced diameter reductions.

4.5.2 Orientation-Dependent 2D GI-XRD

4.5.2.1 Preferred Crystallite Alignment

2-dimensional grazing incidence X-ray diffraction (2D GI-XRD) was used to investigate the influence of electrospinning upon the orientation of crystallites within fibres. Using a 2D area detector, OOP and IP diffraction may be collected simultaneously. Dr Gyula Zilahi at the UK Atomic Energy Authority provided technical assistance for this study including setting up the XRD optics. Details of this set-up are provided in Section 2.2.4.2. Within these experiments, only chain segments involved in crystalline regions, rather than amorphous domains, contribute towards the assessment of alignment.

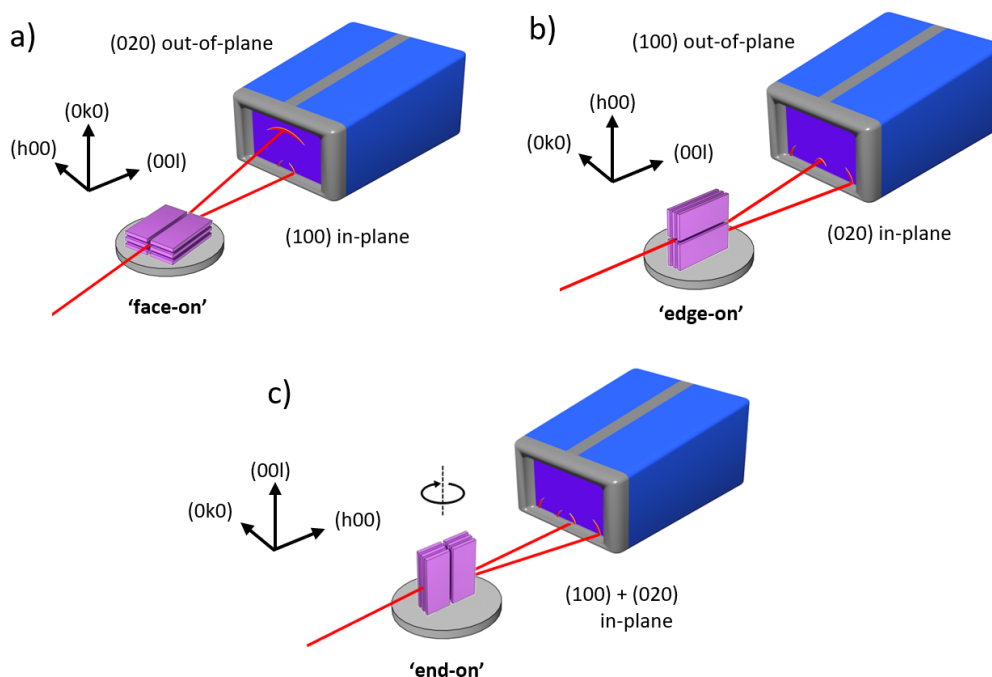


Figure 4.21: Schematic of the (a) OOP and (b) IP diffraction expected to be delivered by the $(h00)$ and $(0k0)$ P3HT reflections in face-on, edge-on and end-on lattice orientations wrt the substrate.

It is possible to determine the orientation of P3HT crystallites wrt the substrate by the position of the scattered intensity along the azimuth of the Debye-Scherrer ring corresponding to the (100) and (020) inter-spacings, as each conformation yields a unique pattern shown in Figure 4.21. Indeed, in Figure 4.22a, the detector image formed by a P3HT thin-film fabricated by spin-coating from chlorobenzene (annealed at 120°C for 20 minutes) reveals a strong preference for edge-on crystallites, driven by the proclivity for alkyl chains to present at the air and substrate interfaces. [71] Edge-on orientations give rise to intense OOP (100) scattering centred at $\sim 5.1^\circ - 5.6^\circ 2\theta$ and IP (020) scattering at $\sim 22.5^\circ - 23.5^\circ 2\theta$. This occurs as the (100) lamellar planes are angled parallel to the substrate (measured with asymmetrical grazing incidence, the planes which may scatter are actually inclined by the θ angle) whilst the $\pi - \pi$ (020) stacking is found to be perpendicular. In fact, this configuration is considered to be sub-optimal for OPVs as charge carriers must be transported in the normal direction to the substrate, thereby through the alkyl chains which reduce mobility in the required direction. [260, 261, 262] Chloroform-derived films generally produces the kinetically-trapped metastable face-on

preference due to rapid solvent evaporation. Yet even so, annealing or chlorobenzene-derived films offer greater efficiencies as they generate higher-quality crystallites. [263]

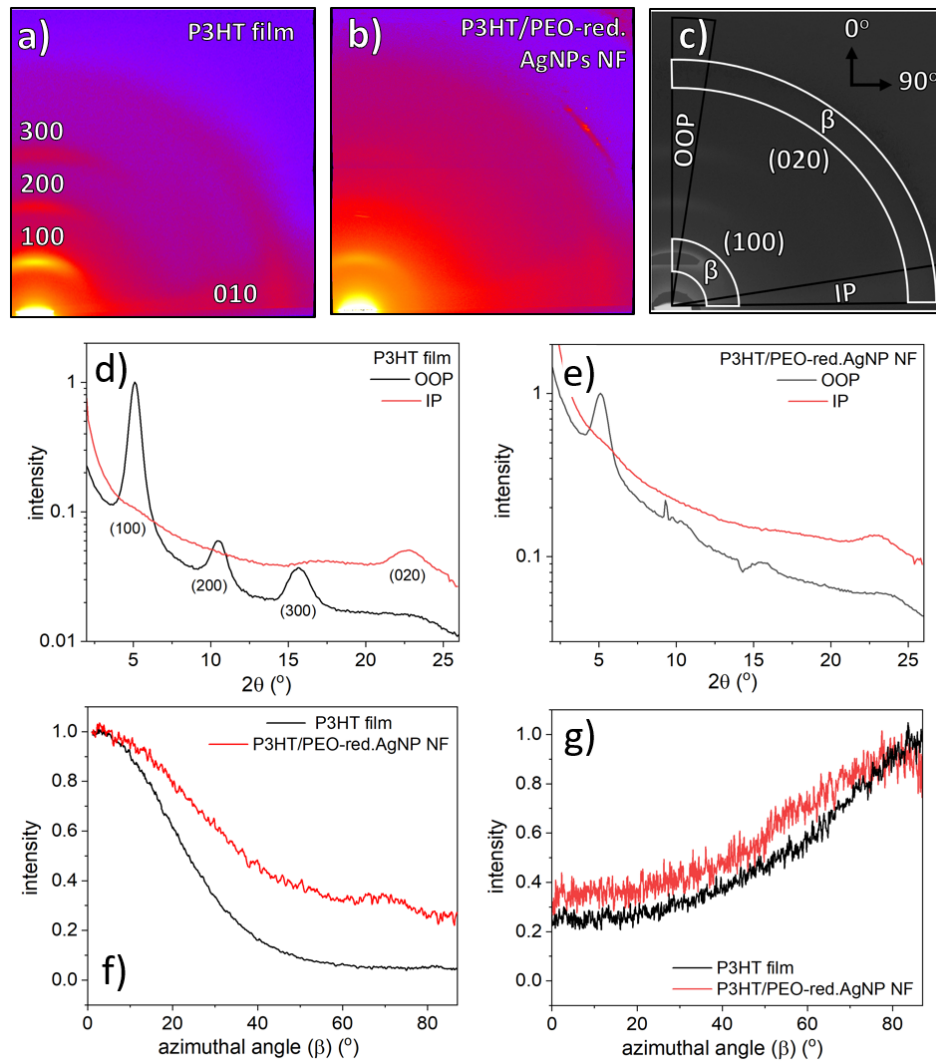


Figure 4.22: GI 2D-XRD raw detector images of a (a) spin-coated P3HT film (deposited from chlorobenzene) annealed at 120 °C and (b) a mat of randomly-oriented and washed P3HT/PEO-reduced AgNP NF. (c) Schematic of the extraction of azimuthal, OOP and IP profiles presented in (d - g), from the 2D-XRD detector image. (100) and (020) azimuthal profiles are traced from 0° (OOP) to 87° (IP) β and averaged between 4° - 7° 2θ and 21° - 25° 2θ , respectively. OOP and IP profiles are extracted from 0° and 26° 2θ and averaged between 0° and 10° (OOP) and 77° and 87° (IP) β . (d - e) 1D profiles of X-ray scattering intensity by the (d) P3HT film and (e) fibres extracted along the IP and OOP axis. (f - g) Azimuthal profiles of (f) (100) and (g) (020) scattering from the P3HT film and fibre mat.

In Figure 4.22b, the nanoweb of randomly-oriented nanofibres offers a similar yet reduced preference for a single configuration. The IP (100) scattered intensity increases relative to its intensity at the OOP meridian, however the peak is also significantly

broader and less intense in the IP direction, conveyed in Figure 4.22e. There is a small region of hot pixels in the OOP direction at ca. $9^\circ 2\theta$ in Figure 4.22e, whilst the drop in intensity at $14^\circ 2\theta$ appears due to imperfect stitching of detector images collected via the ‘multi-capture’ acquisition mode. Due to the greater background scattering and peak spreading towards the IP direction, it is not immediately possible to make comparisons between their intensities. A variable background is shown in the 2D detector image with a bare Si wafer in Figure A.4.7 and occurs due to the knife edge positioned between the incident optics and sample to significantly reduce background scattering at low 2θ angles. However, the knife edge only reduces the air-scattering background in the OOP direction.

The greater peak spreading observed in the IP direction is due to inherent divergence of the beam laterally. IP spreading manifests as the X-rays originate from a line source (0.04 mm high, 8 mm wide). Whilst the parabolic mirror is used to collimate the beam, this only produces a parallel beam in an OOP/vertical direction and has no influence in the still-divergent horizontal direction. Despite the use of a 1.0° IP parallel slit collimator and 5° limiting slit, the beam is still divergent, spreading to a greater extent than in the OOP direction. Therefore, to compare the intensities of OOP and IP reflections, it was necessary to collect azimuthal intensity averaged over the $4 - 7^\circ 2\theta$ and $21 - 25^\circ 2\theta$ regions for the (100) and (020) planes, respectively. The air scattering background was then carefully removed. With (020), subtraction of the corresponding azimuth produced by the bare wafer was found to be effective. For (100) correction, an azimuth was collected just beyond the peak region ($7.5 - 8^\circ 2\theta$), which was then shifted to the appropriate OOP level determined by fitting a baseline to the (100) peak in the OOP 2θ trace.

After correction, the intensity of IP (100) scattering by the fibres is higher than in the film at 0.25 relative to the OOP intensity with a more gradual decay rate when scanning along the azimuth from OOP (0°) to IP ($87^\circ \beta$). (020) scattering along the azimuth is more similar to the characteristics of the film with greater intensity scattered in the IP direction versus OOP. The higher intensity of OOP (100) and IP (020) scattering is indicative of a still-dominant edge-on configuration, but also the existence of either face-on or end-on orientations which introduces IP (100) scattering.

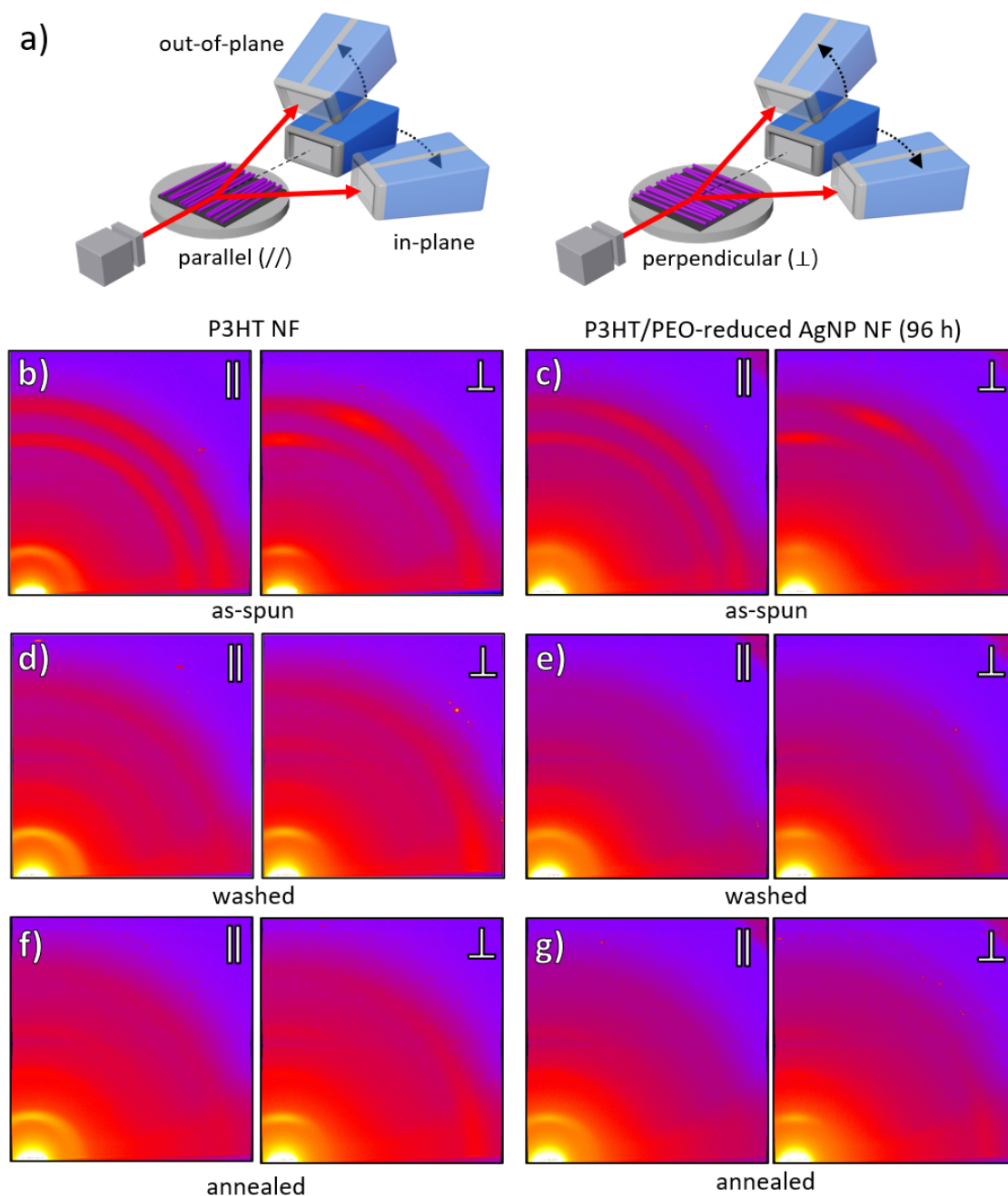


Figure 4.23: (a) Schematic depiction of the parallel and perpendicular orientation of aligned fibre bundles wrt the incident X-ray beam. GI 2D-XRD raw detector images of aligned as-spun (b) P3HT/PEO and (c) P3HT/PEO/PEO-reduced AgNP NFs (spun after 96 h), washed (d) P3HT and (e) P3HT/PEO-reduced AgNP NFs, and annealed (f) P3HT and (g) P3HT/PEO-reduced AgNP NFs. When parallel, the patterns are largely isotropic showing diffraction with a continuum between the OOP and IP extremes. When perpendicular, a preferential orientation is revealed.

To reveal lateral alignment and the nature of the bimodal distribution, one must probe the scattering patterns generated when the X-ray is incident along (parallel to) and across (perpendicular to) the common fibre axis of a nanoweb aligned using a rotating

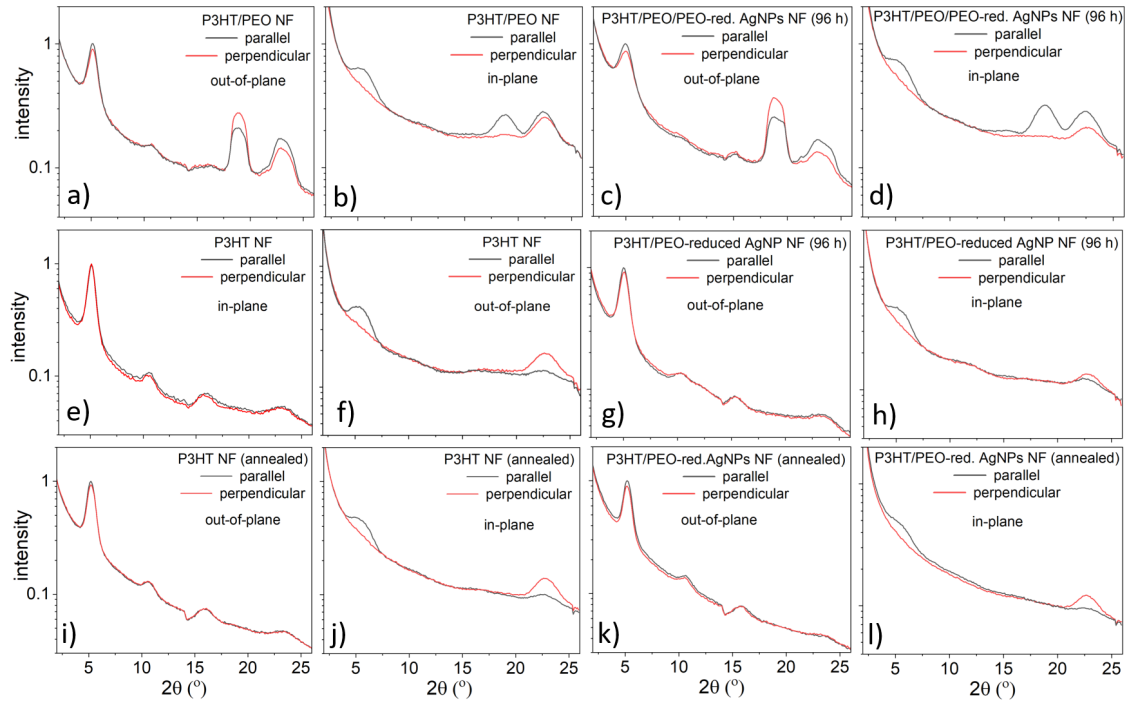


Figure 4.24: 1D XRD profiles of as-spun (a, b) P3HT/PEO and (c, d) P3HT/PEO/PEO-reduced AgNP NFs (spun after 96 h), washed (e, f) P3HT and (g, h) P3HT/PEO-reduced AgNP NFs and annealed (i, j) P3HT and (k, l) P3HT/PEO-reduced AgNP NFs extracted along the (a, c, e, g, i, k) OOP and (b, d, f, h, j, l) IP axis.

collector as depicted in Figure 4.23a. Upon first inspection of the as-spun P3HT/PEO and nanoparticle-containing P3HT/PEO fibres in Figure 4.23b and c, it is clear that when the X-rays are incident along the fibres, the IP (100) scattering increases relative to its still-greater OOP intensity. This is also evident in the respective 1D OOP and IP profiles in Figure 4.24a - d and azimuthal traces in Figure 4.25a and d. The azimuthal profile reveals that the IP (100) scattering intensity can reach 70% of the maximum value found along the OOP meridian, suggesting that the (100) planes can be found oriented both parallel and perpendicular to the substrate, and the continuum of states between. The PEO-associated reflections with X-rays incident along the fibre also present clear isotropic rings, less affected by noise/broadening due to their higher Bragg angle, indicating no orientation preference radially. The peak at $19^\circ 2\theta$ corresponds to the PEO (120) reflection, whilst the peak at $23^\circ 2\theta$ is a convolution of the dominant (112) reflection with contributions by (132), (032), (212) PEO lattice spacings, but also the (020) reflection of P3HT. Analysis of washed pristine and nanoparticle-containing P3HT

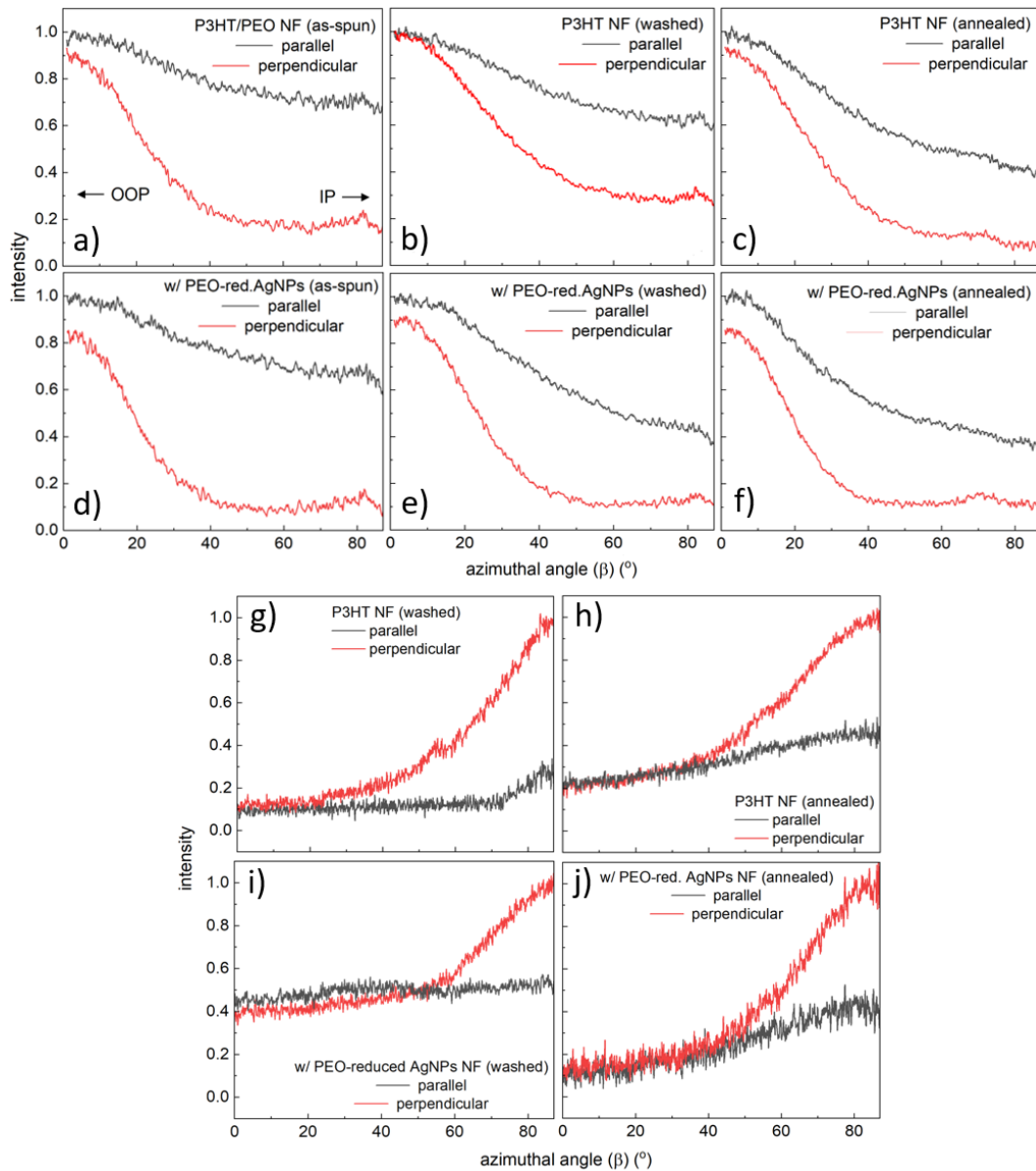


Figure 4.25: Azimuthal traces of the (a - f) (100) and (g - j) (020) scattering intensities of (a) as-spun P3HT/PEO, (b, g) washed P3HT and (c, h) annealed P3HT NFs and (d) as-spun P3HT/PEO/PEO-reduced AgNP NFs (spun after 96 h), and (e, i) washed P3HT/PEO-reduced AgNP and (f, j) annealed P3HT/PEO-reduced AgNP NFs.

nanofibres reveals a weak intensity, largely isotropic (020) reflection in the absence of the PEO reflections, shown in Figure 4.25g and i.

Conversely, when the X-ray beam is incident perpendicular to the fibre axis, different scattering characteristics are observed. In this scheme, fibres deliver a strong preference for OOP (100) scattering with the IP intensity dropping to $\sim 15\%$ of its OOP intensity, presented in Figure 4.25a and d. The contrast between the two beam orientations

suggests that the fibres contain strong anisotropy. In Figure 4.23b-c, the PEO-associated peaks also present localised intensities, at the OOP meridian for (120) and at $23^\circ \beta$ for the (112) peak. In Figure 4.25g and i, washed fibres reveal an increase in scattered (020) intensity towards the IP direction.

Overall, these X-ray characteristics reveal that diffraction is collected from a full continuum of (100) plane orientations when the beam is oriented along the fibre, whilst diffraction is largely obtained from (100) planes parallel to the substrate when the beam is perpendicular to the fibre. Conversely, the weak (020) intensity is isotropic with the beam impinging along the fibre, whereas the diffracting (020) planes are oriented perpendicular to the substrate with the beam incident across the fibre. This behaviour suggests that in a parallel fibre-to-beam configuration, a rotation of the crystallites about the central fibre axis is seen, and when viewed from the side, the edge-on characteristic pattern is created.

Hence, it is proposed that P3HT electrospun fibres contain the preferred crystallite structure depicted in Figure 4.26, involving the rotation of an edge-on crystallite about the fibre axis, resulting in a weak radial preference but strong along-fibre proclivity with the (00l) or polymer backbone direction directed across the fibre axis. Resultantly, the fibre contains a bimodal distribution of end-on and edge-on configurations (and all angles between) wrt the substrate. Low radial preference in the as-spun fibres is logical considering the fibre may twist during flight and that there is no substrate-fibre interface during electrospinning until fibre collection. It is also rational that alignment is produced along the fibre length, as this is the direction of uni-axial elongation. It is also possible that the crystallites produce a ‘radial’ edge-on orientation with respect to the fibre-air interface. [264]

In the parallel fibre-to-beam regime, fibres would generate an isotropic (100) ring, whilst the (020) scattering would be forbidden as they do not meet the Bragg condition (conveyed in Figure 4.26d). In the orthogonal fibre-to-beam orientation, the (020) planes remain perpendicular to the substrate as the crystallite is rotated about the fibre axis (Figure 4.26a and c) allowing only IP scattering. Meanwhile, the (100) lamellae only scatter when in the edge-on configuration with the planes parallel to the substrate,

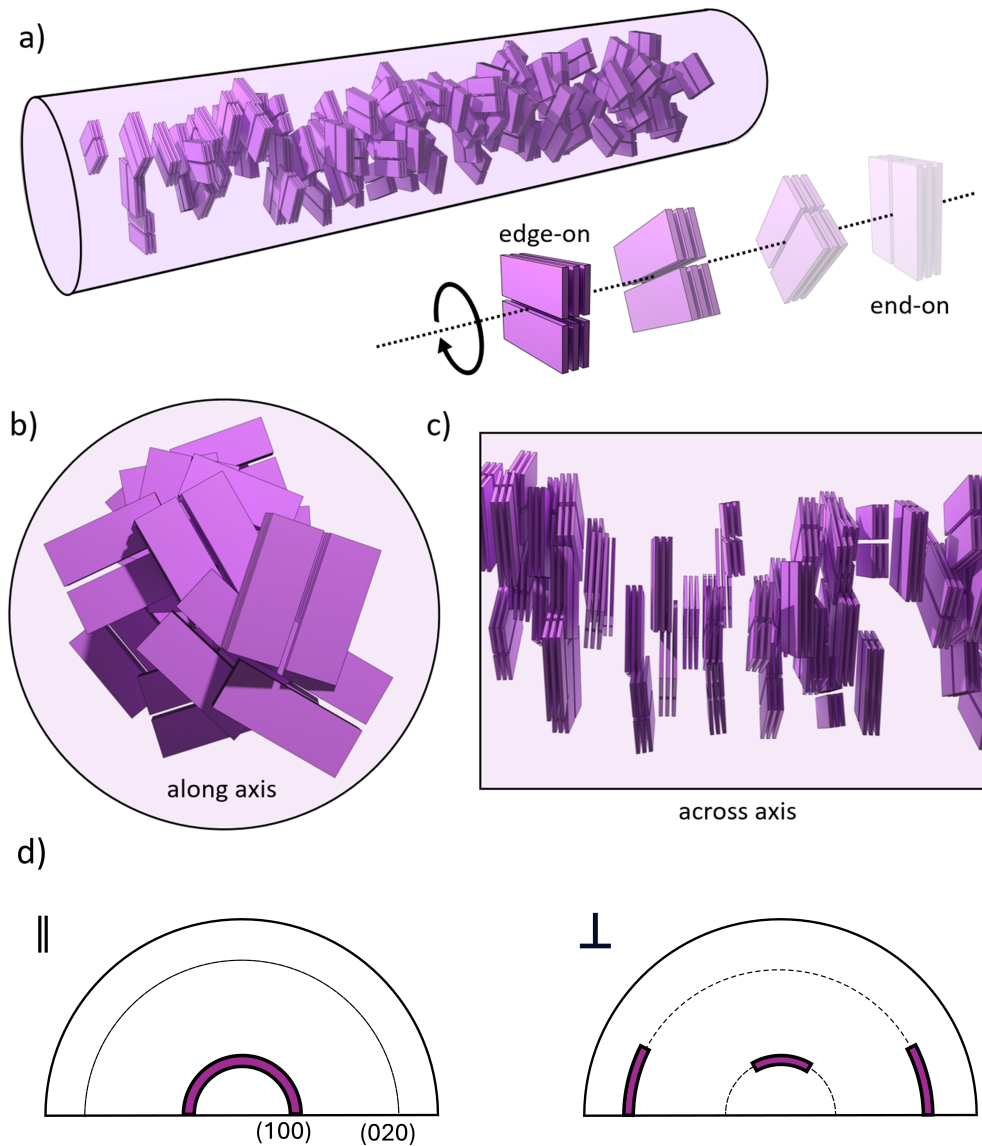


Figure 4.26: (a) Proposed P3HT crystallite distribution within electrospun nanofibres with the $\pi - \pi$ stacking oriented along the fibre axis with little to no preference in the radial direction due to free rotation of the forming fibre. (b) Parallel and perpendicular projections of (a) showing that (100) lamellar stacking is observed isotropically when the fibre is viewed along its axis and that (c) OOP (100) and IP (010) scattering is expected when viewing the fibre across its long axis. (d) Depiction of the expected scattering behaviours from the proposed nanostructure in (a - c).

resulting in OOP scattering. While end-on, the (100) planes are perpendicular to the substrate, they are not in the correct direction for diffraction.

In reality, a weak, isotropic (020) ring is detected in the parallel fibre-to-beam regime due to imperfect crystallite and fibre-to-fibre alignment, and there is a small preference for OOP (100) scattering versus IP. This is attributed to either insufficient treatment of IP

broadening, greater IP attenuation by multiple scattering events, or due to fibre-substrate interfacial interactions following collection. Incomplete solvent evaporation could render the polymer chains labile enough to produce a small edge-on preference overall.

In any case, it is clear in the azimuthal traces in Figure 4.25 that during nanofibre post-processing (washing and annealing), the IP/OOP (100) intensity ratio decreases with the parallel fibre-to-beam orientation. This occurs as thermal treatment promotes a transition towards edge-on orientations at the substrate, solvent or air interfaces. [198] As previously discussed, the fibres 'slump' during PEO removal, producing a non-negligible interface with the substrate for edge-on enrichment at elevated temperatures.

With respect to PEO in Figure 4.23b-c, scattering is isotropic with the parallel beam, however, the behaviour observed when the beam is perpendicular are consistent with patterns from previous studies, wherein the PEO backbone is viewed from the side with rotation about the chain axis. [265, 266] Therefore, the PEO chains are oriented along the electrospun fibre within crystalline regions. This occurs as the polymer chains are aligned prior to crystallisation, during the early stages of electrospinning, which then template the formation of aligned crystallites with the backbones directed down the fibre length.

Given this result, the finding that the P3HT polymer backbones are oriented orthogonally to the fibre axis was initially surprising. Frequently, electrospun fibres including some previously reported P3HT fibres, form crystallites with the (001) axis along the fibre axis. [61] Whilst uncommon, this backbone direction is not unprecedented [264, 267]. However, these researchers determined this by polarized PL emission. Therefore, within their fibres, polymer chains were either orthogonal in both amorphous and crystalline domains, or the measurement was dominated by crystallites, perhaps due to a high degree of crystallinity or lack of alignment in amorphous domains. In any case, the origin for orthogonal orientation was not commented upon.

In this work, the findings propose that the orthogonal backbone alignment in the crystalline regions is produced by the very same driving principle which produces the along-fibre backbone alignment in the amorphous P3HT phase measured in Section 4.5 - uni-axial elongation.

It has already been discussed that a controlled nano-crystallisation of P3HT is detected in the spinning solution. It is well reported that these will most commonly assemble along the (0k0) direction to produce a high-aspect ratio P3HT crystal. Therefore, under the same driving force which causes elongation of the well-dissolved polymer chain backbones along the fibre axis, these anisotropic crystals are similarly aligned. Similar behaviour is reported with the incorporation of inorganic nanorods into electrospun fibres. [268, 269, 270] A single chain has the greater aspect along its backbone but the nano-scale P3HT assemblies are longer in the (0k0) axis direction, reversing the final backbone orientation preference. Therefore, the electrospinning of aged, crystallite-containing P3HT spinning solutions produces a unique internal fibre structure - one where amorphous polymer chains that were well-dissolved within the spinning solution are aligned along the fibre, while crystallites, self-assembled during the ageing period, deliver an orthogonal backbone direction. This suggests that a majority of P3HT crystallisation occurs prior to spinning, and that a relatively low proportion of crystallites form during electrospinning, likely due to its rapid formation time relative to the solution ageing/nano-precipitation time.

4.5.2.2 Extent of Crystallite Alignment

To evaluate the extent of crystallite alignment within the fibres, Hermans' orientation factor, $\langle P_2 \rangle$ was determined for the sets of planes using the 2D-XRD images in Figure 4.27. This parameter compares the distribution of the (100) and (020) scattered intensity, $I(\phi)$, over the azimuthal range using equation 4.2. [271]

$$\langle P_2 \rangle_o = \frac{3\langle \cos^2(\phi) \rangle - 1}{2} \quad (4.2)$$

Where,

$$\langle \cos^2(\phi) \rangle = \frac{\int_0^{\frac{\pi}{2}} I(\phi) \cos^2(\phi) \sin(\phi) d\phi}{\int_0^{\frac{\pi}{2}} I(\phi) \sin(\phi) d\phi} \quad (4.3)$$

Here, $I(\beta)$ information from the azimuthal traces is converted to $I(\phi)$ data via the spherical trigonometric relationship:

$$\cos(\phi) = \cos(\beta) \cos(\theta) \quad (4.4)$$

Where θ is the Bragg angle and β is the azimuthal angle from the OOP meridian (taken to be 0° β). Complete alignment of the lattice planes parallel to the substrate will give a value of 1, whilst a perpendicular orientation will produce a value of -0.5 and an isotropic sample, 0. [272]

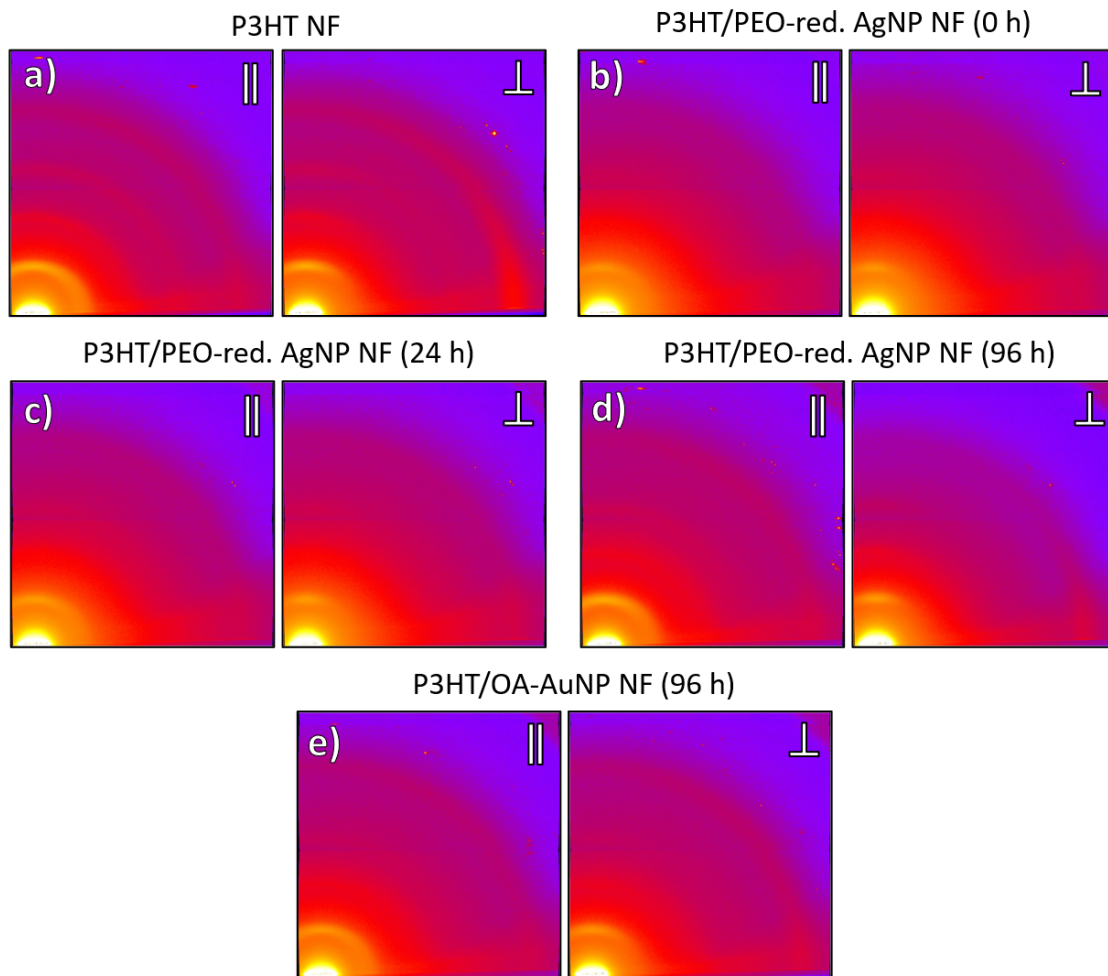


Figure 4.27: GI 2D-XRD pattern of (a) pristine P3HT NFs, (b - d) P3HT/PEO-reduced AgNP NFs spun after (b) 0 h, (c) 24 h and (d) 96 h, and (e) P3HT/OA-AuNP NFs spun after 96 h with the X-ray beam parallel and perpendicular to the fibre axes.

The overall orientation parameter, $\langle P_2 \rangle_o$, given by this calculation is a convolution of the crystallite alignment, $\langle P_2 \rangle_c$, and fibre-to-fibre alignment, $\langle P_2 \rangle_f$ as in Equation 4.5. [273] Fibre orientation was calculated from SEM micrographs of the as-spun, aligned fibre mats by generating an angular fibre histogram using the ImageJ plugin, Directionality

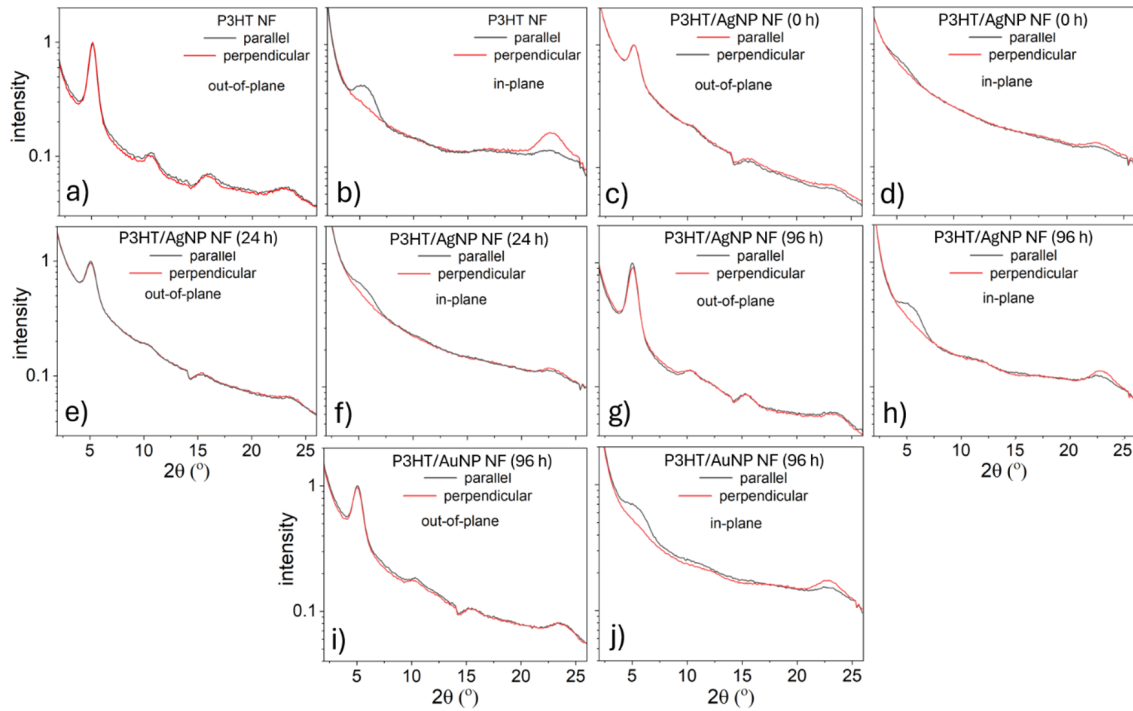


Figure 4.28: 1D XRD profiles of pristine and variably-aged NP-containing P3HT nanofibres extracted from the 2D patterns at the OOP and IP axis.

(output in Figure A.4.6 and Table A.4.1) and applying Equation 4.2. The overall and fibre-to-fibre orientation factors are found in Figure A.4.8. Due to the similar $\langle P_2 \rangle_f$ for each nanoweb, relative changes were inconsequential.

$$\langle P_2 \rangle_c = \frac{\langle P_2 \rangle_o}{\langle P_2 \rangle_f} \quad (4.5)$$

Along-fibre alignment, $\Delta \langle P_2 \rangle_c$, was ultimately determined by the difference in the $\langle P_2 \rangle_c$ factor with the parallel and perpendicular beam configurations using Equation 4.6. This helps to account for edge-on enrichment during processing and isolate the improvements in along-fibre alignment provided it affects both traces similarly. The influence of edge-on enrichment during processing can be seen in $\langle P_2 \rangle_c$ given in Figure 4.31. Here, $\langle P_2 \rangle_c$ in the parallel beam configuration display progressive magnitude increases upon successive processes at elevated temperatures.

$$\Delta \langle P_2 \rangle_c = \langle P_2 \rangle_{\perp} - \langle P_2 \rangle_{\parallel} \quad (4.6)$$

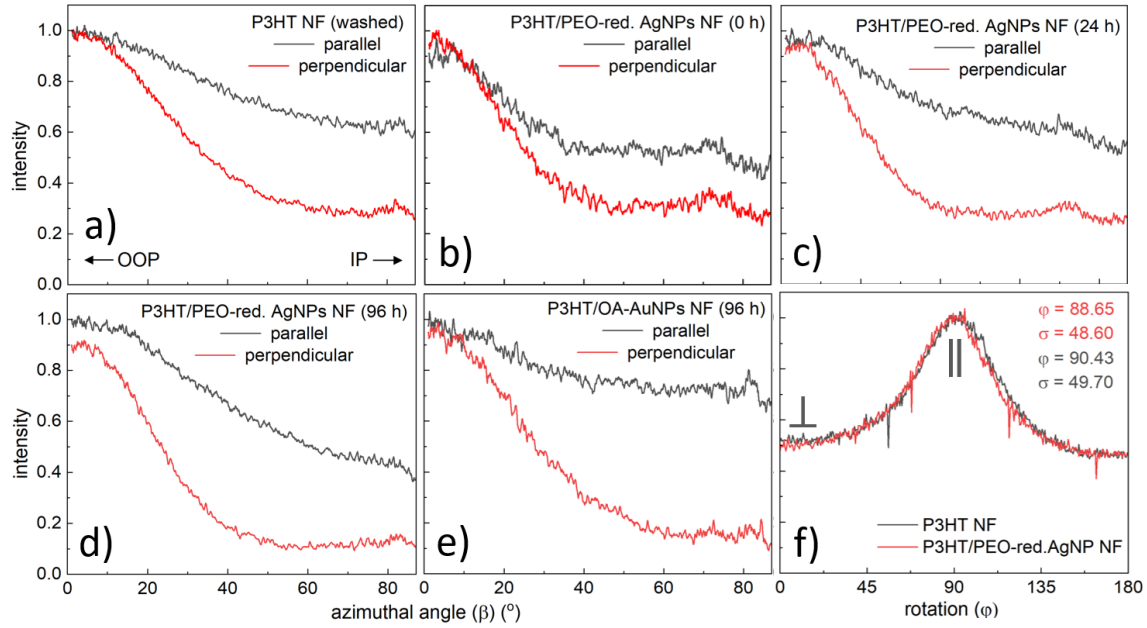


Figure 4.29: Azimuthal traces from OOP ($0^\circ \beta$) to IP ($90^\circ \beta$) of the (100) lamellar reflection between $4^\circ - 7^\circ 2\theta$. When parallel, there is less dependence on the β angle, whilst perpendicular to the axes, there is a lower intensity IP than OOP. (f) Evolution of (100) scattering intensity as thicker pristine and ultra-thin P3HT/AgNP NFs are rotated about a $180^\circ \phi$ rotation.

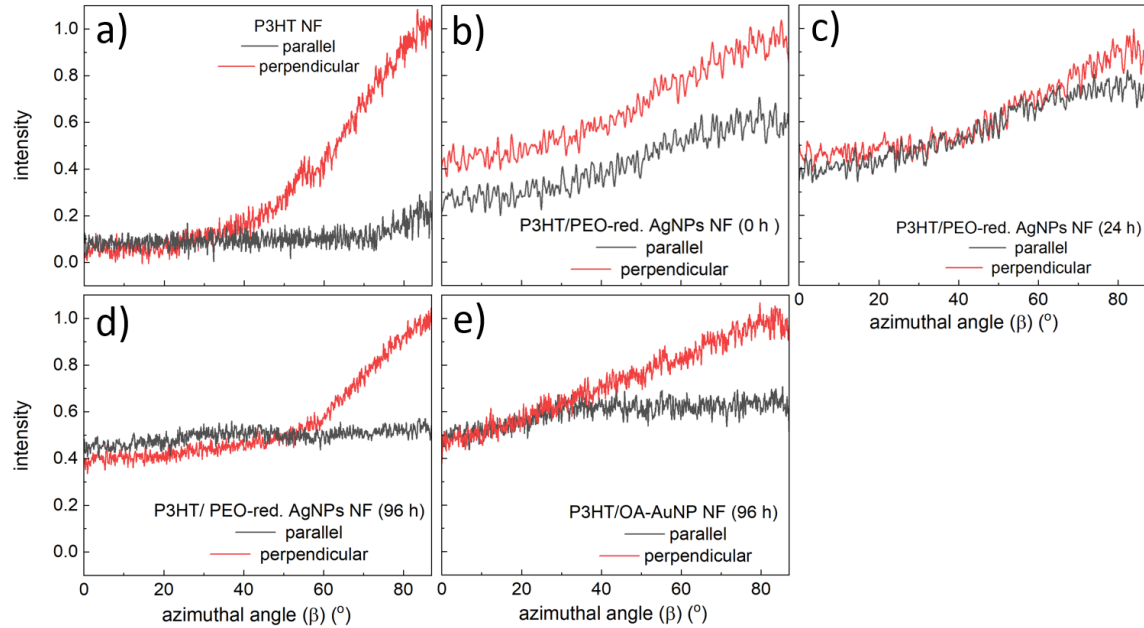


Figure 4.30: Azimuthal traces from OOP ($0^\circ \beta$) to IP ($90^\circ \beta$) of the (020) $\pi-\pi$ reflection between $21^\circ - 25^\circ 2\theta$. When parallel, there is weak dependency upon the β angle, whilst perpendicular to the axes, there is greater intensity when IP than OOP.

In Figure 4.28, after extraction of the 1D profiles from the detector images, AgNO_3 addition appears to initially (0 h) reduce the degree of crystallinity, which subsequently recovers as the spinning solution is aged prior to fibre formation.

To more accurately assess the (100) distribution, azimuthal traces are given in Figure 4.29. The difference between the parallel and perpendicular fibre-beam azimuths clearly reduces and the two traces initially converge together following salt/particle addition (Figure 4.29b) versus their pristine counterpart in Figure 4.29a. This is reflected in the P3HT fibre's $\Delta < P_2 >_{c,(100)}$ which decreases from 0.134 for pristine fibres, to 0.088 for fibres spun immediately after AgNO_3 addition (0 h). As the PEO-reduced AgNP-containing spinning solution is aged before spinning, the traces diverge, indicating an improvement in along-chain alignment. Whilst the 24 h fibre $\Delta < P_2 >_{c,(100)}$ is similar (0.089), the 96 h, ultra-thin fibres possess a greater $\Delta < P_2 >_{c,(100)}$ than their pristine counterparts at 0.236 (PEO-reduced AgNPs) and 0.302 (OA-capped AuNPs).

Figure 4.29f compares the crystallite alignment within the pristine and PEO-reduced AgNP-containing P3HT fibres (96 h) by rotating between 0° and 180° ϕ (parallel fibre-to-beam orientation at 90° ϕ) whilst the detector (in 1D mode) tracks the evolution of the IP (100) intensity. As the background could not be subtracted, the parallel to perpendicular beam-fibre intensity ratio and FWHM of the formed peak were used to gauge the extent of alignment. It is immediately clear that the alignment in the pristine and particle-containing fibres are equal, suggesting no improvement in (100) alignment following diameter reduction. However, the nanoparticle-containing fibres possessed a marginally lower fibre-to-fibre alignment of 0.787 versus 0.828 for the pristine web (Figure A.4.6). Therefore, with correction, one would expect a slight improvement in crystallite alignment in thinner fibres.

(020) scattering shows a similar trend with negative $< P_2 >_c$ values (due to higher IP intensity) in Figure 4.32. The relatively large -0.368 $\Delta < P_2 >_{c,(020)}$ of the pristine P3HT nanofibres, drops to near-zero with fibres spun up to 24 h after PEO-reduced AgNP addition. This is also evident in Figure 4.30b-c, which clearly demonstrates that the differences in the distribution between the two beam orientations disappears and then re-emerges for fibres spun after 96 h, with the parallel beam trace becoming flatter and the perpendicular beam delivering a greater weighting towards IP scattering. With respect to the (020) planes, the $\Delta < P_2 >_{c,(020)}$ of the 96 h nanoparticle-containing P3HT

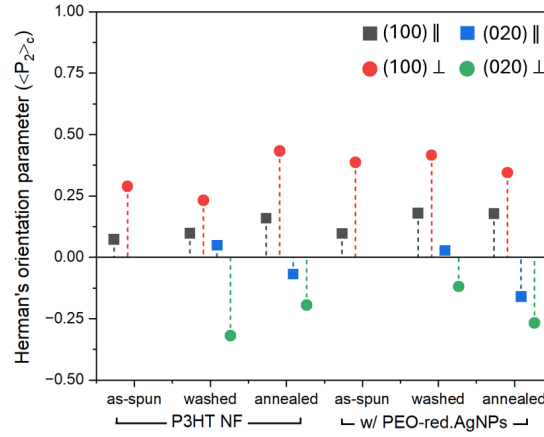


Figure 4.31: (100) and (020) crystallite orientation factors, $\langle P_2 \rangle_c$, (corrected for the degree of fibre-to-fibre alignment) determined from the azimuthal traces of pristine and NP-containing P3HT fibres with parallel and perpendicular X-ray configurations in Figure 4.25, presenting the influence of the washing and annealing processes.

fibres only reach values of up to -0.146, therefore suggesting that (020) alignment did not recover to the levels generated within the pristine fibres.

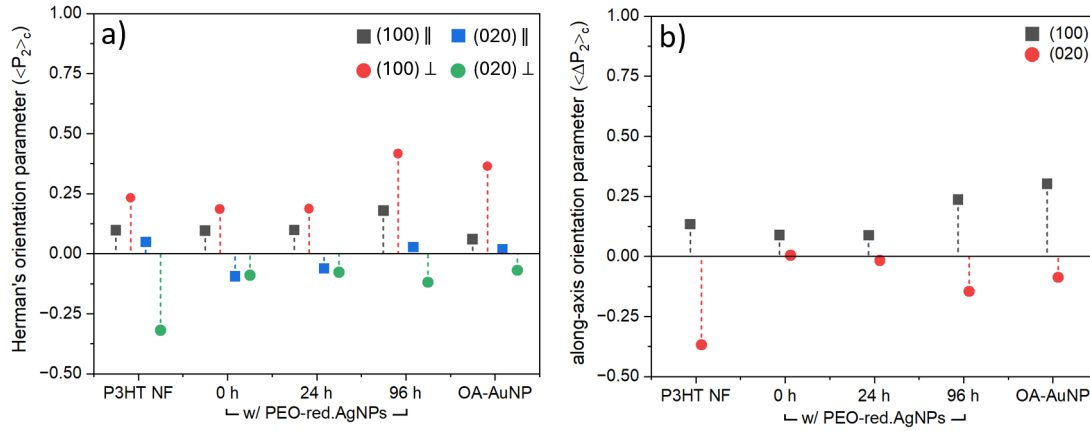


Figure 4.32: (a) Crystallite orientation factors ($\langle P_2 \rangle_c$) determined from the (100) and (020) azimuths of pristine and NP-containing fibres in Figure 4.29 - 4.30, corrected for fibre-to-fibre alignment. (b) Along-axis fibre alignment factor, $\Delta \langle P_2 \rangle_c$, the difference between the parallel and perpendicular orientation factors. A value of 1 indicates the set of planes are parallel to the substrate (or reference plane), 0 presents an isotropic distribution, and -0.5 is given to planes found perpendicular to the substrate.

In summary, GI 2D-XRD reveals that crystallites within electrospun P3HT fibres are oriented with the $[0k0]$ axis along the fibre. This arrangement may provide effective in-plane/along fibre mobility versus the edge-on configurations in thin-films which lack lateral alignment. As the fibres rotate during flight, there is only a weak ‘radial’ preference. This generates a population of P3HT crystallites with a end-on orientation, not typically

found in films, which may provide a mechanism for out-of-plane transport along the polymer backbone (theoretically the direction of greatest mobility). However, exposure of the fibres to elevated temperatures during washing or annealing promotes the transition of crystallites to an edge-on configuration.

4.5.3 Nanobeam Electron Diffraction (4D-STEM)

Direct observation of P3HT and other organic crystallites through electron diffraction is challenging due to their beam-sensitive nature. Even so, low-dose nanobeam diffraction is demonstrated to reveal the location, shape and alignment of crystalline features within single electrospun fibres without the requirement for cryogenic conditions.

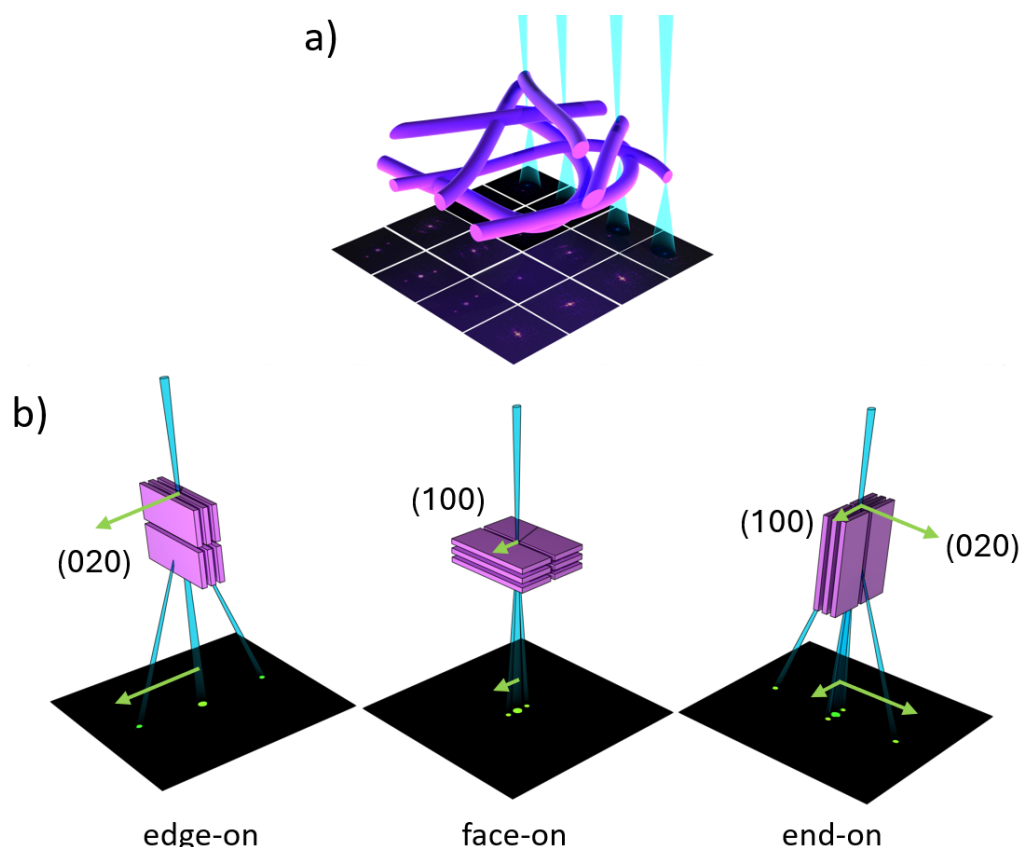


Figure 4.33: (a) Schematic of the nanobeam electron diffraction experiment. (b) The expected diffraction patterns arising from each crystallite orientation.

Under higher magnification or with repeated acquisition, the accumulated dosage degraded the polymer's crystallinity, however by employing a 'blind selection' procedure, it was possible to collect clear diffraction images of P3HT with an electron fluence of

$\leq 6 \text{ e}^- \text{ \AA}^{-2}$. Further details of this experiment are provided in Section 2.2.1.6. Whilst I guided the experimental process, the microscope was operated by Dr David Hopkinson at Diamond Light Source.

A sampling of the diffraction patterns generated by the nanofibre at their respective location is shown in Figure 4.34. Generally, the (100) and (020) spacings are visible, and in some cases, the (200), (120), and (040) reflections alongside various d-spacings corresponding to the OA-capped AuNPs within the fibre. The presence of (002) reflections could not be confirmed. The virtual dark-field (vDF) images at the centre of Figure 4.34 are created by integrating the diffraction-space coordinates within a region of each pattern, leading to the generation of pixel intensities in real-space. [274] In conventional TEM, an aperture in the diffraction plane can be used to isolate a region of interest and produce a dark-field image at the imaging plane comprising solely of electrons diffracted through this area. The vDF is analogous, and can provide a real-space representation to help visualise the location and form of crystalline features. Here, the left-hand vDF is integrated over the full diffraction area, whereas the right-hand image is generated by masking only the central disc.

The ‘mean’ diffraction pattern in Figure 4.35a resembles those produced in SAED and offers an overview of the most prominent diffraction behaviour such as the strong (020) Debye-Scherrer rings. However, other Bragg discs may be obscured if they occur at only a few of positions or are masked by the drift of the direct beam. Instead, the ‘maximum’ diffraction pattern reveals the maximum diffracted intensity at each pixel across all probe positions. This allows visualisation of Bragg scattering even if it was only detected at a single probe position. In Figure 4.35b, the ‘maximum’ diffraction pattern reveals the presence of (100) Bragg scattering, close to the central disc, not seen in mean pattern or by SAED.

Both (100) and (020) scattering is confined to a specific, local angular range along the Debye-Scherrer ring, corroborating preferential alignment of the polymer crystallites. The observed spot configuration, being separated by an azimuthal rotation of 90° , is expected in the presence of end-on crystallites as in Figure 4.33b. At this stage, before

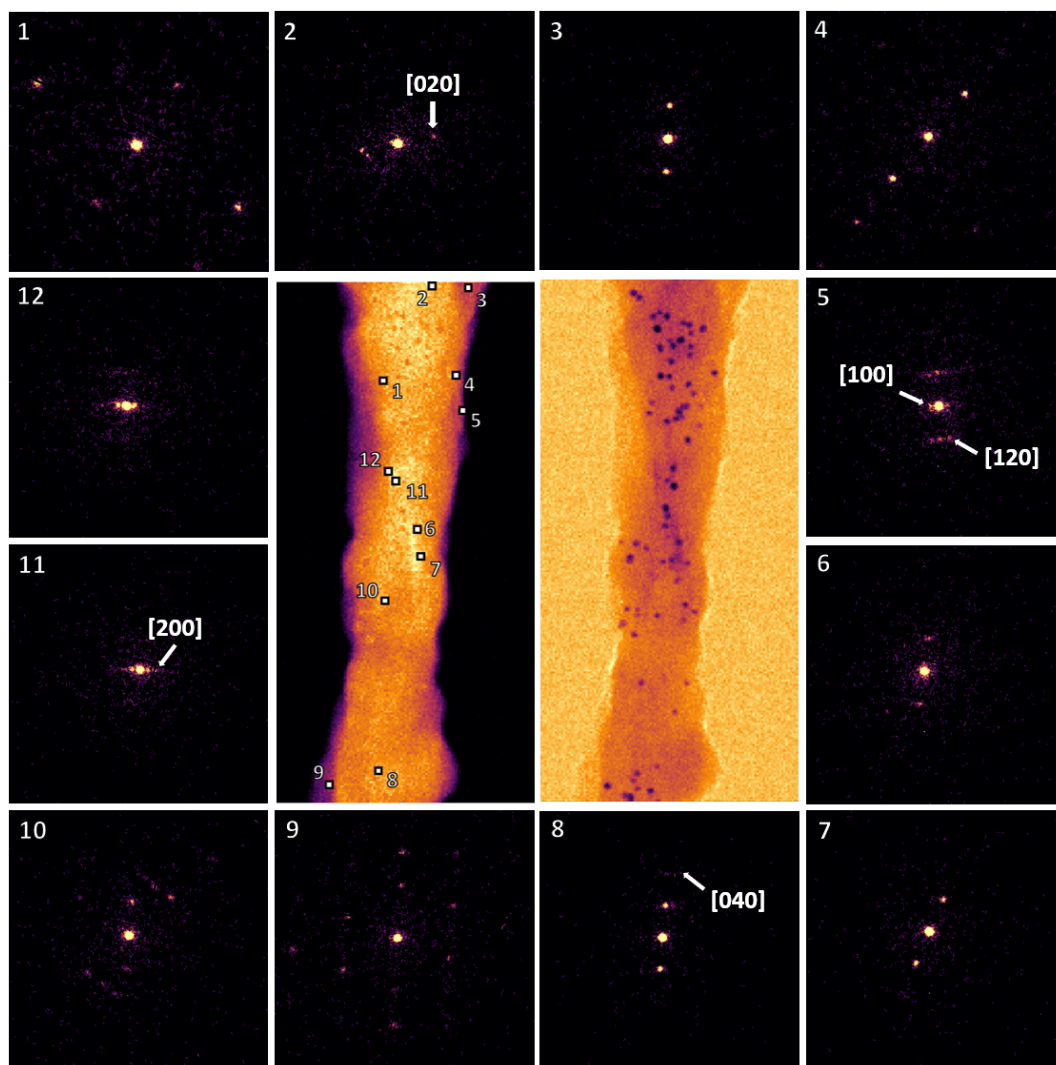


Figure 4.34: Representative selection of diffraction patterns from the labelled pixel in the left-hand vDF of the P3HT/OA-AuNP NF. This vDF was integrated over the entire diffraction pattern, and the right-hand side vDF masked over the central disc. Patterns were rotated by 257° anti-clockwise as determined by Figure A.4.10.

determining the relative rotation between real-space and diffraction space, the assumed orientation wrt the fibre cannot yet be commented upon.

In Figure 4.36, vDF images are generated using an annular mask over the (020) d-spacing region revealing the distribution and anisotropic morphology of these features. These structures form anisotropic ‘striations’ oriented along the axial direction. They are narrow but can span tens of nm along the fibre length. Masking (111) and (200) Au regions analogously reveals the location of the metallic nanoparticles. The P3HT lamellae vDF is not as distinct due to its proximity to the central disc.

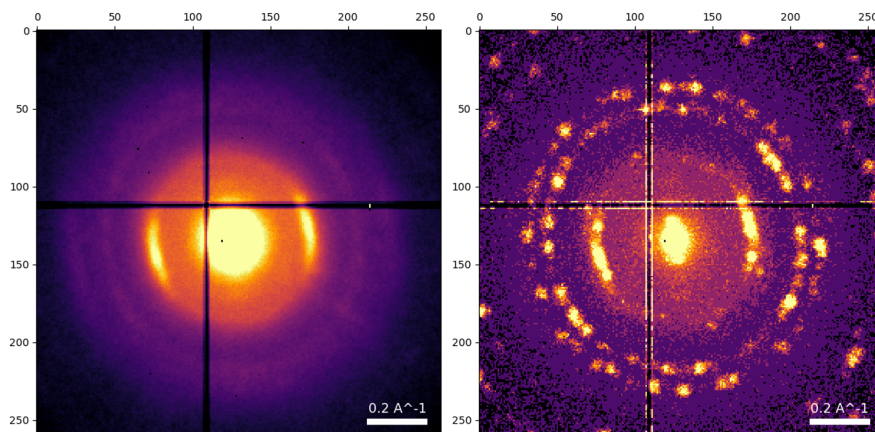


Figure 4.35: (a) Mean diffraction pattern - mean intensity from all diffraction patterns and (b) Maximum diffraction pattern - the maximum intensity pixel from each diffraction pattern of the P3HT/OA-AuNP NF.

At 300 kV and 0.8 mrad convergence semi-angle probe, an effective depth of focus of $\sim 3 \mu\text{m}$ is expected, thereby the beam samples the full nanofibre. [275] This has been shown experimentally with a pencil beam probe, where changing the sample height over hundreds of nanometres did not impact the clarity of the ADF image. [276] However, just because a region does not produce meaningful diffraction for Bragg detection, does not necessarily mean that region contains only amorphous material. Instead, the lattice planes may not have the correct orientation for effective scattering. Simulation of P3HT electron diffraction with Singlecrystal software in Figure A.4.9 proposed that an off-axis rotation of 2 or 8° is sufficient to attenuate diffraction of a crystal initially viewed along (001). Furthermore, in thicker samples, greater perturbation of the diffracted intensity is expected which may attenuate its focus/intensity at the detector.

A selection of diffraction patterns are then chosen to refine the Bragg vector cross-correlation detection method. Often a ‘vacuum probe’ is generated from images of the central beam over the vacuum in diffraction space. Next, py4DSTEM subtracts a Gaussian wider than the probe to produce a negative intensity region encompassing the kernel to improve Bragg peak detection. [84] Here, a synthetic probe offered greater control over this negative intensity region, (Figure A.4.10) enabling detection of (100) Bragg peaks close to the direct beam without excessive false positives.

After cross-correlation, the Bragg vector map (BVM) can be constructed containing

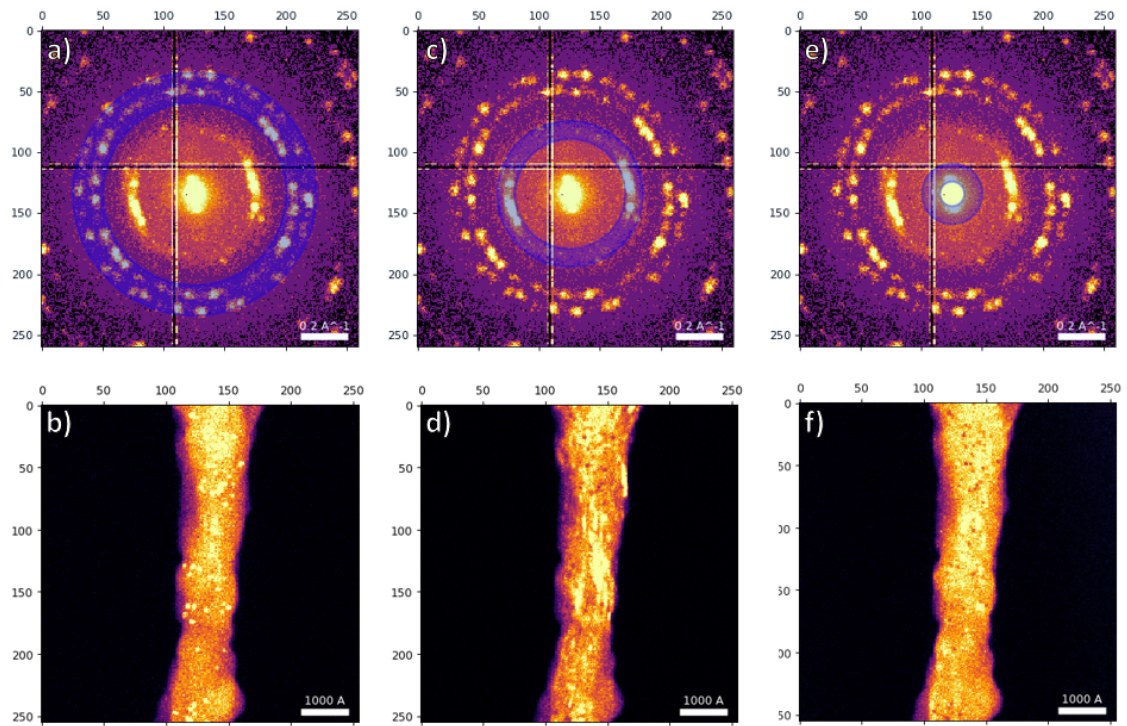


Figure 4.36: (a, c, e) Annular masks applied to the Bragg disc detection map and (b, d, f) vDF images showing the real-space features which give rise to the intensity collected for the (a,b) (111) and (200) reflection of AuNPs, and the (c, d) (020) $\pi - \pi$ stacking and (e, f) (100) lamellae of crystalline P3HT.

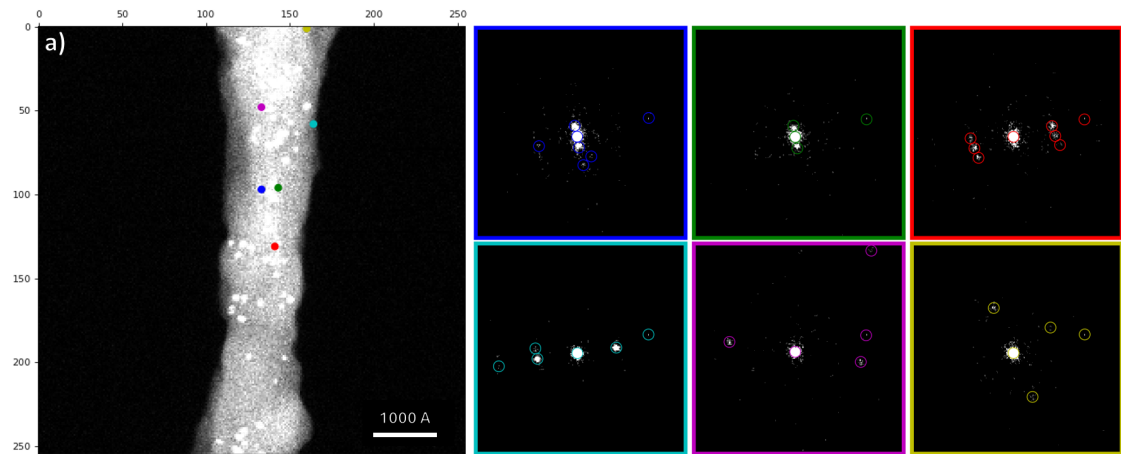


Figure 4.37: Probe positions/diffraction patterns chosen for hyper-parameter tuning of the cross-correlation detection method of Bragg reflections.

a 2D histogram of all vectors and intensities of the detected Bragg points. The BVM has been defined as the ‘position-averaged probability distribution of reciprocal lattice points’. [84] The map should not contain information from amorphous regions, however, false positives generate a haze accentuated by the logarithmic scale used for visualization,

particularly at low angles. Relative to (020), the (100) lamellar stacking provides significantly fewer diffraction patterns.

Several calibrations were applied to the BVM - the difference pre- and post-calibration is highlighted in Figure 4.38. Dr Mohsen Danaie provided the basic Python code which was then adapted for the workflow discussed here. The beam disc is first centralised within each diffraction pattern and the BVM re-composited (Figure 4.38c-d) and the rotation between real and diffraction space is applied. This 257° anticlockwise rotation was determined separately using a highly defocussed shadow image of a gold cross-grating standard. [84] After correction, with the probe above the sample, the probe raster direction may be visualised by the movement of features from right to left during the scan. Additionally, the real and reciprocal pixel size, and an affine elliptical transformation, were determined using the same cross-grating with known grating pitch and scattering vectors. The general procedures for each calibration can be found in Figure A.4.10 - A.4.14.

To explore the preferential alignment direction, an annular mask is applied to the BVM. Probe/real-space positions that give rise to Bragg spots within this annulus are assigned two values. The first is the maximum intensity found in the (020) or (100) mask region of the diffraction pattern, and the second is the angle between the central disc to maximum intensity pixel vector, and the vertical y-axis. Finally, the vDF is reconstructed from the masked BVM region and each pixel is allocated colour based upon its angle (Figure 4.39a,c) and intensity (Figure 4.39b,d). Following the Bragg disc detection protocol, the crystalline features are far more distinct than the corresponding vDF images formed earlier with the raw data in Figure 4.36, now with low contribution from amorphous material.

These angle and intensity maps reveal an impressive degree of common orientation present within the fibres. After diffraction to real-space rotation calibration, one can see that the (020) planes are overwhelmingly found orthogonal to the fibre axis and the (100) lamellae located parallel. This is consistent with the proposed nanostructure from the X-ray studies, with crystallites aligned with the (0k0) axis oriented along the fibre length.

X-ray diffraction suggested that there was low radial preference generating a mixture of end-on and edge-on crystallites (wrt the substrate). In 4D-STEM, the nanoprobe impinges at a normal to the fibre with the substrate (TEM grid) below the fibre. Although nanobeam

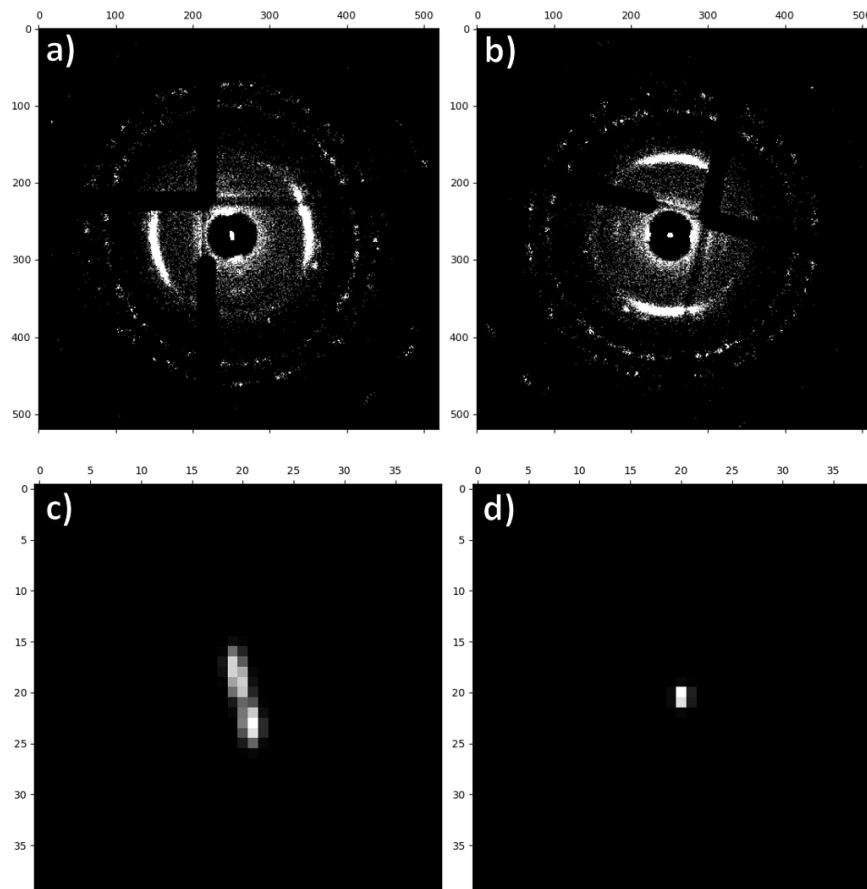


Figure 4.38: The BMV (a) before and (b) after calibration of the pixel size, correcting shifts of the direct beam disc, applying an affine transformation to account for elliptical distortion and a diffraction to real-space rotation offset. Enlarged view of the central disc (c) before and (d) after calibration.

diffraction was conducted on fibres over the vacuum, for the purpose of end/edge/face-on nomenclature, the grid is imagined to be continuous beneath the fibre. When considering the rotation of an end-on crystallite (wrt to the TEM grid) about the fibre axis, one would initially expect both (020) and (100) scattering. Once rotated about the (0k0) axis, the lamellar scattering deviates from the Bragg condition, while the (020) scattering is maintained. This provides an explanation for the ubiquity of (020) scattering versus (100). The close proximity of the (100) Bragg spots to the central beam at 40 cm camera length increases difficulty in their detection which may also act to reduce its prevalence in the BVM versus $\pi - \pi$ stacking. As mentioned, a rotation of just 2 and 8° off-axis is sufficient to prevent scattering by either the (100) and (020) planes (Appendix A.4.13), explaining why they are generally observed separately, with relatively few instances of

detection at the same probe position.

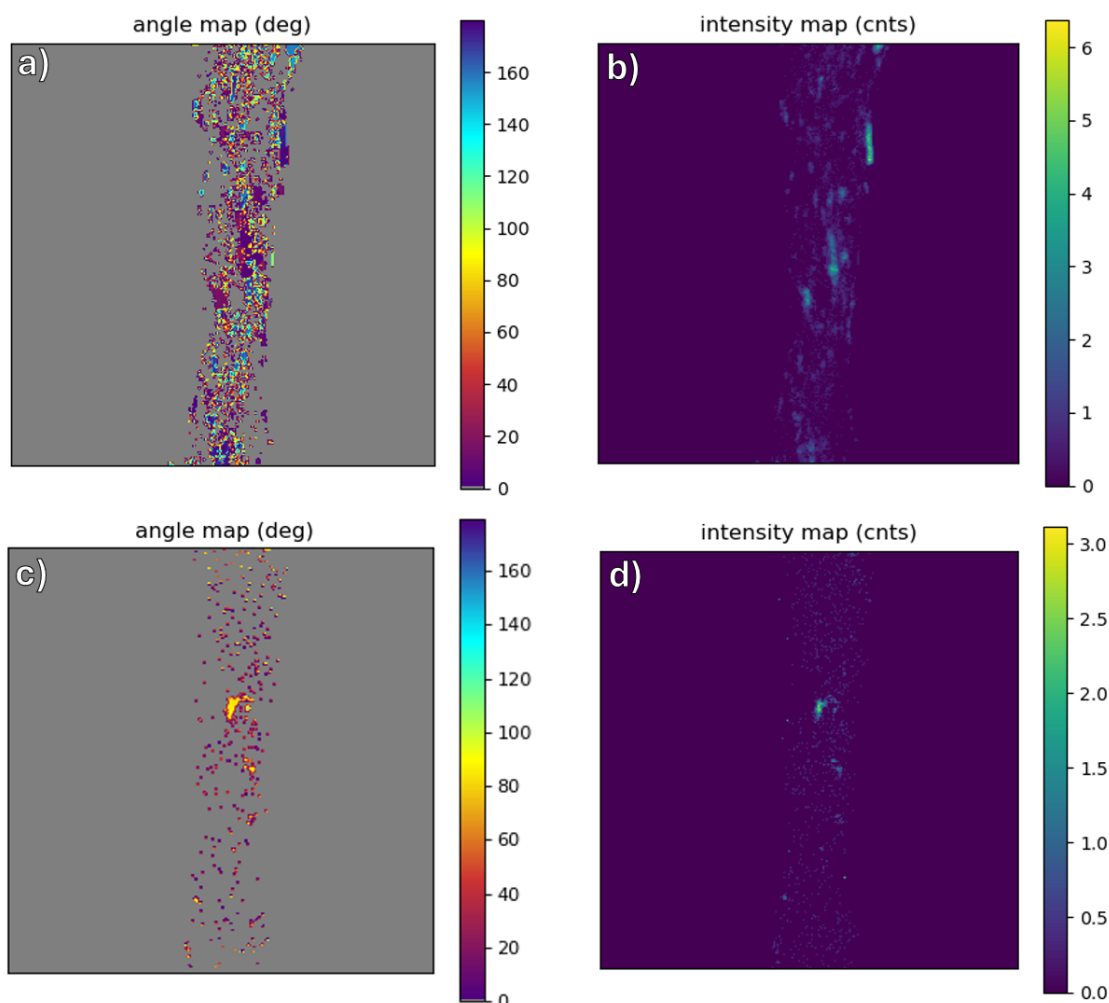


Figure 4.39: Orientation and intensity maps revealing (a, b) the angle between the (020) and (c, d) (100) Bragg vector wrt the vertical axis at each probe position. These orientations indicate that the c-direction of the crystallites are oriented across the fibre axis.

Combining the angle and intensity maps in Figure 4.39 produces an intensity-weighted angle map, as presented in Figure 4.40, with reduced SNR which accentuates the extent of alignment. In Figure 4.41a, the BVM of a web containing several fibres initially appears to show isotropic behaviour, however 4D-STEM reveals a high degree of alignment within each individual fibre, with the (020) Bragg vector angles running along its fibre length. The vDF images of the raw data are displayed in Figure A.4.15. The ability for nanobeam diffraction to reveal both the orientation and shape of individual crystals reveals that the longer aspect of the anisotropic crystals is along the (0k0) direction. Hence, nanobeam diffraction corroborates that the observed nanostructure is generated from electrospinning

alignment of self-assembled nanocrystals formed within the spinning solution. Additional intensity-weighted orientation maps can be found in Figure A.4.16 and A.4.17 for the (020) and (100) planes, respectively, showing how consistent orientation can be observed.

In Figure 4.42, plotting the pixel- and intensity-weighted angle maps as 2D histograms (Figure 4.39 and 4.40), one can finally appreciate the outstanding degree of common orientation imparted by electrospinning (additional histograms in Figure A.4.18).

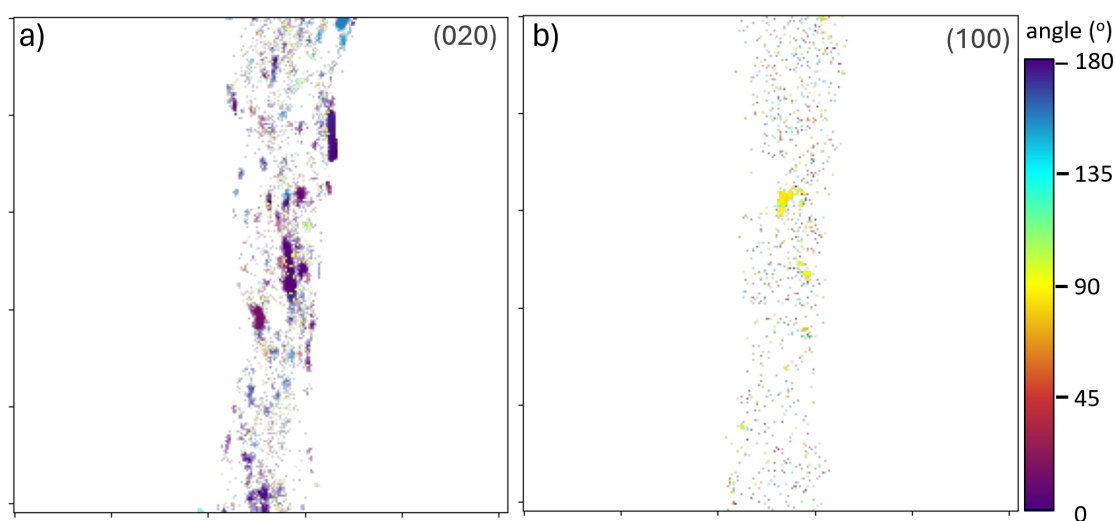


Figure 4.40: Combined (a) (020) and (b) (100) orientation and intensity map. The pixel colour is determined by the angle of the Bragg vector at that probe position, and the opacity determined by the normalised intensity count, producing an intensity-weighted orientation mapping. This approach allows for significant noise reduction and clear visualisation of alignment within single electrospun fibres.

At a 90° β angle to the major (020) peak in Figure 4.42, a smaller peak is observed (centred in Figure A.4.19). This may be attributed to order in the (002) direction or to (020) d-spacings arising from crystallites with axially-aligned polymer backbones, perhaps those which crystallise during electrospinning, which would result in a bimodal preference. Inspection of the intensity-weighted map suggests that pixels assigned this angle are found nearby to regions contributing to the main peak. This increases the likelihood that this is (002) scattering. However, (002) scattering could not be confirmed in the raw data. It is also possible that the existing crystals act as nucleation points for additional crystallisation during spinning. The standard deviation of this second peak is marginally higher at $11 - 19^\circ$, and in this example, possesses around $15 - 30\%$ of the integrated intensity of the major (020) peak.

Hermans' crystal orientation parameter, $\langle P_2 \rangle_c$, (Equation 4.2) was again applied to the raw 2D histograms with pixel/number- and intensity-weighting. The number-weighted (020) distribution provides an $\langle P_2 \rangle_{c,(020)}$ of 0.639, rising to 0.743 when weighted by intensity. The mean number-weighted $\langle P_2 \rangle_{c,(020)}$ was 0.593 ± 0.116 and intensity-weighted $\langle P_2 \rangle_{c,(020)}$ was 0.636 ± 0.110 across the dataset ($n = 7$). The aforementioned sub-peak would also act to reduce the orientation factor. The higher orientation factors calculated from 4D-STEM, relative to X-ray studies, originates from the cross-correlation protocol which removes a large proportion of scattering contribution from amorphous material.

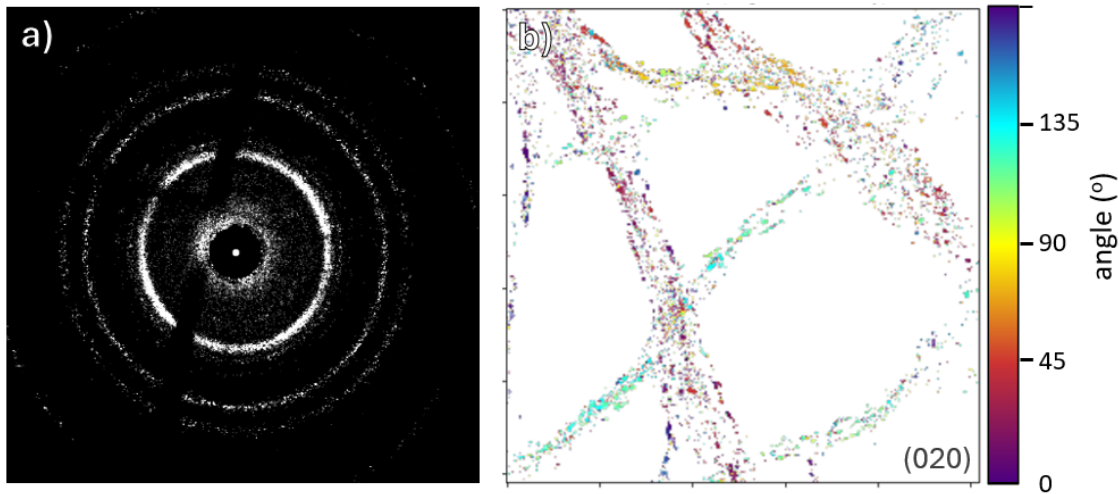


Figure 4.41: (a) BVM and (b) intensity-weighted orientation map of the (020) reflection of a P3HT/OA-AuNP nanoweb containing several fibres.

In conclusion, 4D-STEM reveals that the crystallites possess dimensional anisotropy with the longer $[0k0]$ axis oriented along the fibre. This finding reveals that anisotropy provides the driving force for uni-axial elongation to generate crystallite alignment during spinning. Secondly, it suggests that crystallites are predominantly formed in solution before electrospinning.

4.6 Conclusions

The photoelectric performance of an active material is heavily influenced by its internal nanostructure which is, in turn, dictated by the processing methodology from solution. Within this chapter, the process-structure relationship within electrospun P3HT, and

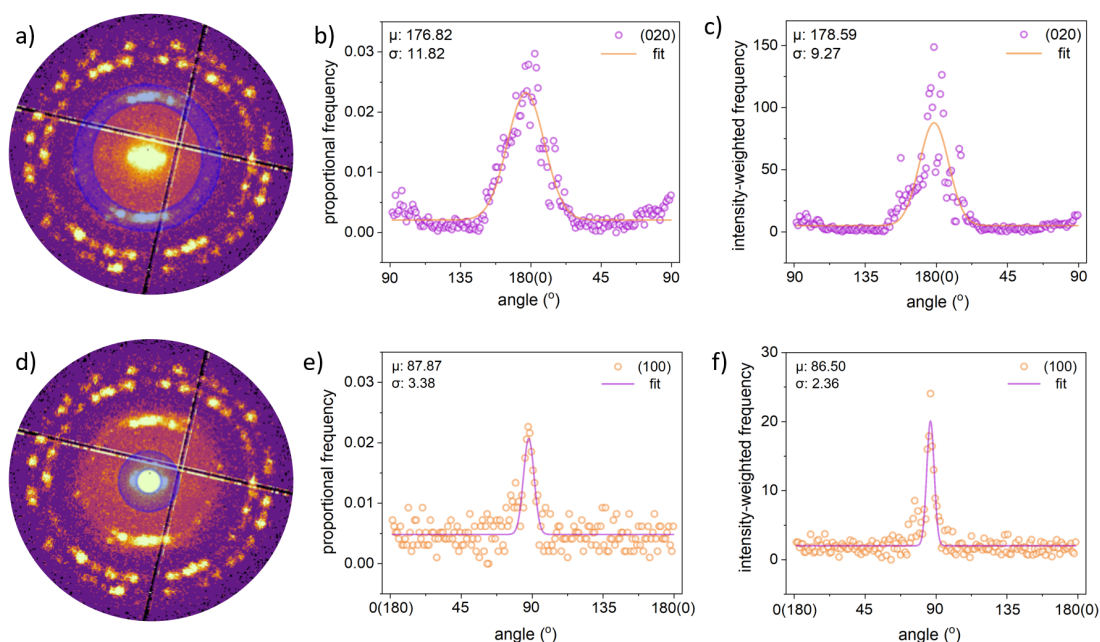


Figure 4.42: (a, d) Masking annulus, (b, e) pixel number-weighted and (c, f) intensity-weighted orientation (angle) histogram of (a, b, c) (020) and (d, e, f) (100) scattering, revealing the angular distribution of crystallites. A 0° angle refers to Bragg vector parallel to the y-axis.

the effect of washing or annealing processes, is explored. This is achieved by probing the composition, morphology, molecular orientations, and crystallinity of nanoparticle-containing P3HT fibres produced by electrospinning.

Initially, thermal analysis is used to ensure the insulating polymer is efficiently removed from the P3HT/PEO blend fibres upon washing, in an attempt to prevent inhibition of the charge transport qualities of the conjugated polymer. The most effective solvent for this selective deposition was hot IPA capable of removing up to 98.5% of the PEO. Effective washing is dependent upon the phase separation reported by Kim et al. to prevent isolated PEO regions forming. [67] Herein, it is demonstrated that nanoparticle introduction does not impede the formation of the P3HT core and PEO sheath. Due to the expense of silver and gold, it is vital that a significant proportion remains, and so TGA analysis was once again employed to show that up to 85 % of PEO-reduced AgNP content remains after washing. TEM and STEM-in-SEM imaging techniques reveal the absence of nanoparticle aggregates, and that effective particle dispersion is achieved, perhaps due to repulsion generated during electrospinning. The P3HT starting material

presented a large influence upon the final dimensions and morphology of the nanoweb regarding size, junction fusion and surface texture.

Through complementary techniques, polarized UV-Vis, and X-ray and electron diffraction, a unique nanostructure is proposed to have been imparted by electrospinning, due to shear forces and uni-axial elongation. Overall, extension of the P3HT chains along the fibre axis (in particular in amorphous regions) is revealed using polarized UV-Vis spectroscopy, with greater absorption of light when polarized along the fibre axis. Whilst alignment is commonly associated with electrospinning, to my knowledge, no study has investigated the effect of P3HT fibre diameter upon the extent of this alignment. Herein, the polarized-light absorption anisotropy increases from a ratio of 0.88 for pristine P3HT fibres (220 nm before washing) to 0.62 for sub-100 nm PEO-reduced AgNP-containing fibres (spun after 96 h ageing), suggesting a significant improvement to chain alignment. Concurrently, an increase in J-aggregate behaviour is observed, associated with greater intra-chain interactions. Enhanced orientation of polymer chains in-plane with the substrate upon fibre collection may provide optimal polymer orientation for light harvesting. [61, 62, 68] Linear transmission measurements were shown to be inadequate for these studies, due to the diffuse light scattering. Instead, the use of an integrating sphere to collect total reflectance and transmittance spectra was shown to be effective.

Conversely, X-ray and electron diffraction studies reveal that polymer backbones located within crystalline regions are oriented orthogonally to the fibre length, demonstrating that the polarized UV-Vis measurements are dominated by the amorphous content of the fibres. The X-ray scattering characteristics are most consistent with P3HT crystallites oriented with their (0k0) axis along the fibre length. There is only a weak radial preference as the fibre, and therefore the crystallite, is free to twist/rotate during electrospinning. This creates a full distribution of edge-on to end-on crystallites wrt the substrate. Hermans' orientation parameters, calculated from azimuthal scans, demonstrate that the initial addition of AgNO₃ degrades the extent of crystalline alignment. However, following reduction to PEO-reduced AgNPs over 96 h, the fibres contain equivalent or greater alignment along the fibre axis versus their pristine counterparts.

Nanobeam electron diffraction or 4D-STEM experiments represent the first report of crystallite distribution and alignment mapping within single electrospun fibres of organic semiconductors. The spatial resolution of the crystallites reveal anisotropic nano-crystals with a width of ca. 10 nm but up to 80 nm in length. Steady-state UV-Visible absorption measurements of the spinning solutions reveals the presence of nano-precipitates formed during ageing. Generally, P3HT crystals grow preferentially along the (0k0) axis, and therefore possess a longer length in the $\pi - \pi$ direction. Hence, the very same driving forces of uni-axial elongation, orient the (0k0) axis along the fibre length, delivering the reverse backbone orientation to polymer found in amorphous regions. These findings suggest that these nano-crystals comprise a majority of the crystalline content within the fibres with comparatively low crystallisation during the spinning process itself. It is also suggested that solution ageing is vital to allow time for self-assembly of anisotropic nanocrystals, and to promote a greater extent of crystallinity in the final product. Fibres electrospun from unaged particle-containing solutions appear to possess a lesser extent of crystallinity which may deliver poor charge mobility, evident from the lower total scattering intensity versus pristine and optimally aged nanoparticle-containing fibres.

This process-driven fibre nanostructure provides a strong platform for long-range lateral charge transport along crystalline domains, continuous for up to tens of nanometres. Long persistence lengths of highly-ordered $\pi - \pi$ stacking have previously been linked with long-range exciton diffusion lengths up to 300 nm. [245] Meanwhile the increased prevalence of end-on crystallites may enhance vertical transport potential versus edge-on thin-films. Within other organic electronics, such as Organic Field-Effect Transistors (OFETs), the lateral charge transport potential through long-range $\pi - \pi$ stacks is highly advantageous and consequently, enhanced mobility of fibrous OFETs has been reported. [264, 277]

The realisation of thinner fibres has been demonstrated to enhance the alignment effects of electrospinning, having undergone more stretching to have reached this diameter. Given that the diameter reduction strategy described in Chapter 3 has produced the thinnest instance of P3HT fibres, superseding previous reports, it offers the possibility of also generating greater degrees of chain and crystallite alignment.

5

Assessing the Photovoltaic Potential of Plasmonic Nanofibrous Active Layers

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5.1 Highlights

Within this chapter, it is demonstrated that the fibres' light-harvesting capabilities rise with solution ageing before electrospinning, concurrent with diameter reduction and the formation of PEO-reduced AgNPs. As a result, fibres spun after 96 h of ageing offer 84% (relative) higher photon absorption between 350 and 800 nm than those spun immediately after AgNO₃ addition. When compared to the equivalent mass thin-film,

nanoparticle-containing P3HT fibres deliver up to 58% higher photon harvesting, owing to polymer alignment and the LSPR effect.

Whilst these findings indicate enhanced exciton generation, excitons must be dissociated into free charges to generate current. PL quenching efficiency reveals that up to 95 - 97% of excitons are non-radiatively quenched, independent of fibre diameter, likely proceeding via dissociation at the PCBM interface. This suggests significant acceptor diffusion into the fibres upon backfill. Transient absorption is studied between 40 fs and 3 ns, across 6 orders of magnitude, to probe the charge carrier (polaron) conversion rates and lifetimes. PEO-reduced AgNPs are shown to offer 59 % greater polaron populations (measured at 1 ns) per exciton formed. This manifests due to longer exciton/polaron lifetimes and/or improved polaron formation. Compounded with light-harvesting improvements, these active layers show significant promise.

Finally, proof-of-principle OPV devices are produced with an inverted structure. Unoptimised devices present PCEs of $\leq 1.74\%$, inferior to the BHJ at 2.18%. However, PEO-reduced AgNPs induce a V_{OC} enhancement from 0.49 V (BHJ) to 0.57 V. Whilst the ultimate potential of these nanofibrous active layers is considered high, it is postulated that currently the performance is limited by the morphology of the infiltrated acceptor layers which attenuates carrier extraction.

5.2 Background

Outlined in Section 1.2, a productive OPV photoactive layer must form large exciton populations following high photon absorption. Vitally, it must then efficiently separate these excitons at the heterojunction, and ultimately extract these carriers to the external electrodes. If just one of these three key steps is found to be ineffective, it will act as a bottleneck and impede final performance.

In the previous experimental chapter, enhanced in-plane polymer chain alignment with fibre diameter reduction has been presented, whilst a strong plasmonic response was recorded for nanoparticles encapsulated within the electrospun polymer. These dual-modes have been well reported to provide enhancement in photon absorption (the relevant literature is collated in Appendix Table A.1.1 - A.1.2).

However, it is also vital to evaluate whether the fibres possess diameters allowing for effective exciton dissociation, and appraise the influence of the metallic nanoparticles, to assess the ultimate PCE potential of the nanofibrous active layers.

Reproduced in Figure 5.1, Kim et al. demonstrated the efficiency of exciton dissociation as a function of fibre diameter using PL emission. [64, 67] PL quenching can be used as a predictor of eventual device performance, with greater PCE generally coinciding with higher quenching efficiency. [278, 279, 280] Given that few excitons are spontaneously dissociated in neat P3HT, PL emission of the nanoweb prior to acceptor backfill is assumed to be representative of the total exciton population. After PCBM introduction, the researchers presented that quenching efficiency increased as the diameter of electrospun fibres was reduced. Within these works, fibre with diameters of 80 nm (P3HT) and 50 nm (PCDTBT) were required to enable good charge separation. [64, 67]

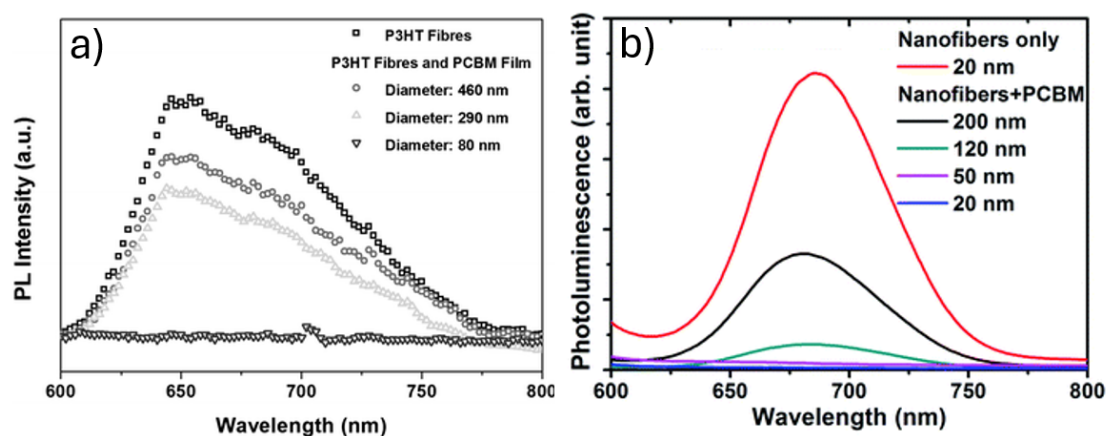


Figure 5.1: PL spectra of (a) P3HT and (b) PCDTBT nanofibres and increasing PL quenching efficiency upon PCBM infiltration of lower diameter fibres. Reprinted with permission from references [67] and [64], respectively. Copyright 2011 The Royal Society of Chemistry, Copyright 2014 The Royal Society of Chemistry.

Introduction of AgNPs or AuNPs into BHJs has reproducibly offered an attractive approach to increasing light harvesting and hence, exciton generation. However, the ability of particle-containing BHJ blends to produce a correspondingly high population of separated charge carriers is more controversial. [281] Nanoparticles may introduce additional recombination mechanisms for either excitons or charge species, which ultimately prevents the consistent observation of final PCE enhancements. [155, 282, 283, 284] Notably, Topp et al. demonstrated that nanoparticles degraded device performance by 40

%, despite a greater initial generation of excitons. [134] For this reason, nanoparticles are often segregated from the photoactive material, and moved to the charge transport layers. However, this means the initial LSPR enhancement potential will be lower.

Nanoparticles have been shown to quench [129] or dissociate excitons, [285, 286, 287, 288] thereby acting as recombination centres or electron acceptors, evaluated by transient absorption and time-resolved PL emission spectroscopies. Other researchers have shown exciton dissociation rates to be invariant of particle presence. [155] If the charges from dissociation at the metal centres are extracted, nanoparticles provide a photocurrent improvement. However in other devices, the additional charges quickly recombine or become trapped. Salvador used ‘steady-state’ photoinduced absorption (Figure 5.2a) to reveal that fullerene molecules could transfer charges to Ag nanoprisms, where they accumulate until recombination, perhaps proceeding via transfer back to the fullerene domain. This was indicated by the evolution of the bleach and adjacent photoinduced absorption (PIA) signal arising from a blue-shift in the nanocrystals plasmonic resonance upon electron injection.

Studies conducted by Du and Wu in Figure 5.2b-d, showed faster decay kinetics upon AgNP addition, and invariance of polaron signal (at 1000 nm, 1 ns) in Figure 5.2c, suggesting that increased exciton populations did not translate into greater polaron populations using fs-TAS. However, by insulating the metal with an oxide coating, polaron generation and/or lifetimes could be improved versus a pristine BHJ (Figure 5.2b). [155, 288]

Therefore within this final experimental chapter, absorption enhancements must be evaluated, and furthermore, it must be ensured that any additional excitons are effectively dissociated to show that particles do not have a detrimental influence upon excitons or polarons.

5.3 Total Light-Harvesting Properties

5.3.1 Ageing Time and Diameter-Dependent Absorptance Enhancements

Concomitantly with reducing diameter, the absorptance of the nanowebs increases by 84% between fibres spun immediately after salt/nanoparticle addition, and those processed

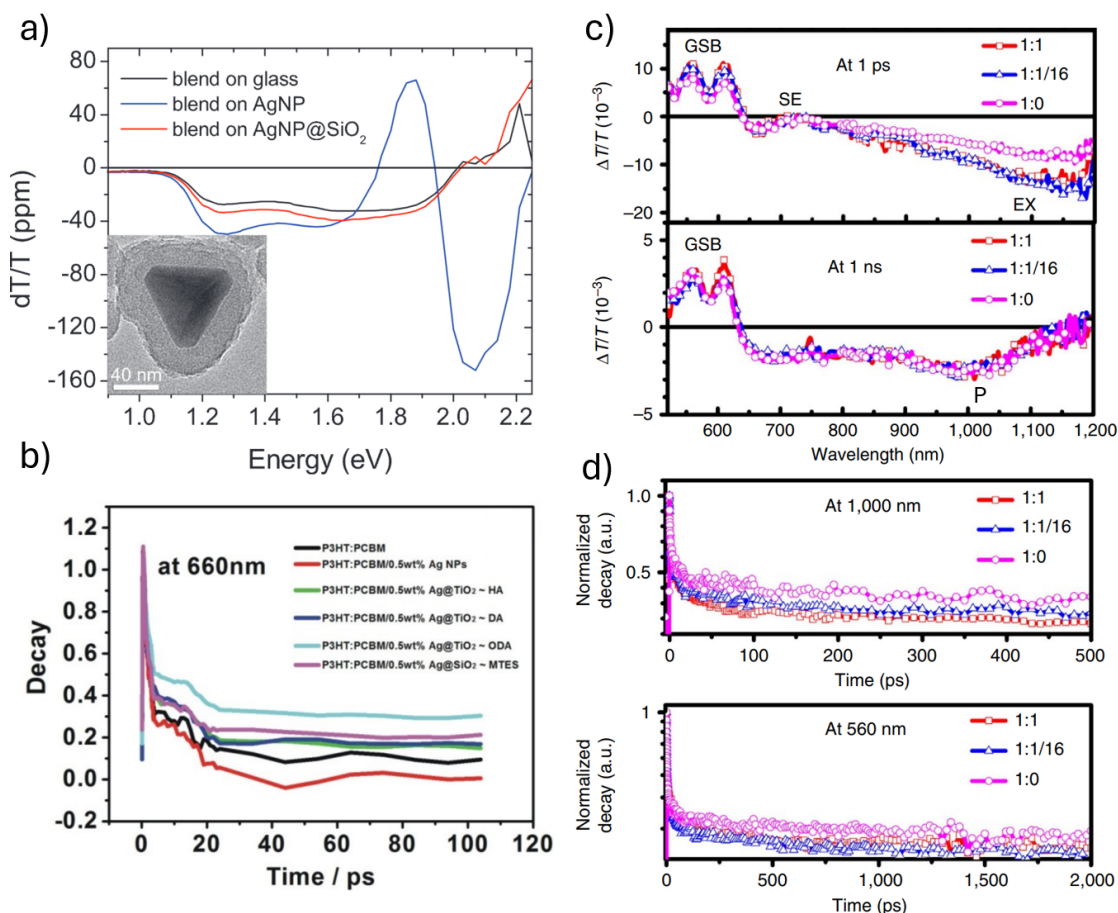


Figure 5.2: (a) Photo-induced absorption spectra of P3HT:PCBM BHJ blends presenting an electron accumulation upon AgNP introduction indicated by the evolution of the concomitant bleach/PIA peak. Reprinted with permission from reference [289]. Copyright 2011 Elsevier B.V. (b) BHJ polaron pair transient decays presenting faster signal relaxation upon the addition of bare AgNPs and slower relaxation with oxide-coated AgNPs. Reprinted with permission from reference [288]. Copyright 2015 Wiley-VCH Verlag GmbH Co. KGaA, Weinheim. (c) fs-TAS spectra of pristine and plasmonic (at low, 1:1/16, and high, 1:1, AgNP concentrations). Plasmonic BHJs present greater exciton generation (1150 nm, 1 ps) yet no polaron population enhancement (1000 nm, 1 ns). (d) Reduced polaron generation in plasmonic BHJs revealed by faster decay associated by exciton/polarons (1000 nm) and GSB (560 nm) recovery. (c) and (d) are reprinted with permission from reference [155]. Copyright 2013 Springer Nature Ltd.

after 96 h ageing. Figure 5.3 presents a sharp increase in the absorbance of fibre mats with an equal mass of P3HT (within 5%) over the first 72 - 96 h of ageing. Fibres spun 0 h after AgNO₃ (240 nm before washing) produced a maximum (0-1) transmission absorbance (560 nm) of 45%. The fibre mats spun from aged solutions deliver incremental absorbance increases until a plateau was observed at 72 - 96 h (83% absorbance at 560 nm). The absorbance maxima coincide with the minimum fibre diameter. Subsequently, by 168 h ageing, the fibres deliver a low absorbance of 71%.

By this time, fibre beading has begun to occur.

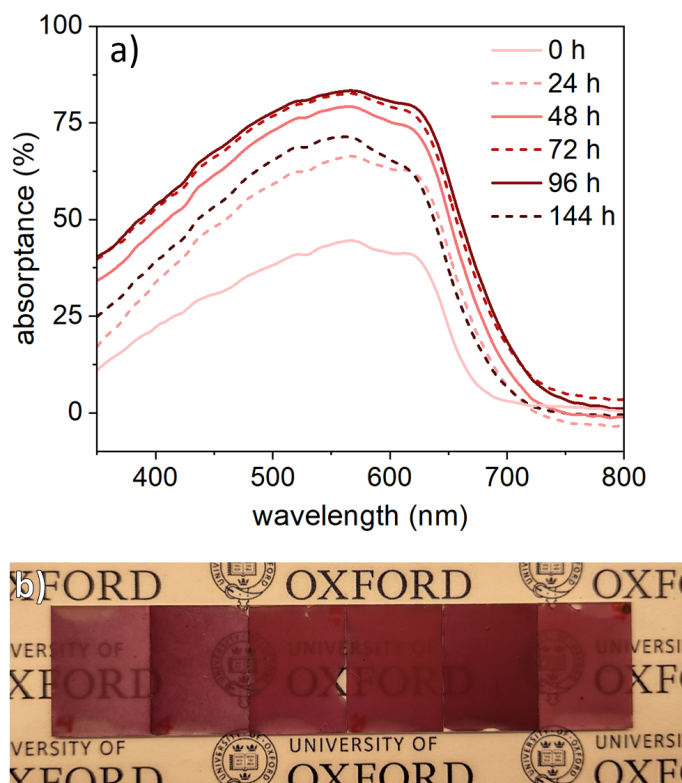


Figure 5.3: (a) Absorbance of PEO-reduced AgNP-containing P3HT nanowebbs (determined using an integrating sphere) revealing a substantial improvement in light-harvesting ability upon solution ageing before spinning. (b) Digital photographs of electrospun nanowebbs spun after 0 h, 24 h, 72 h, 96 h and 144 h of ageing (from left to right).

In Section 3.3.1, it was identified that PEO-reduced AgNPs form over a similar time-scale and the plasmonic intensity increases over time. However, relative to the semiconductor, absorption by the nanoparticles themselves is low, and cannot account for up to 80% greater harvesting alone. Therefore, the first contribution to enhanced photon absorption is an increase in the P3HT absorption cross-section due to an evolving LSPR effect. rather than As the concentration of nanoparticles increases, as will the plasmonic intensity, and therefore LSPR enhancement of the semiconductor. Furthermore, in Figure 3.3, the plasmonic intensity drops beyond 96 h of ageing, coinciding with the absorbance drop.

Therefore, this enhancement is also attributed, in part, to a similar physical phenomenon used to quantify fibre alignment with parallel and perpendicularly polarized light. When the polymer backbone is aligned within the plane of the substrate, this generates

a higher-probability of absorption of light impinging normal to the nanoweb due to the orientation of the transition dipole. [61, 62, 68] Given that the electrospinning process aligns amorphous polymer chains along the fibre axis, this will translate into a higher proportion of chains being oriented in-plane with the substrate upon collection, as the fibres lay approximately flat. As thinner fibres possess increasingly aligned polymer chains, they possess more effective light-harvesting properties for a given mass of active material.

Thirdly, thinner fibres possess increased surface area, and thus, could scatter more light. Scattering increases the average pathlength of light through the nanoweb. Therefore, light interacts with more molecules, increasing the absorption probability. These three effects enable thinner diameter fibres, spun from solutions aged for longer, to provide greater optical absorption than thicker fibres.

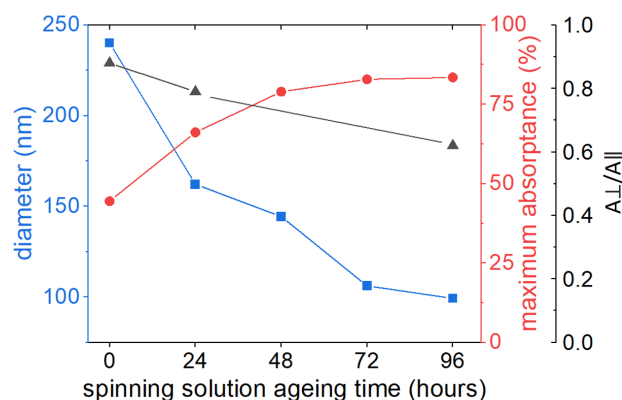


Figure 5.4: The reducing P3HT fibre diameters generated from increasingly aged PEO-reduced AgNP-containing spinning solutions promotes amorphous polymer alignment, given by the ratio of absorbed parallel and perpendicularly polarized light (a lower value indicates better alignment). This, in turn, enhances light-harvesting properties of the nanoweb.

In contrast, peak absorbance with OA-NPs in Figure 5.5 was recorded after 48 h ageing, and subsequently reduces despite similar diameter behaviour. OA-AgNPs precipitate over time which reduces any LSPR enhancement in fibres spun from aged solutions, however this is not the case for OA-AuNPs. (Section 3.3) The stable plasmonic response of OA-AuNPs should allow for isolation of diameter effects. However, there is still a strong absorbance improvement over the first 48 h, during the time of greatest diameter reductions.

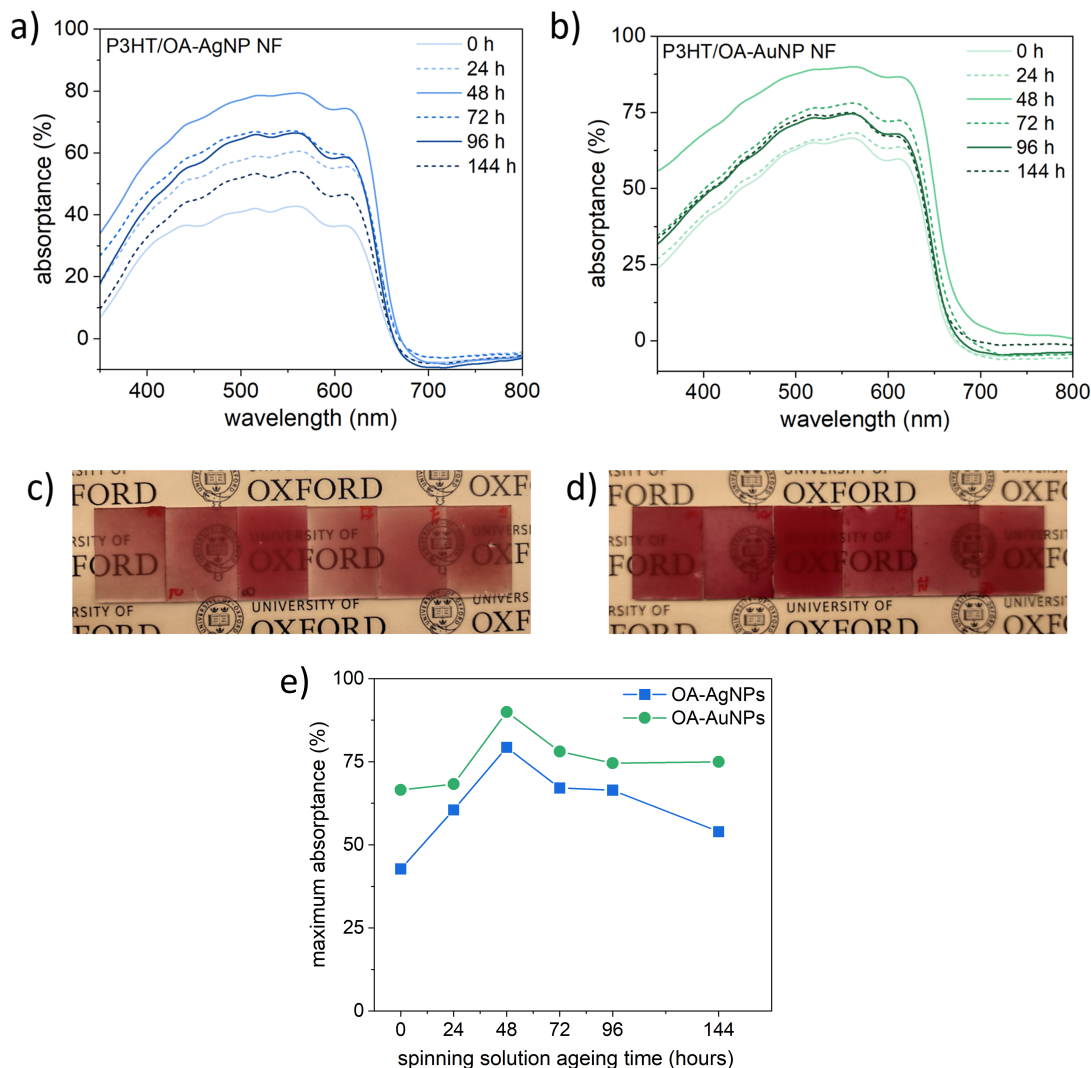


Figure 5.5: Effect of solution ageing (before spinning) upon the absorbance spectra of (a) OA-AgNP and (b) OA-AuNP containing P3HT NFs on ITO-coated glass. Maximum light harvesting properties were recorded after 48 h, earlier than with PEO-reduced AgNPs. Digital photographs of the nanofibrous films containing OA-capped (c) Ag and (d) AuNPs spun after 0 h, 24 h, 48 h, 72 h, 96 h and 144 h of ageing (from left to right). (e) Peak absorbance of OA-capped NP-containing P3HT fibres spun after a 0 - 144 h solution ageing period.

5.3.2 Light-Harvesting by Nanofibres versus Thin-Films

Ultimately, the absorbance of the electrospun fibre films were compared to conventionally spin-coated thin-films. For this analysis, thick films were spin-coated from chloroform solutions upon large ITO substrates to produce a film mass of 0.20 mg. Nanowebs were then produced to equal mass (within 5%), and absorbance was determined by total integrated transmittance and reflectance.

The electrospun material presented far greater levels of diffuse scattering, as represented by the high attenuation of transmittance > 700 nm. In comparison, due to the reduced interface found in films, scattering is substantially lower (Figure A.5.1). Upon first inspection, the total amount of light harvested by the film and pristine fibres in Figure 5.6a is similar. However, in Figure 5.6d, the increase in J-aggregate character in the fibres provides additional photon absorption for wavelengths between 550 and 650 nm. Additionally, an absorption ‘tail’ below 450 nm was observed, ascribed to amorphous content which absorbs light over a wide energy range continuum (similar to when dissolved in solution). Lower extent of crystallinity is also consistent with the lower total X-ray scattering observed in Chapter 4 versus films. Between ~ 450 and 550 nm, the thin-film provides greater harvesting ability, but integrated across the entire wavelength range, the cumulative absorptance of the fibre in Figure 5.6g increases from 31.2% to 36.6%, or a factor of 1.14x, versus the thin-film.

This suggests that electrospinning produces greater in-plane polymer chain alignment versus the driving force which promotes alkyl chains to present at the substrate and air interface during spin-coating. Thereby, spinning produces a better overlap between the polymer’s $\pi - \pi^*$ transition dipole moment and the electric field vector of radiation. However, considering the variance between repeat samples, the electrospinning enhancement in the absence of nanoparticles is small. Taking into account the more straight-forward fabrication approach of films, previously reported strategies to P3HT fibres may not provide a significant enough enhancement to warrant the complexity of processing by electrospinning.

More significant enhancements were found upon the introduction of nanoparticles in Figure 5.6b and e. The incorporation of PEO-reduced AgNPs and OA-AuNPs delivered a strong broadband enhancement across the entire visible light region versus pristine nanofibres, delivering enhancements of 1.30x and 1.38x, respectively (Figure 5.6h). Surprisingly, there was no evident enhancement (1.04x) from OA-AgNP addition. Compared to the pristine P3HT films, PEO-reduced AgNP and OA-capped AuNP-containing P3HT nanofibres provide an enhancement of 1.48x and 1.58x, respectively.

At almost 60% additional light-harvesting, nanoparticle infusion produces fibres with impressive absorption properties, justifying the complexity of their fabrication.

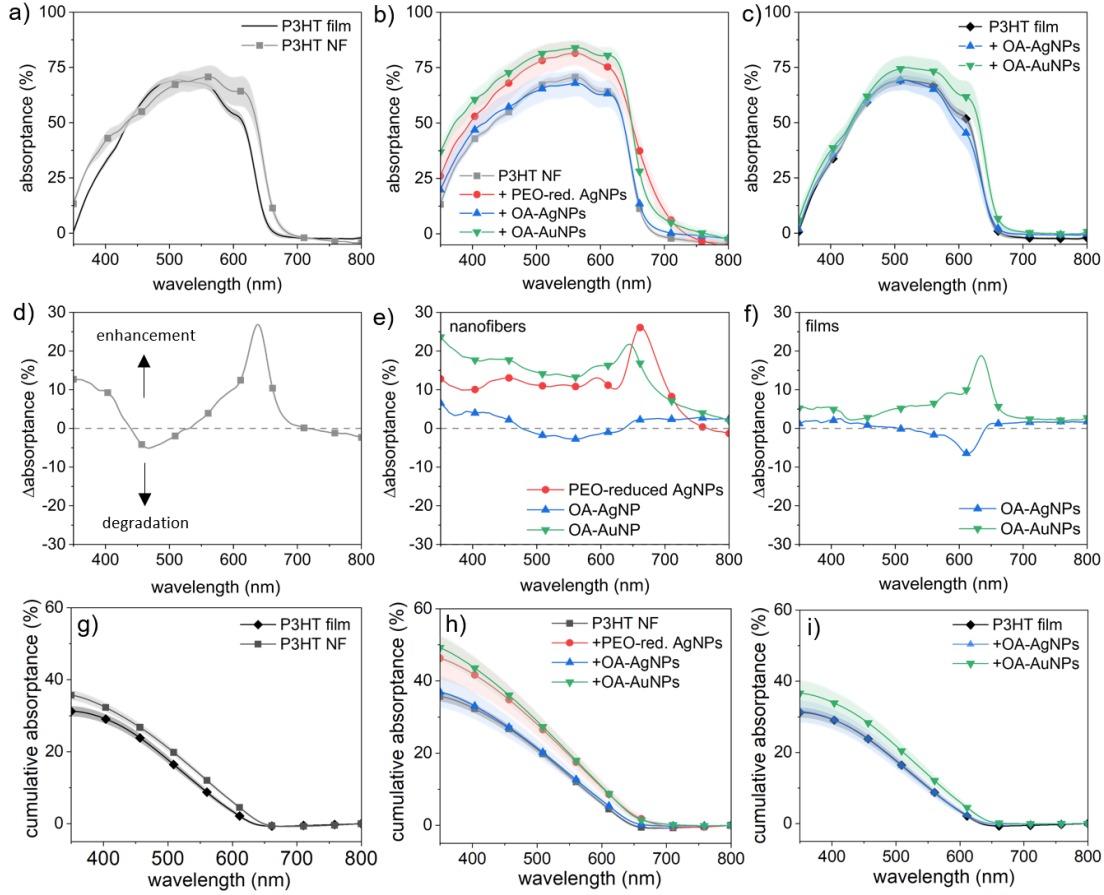


Figure 5.6: Absorbance spectra of (a) electrospun P3HT nanofibres and films, and NP-containing (b) nanofibres and (c) films, presenting dual absorption enhancement modes from electrospinning and plasmonic effects. Change in the absorbance spectra upon (d) electrospinning P3HT in comparison to a spin-coated film, and upon NP addition to (e) fibres and (f) films compared to their pristine counterparts. Integrated, cumulative light-harvesting from the absorbance spectra of (g) P3HT films and fibres, (h) P3HT and NP-containing P3HT fibres and (i) P3HT and NP-containing films.

LSPR enhancement was not unique to fibres, as OA-capped NP-containing P3HT films showed an analogous yet lesser results, with OA-AuNPs producing a 1.17x enhancement. OA-AgNPs again had no effect (1.01x) in Figure 5.6c, despite presenting the greatest plasmonic intensity at a given loading (Figure A.5.2). Furthermore, with a larger diameter than the PEO-reduced AgNPs, OA-NPs offer greater scattering properties. Although lower intensity, PEO-reduced AgNPs possess an LSPR shifted 40 nm red of OA-AgNPs in chloroform. Due to the greater absorption coefficient of P3HT, and the composition of

the fibres, the nanoparticles' plasmonic peak cannot be directly observed in the composite. Instead, using FDTD as outlined in Section 2.2.2.5, it is simulated that when dispersed within a refractive index of P3HT (taken to be 1.95), OA-AgNPs produce an LSPR centred at 480 nm, 70 nm red-shifted from when dispersed in chloroform. (Figure A.5.2) Assuming a consistent 40 nm shift, PEO-reduced AgNPs may produce LSPR at 520 nm. OA-AuNPs were simulated to give LSPR at 580 nm, meaning these particles possess a better spectral overlap with light absorption by the semiconductor. Prospectively, OA-AgNPs may not deliver the same enhancements due to worse spectral overlap.

Sample	Integrated Absorbance (%)	Enhancement vs P3HT film	Enhancement vs P3HT NF
P3HT film	31.2	-	0.87
P3HT NF	35.7	1.14	-
P3HT/PEO-red. AgNP NF	46.3	1.48	1.30
P3HT/OA-AgNP NF	37.0	1.19	1.04
P3HT/OA-AuNP NF	49.2	1.58	1.38
P3HT/OA-AgNP film	31.5	1.01	0.88
P3HT/OA-AuNP film	36.6	1.17	1.03

Table 5.1: Total light-harvesting properties of pristine and NP-containing film and fibre samples determined by integrating the absorbance trace between 350 and 800 nm, and overall enhancement versus their pristine counterparts.

FDTD in Figure 5.7 was also used to simulate the electric field enhancement generated by the plasmonic particles in the P3HT matrix at the (0-0), (0-1), and (0-2) vibronic transition wavelengths (515 nm, 565 nm and 615 nm, respectively) These fields are responsible for the LSPR effect and the strongest electric fields are produced at wavelengths close to the plasmon resonance. OA-AgNPs produce a maximum field strength enhancement of 12.4x at 515 nm, dropping to 7.0x and 5.7x by 565 nm and 615 nm, respectively. In contrast, a 2 nm 'PEO-reduced AgNP' offers larger field enhancements at the (0-1) and (0-2) transitions of 7.5x and 6.5x. Likewise, OA-AuNP produces a substantially higher field strength of 20x and 9.5x at these wavelengths for which P3HT has the highest absorption coefficient. The OA-AgNP electric field propagates further from its surface versus PEO-reduced AgNPs, providing a greater overall field strength for a single particle. However, being smaller, PEO-reduced AgNPs are roughly 125 x more numerous at the same loading. This may offer a greater overall electric field enhancement.

P3HT was modelled using isotropic, scalar parameters, considered adequate for the scope of this thesis. However, the studies on polymer and crystallite alignment suggests that the fibres exhibit significant optical anisotropy. As the dielectric function of P3HT is greater when probed with radiation polarized parallel to the polymer backbone, versus perpendicular, [290] therefore, a more accurate FDTD model would employ an anisotropic environment captured using vector/matrix tensors. [291, 292] The injection axis of light should also be considered. It should also be noted that due to the step size (0.1 nm) used for the simulation, the 3 nm ‘PEO-reduced AgNP’ has a blocky surface. This can lead to spurious regions of increased electric field at these pixelated edges which may be more intense than the true value. For accuracy and confidence in these comparisons, the mesh step size should be decreased, however in this case, available computational power was limited.

The lesser absorptance enhancement by OA-AuNP infusion to films versus the fibres provides a means to deconvolve the contributions by LSPR and diameter-reduction/alignment enhancements. Of the 1.58x, 1.17x is ascribed to LSPR and the remainder from the nanoparticle-induced changes to the electrospun fibres. The difference is attributed to the increased amorphous polymer alignment and scattering by the thinner fibres. Combining the 1.17x LSPR enhancement (P3HT vs P3HT/OA-AuNP film) and 1.14x electrospinning enhancement (P3HT film vs fibre) is also lower than the enhancement demonstrated by OA-AuNP infusion to fibres. This provides evidence that the dual enhancement modes act synergistically, providing a greater enhancement than the sum of their parts due to the improved diameter-dependent amorphous chain alignment.

5.4 Active Layer Fabrication

5.4.1 Infiltration of Nanoweb with Electron Acceptor

Nanoweb infiltration with PCBM is not trivial due to the difficulty in spin-coating continuous films in the presence of the complex topology imparted by the fibre template. The fibres disrupt the spin-coating process causing ‘pile-up’ and ‘wakes’ to form on either side. Prevention of comet streaks, pinholes and divots was not straight-forward, which commonly occur in the presence of dust on the substrate.

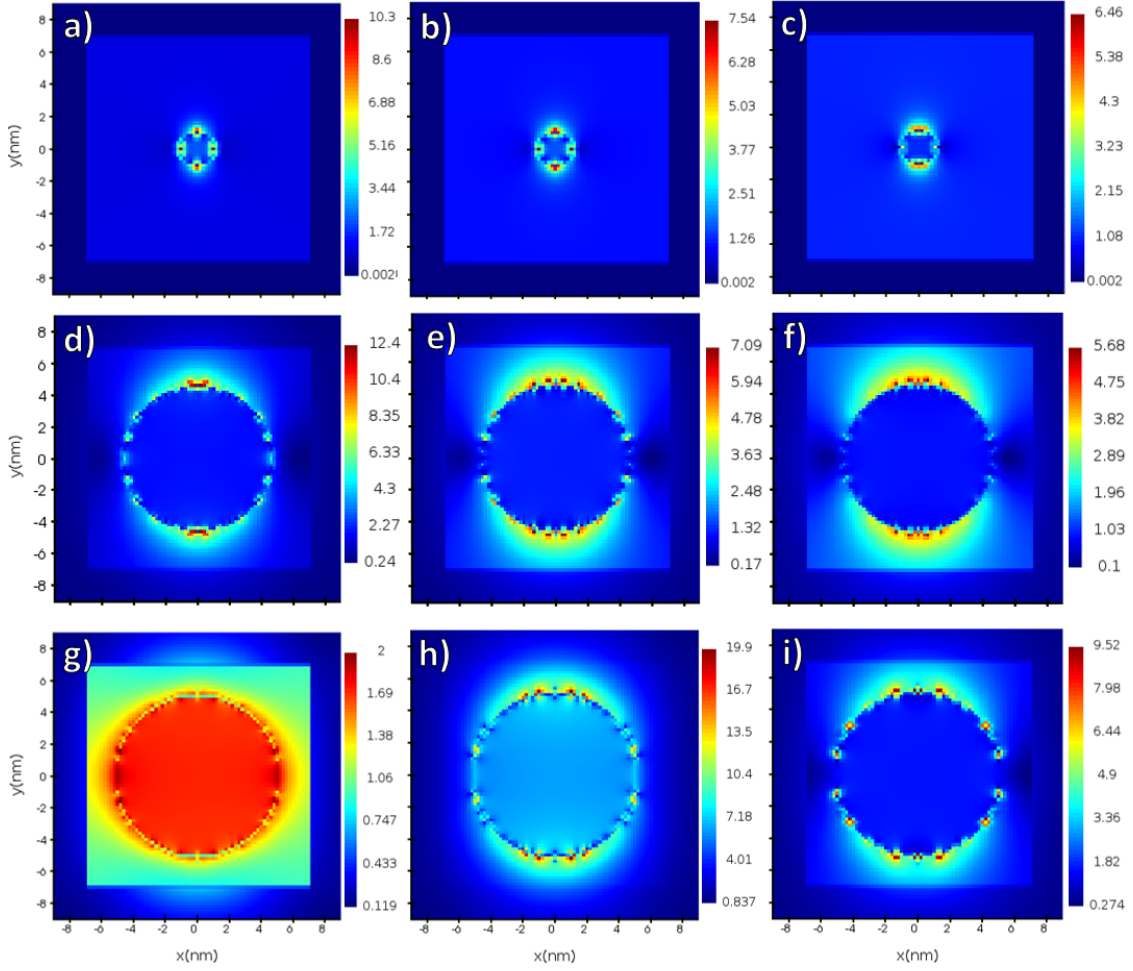


Figure 5.7: FDTD simulations of a single (a - c) 3 nm ‘PEO-reduced AgNP’, (d - f) 10 nm ‘OA-AgNP’ and (g - i) 10 nm ‘OA-AuNP’ dispersed in a refractive index of 1.95, showing the electric field strength generated by the plasmonic resonance at (a, d, g) 515 nm, (b, e, h) 565 nm and (c, f, i) 615 nm.

Kim et al. conducted infiltration using a 5000 rpm rotation speed with a PCBM solution in DCM (16 mg mL^{-1}), however no further details were shared. [64, 67] A spin-coating solution can be dispensed onto the substrate either from static start (prior to rotation) or dynamically (once at full rotation speed). Using a dynamic approach, the SEM micrographs in Figure 5.8a-b show poor film uniformity and continuity.

In Figure 5.8c-d, PCBM dissolved in neat DCM (at saturation concentration of 14 mg mL^{-1}) was dispensed via a semi-static approach onto the substrate at a low rotation speed (200 rpm, 5 s), followed by a ‘spin-off’ stage at 1500 rpm. The initial step allowed additional time for the solution to infiltrate the web and spread over the substrate. This strategy was found to produce more continuous, thicker interstitial films versus the

dynamic approach. Varying the rotation speed during the second spin-off stage did not produce a consistent trend in active layer thickness (not shown here) suggesting that trapping of the solution by the fibres dominates the film formation behaviour. However at the macroscale, greater rotation speeds (up to 5000 rpm) increased the prevalence of cometing, evaluated by eye. Final active layer thicknesses (where fibres were collected for 120 s to yield a ~ 500 nm nanoweb) were 200 - 300 nm, estimated from the cross-sectional SEM micrographs. Under all conditions tested, pinholes were persistent, perhaps due to rapid solvent evaporation (Figure 5.8c-d).

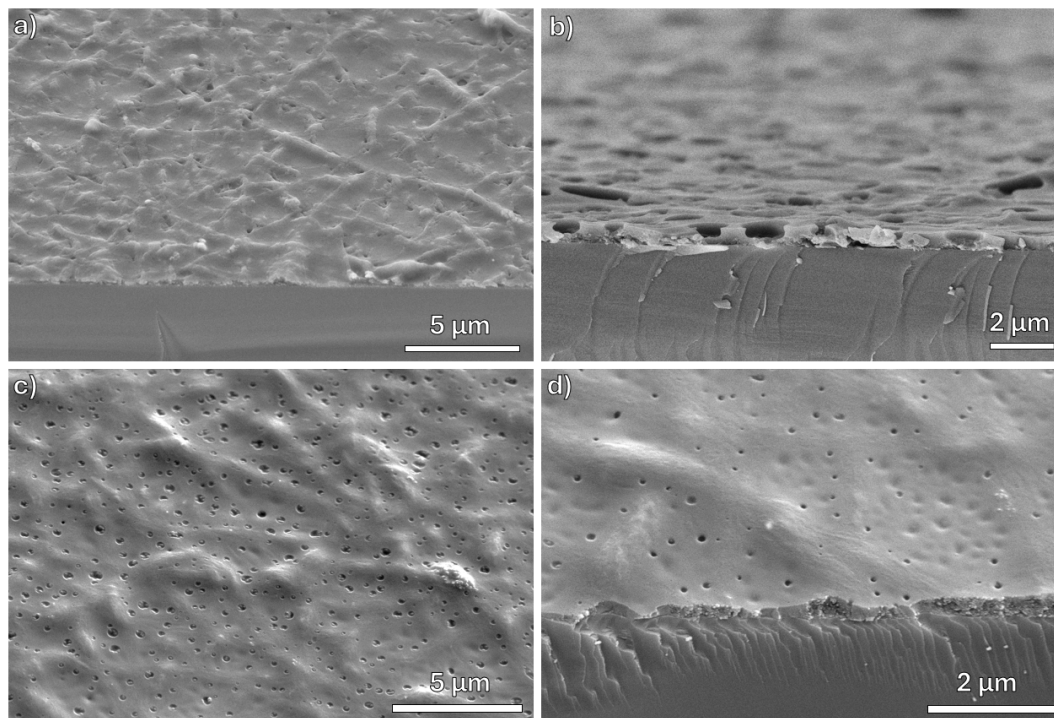


Figure 5.8: (a,c) Tilted and (b,d) cross-sectional SEM micrographs of the nanofibrous active layer achieved via spin-coated PCBM infiltration from an orthogonal solvent solution (DCM) when dispensed (a,b) dynamically after reaching maximum rotation speed and (c,d) prior to ramp up. Pristine P3HT NFs were spun onto Si and the active layer was fractured to reveal its cross-section. Larger diameter, pristine P3HT fibres were used for optimisation as their infiltration was considered more complex.

The SEM and AFM topographic micrographs in Figure 5.8 and 5.9 show that the surface of the active layer possesses greater RMS roughness (1.31 ± 0.19 nm) and average waviness (4.92 ± 2.23 nm) than the BHJ (0.49 ± 0.07 nm and 0.50 ± 0.11 nm determined from AFM images, respectively). The uppermost fibres protrude from the PCBM layer, vital to enabling hole extraction in an inverted OPV structure. Here, roughness is defined

as surface height deviations over small scales, whereas waviness captures more gradual variation in height. However, the threshold between the two is poorly defined in literature.

Surface roughness and waviness of an active layer can influence device performance. Increased roughness/waviness can provide increased surface area for charge collection, [293, 294] but if too high, it may complicate the deposition of conformal transport layers upon it. Optimisation of the infiltration procedure may allow for full encapsulation, control of the roughness/waviness, and avoidance of pinholes. This should be a focus of future work.

DCM is the most frequently used solvent for P3HT:PCBM bilayer fabrication, [295] and allows one to limit the dissolution/degradation of the fibre nanostructure. If morphology were to deteriorate, the proportion of polymer chains oriented in-plane and long-range crystallite alignment would likely be disrupted, attenuating the electrospinning-induced properties. Spin-coating pure DCM (without PCBM) at 1500 rpm over the nanoweb, demonstrates the resistance of the fibres to orthogonal solvent exposure. In Figure 5.9d and e, the SEM micrograph reveals that the fibres are intact, whilst AFM reveals that the fibres are densified/planarized as the maximum depth of the nanoweb is compacted from ~ 500 nm before spin-coating (Figure 5.9c) to ~ 140 nm (Figure 5.9d). The SEM images of the nanofibrous active layers in Figure 5.8 suggest that the fibre structure is retained.

Finally, a nanoparticle-containing P3HT nanoweb is briefly electrospun directly onto a carbon film TEM grid to achieve a low fibre density. After the fibres were subsequently infiltrated with PCBM, STEM-in-SEM analysis in Figure 5.10 reveals that long-range nanoparticle ‘pathways’ are still present within the active layer. EDX linescans drawn across these nanoparticle pathways confirm that sulfur, and therefore P3HT, remains localised to this region.

Other studies have infiltrated P3HT nanoweb using a BHJ blend in chloroform (in which P3HT is soluble). [61, 63] To produce pinhole-free, uniform films, PCBM infiltration was also attempted from semi-orthogonal co-solvent systems, namely 50:50 v/v DCM:chloroform and DMF:chlorobenzene. To avoid excessive fibre dissolution and resultantly, the loss of nano-structure and ‘spin-off’ of electrospun material, a minimal elution volume ($20 \mu\text{L}$) was dynamically dispensed at 1500 rpm. In Figure 5.11, SEM

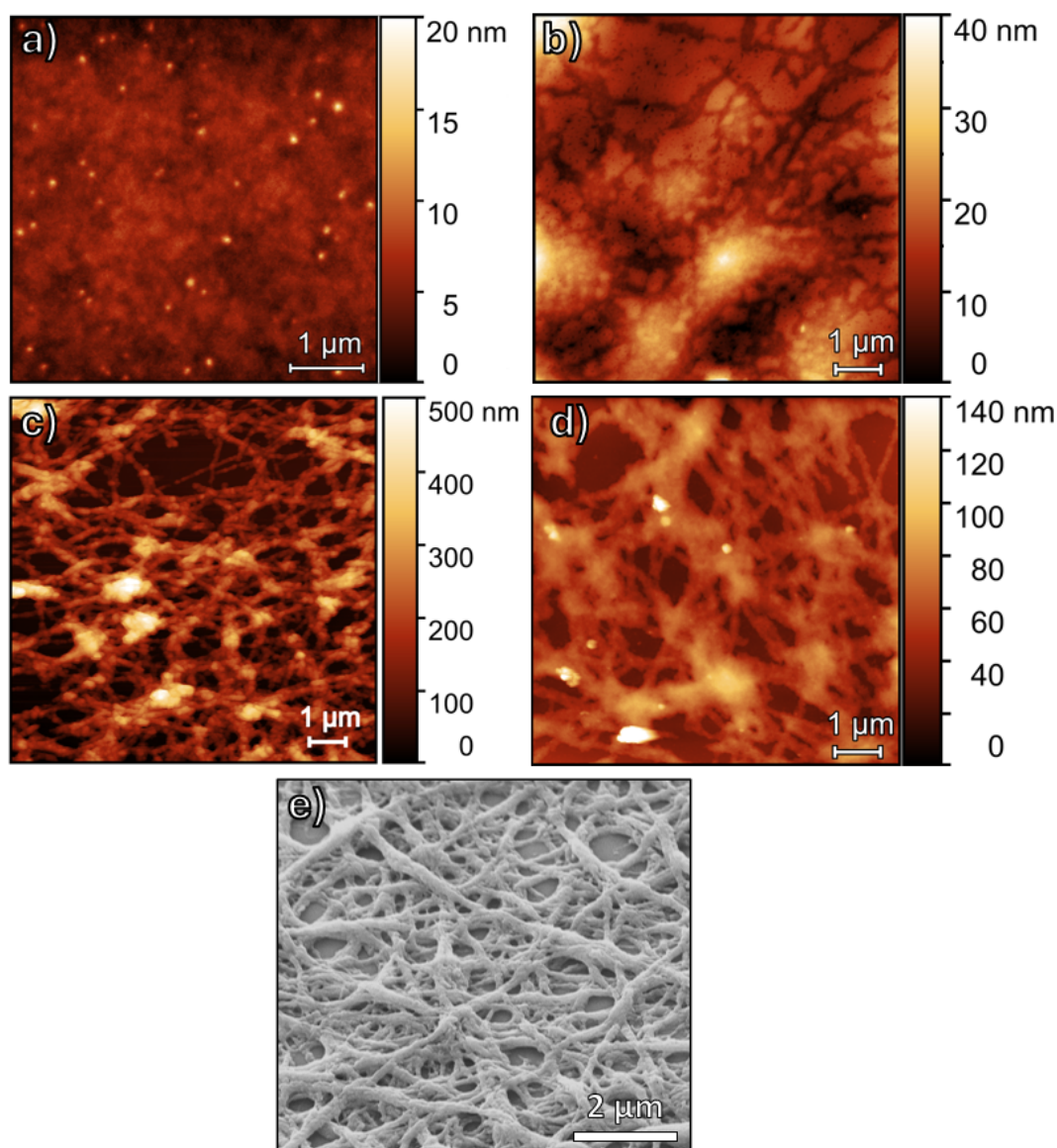


Figure 5.9: AFM topography images of a conventionally spin-coated (b) P3HT:PCBM BHJ and (b) the nanofibrous active layer after backfill using DCM. (c) AFM images of the nanoparticle-containing P3HT nanofibre mat after washing, and (d) AFM and (e) SEM micrograph of the P3HT nanofibre mat after spin-coating with pure DCM without fullerene ($50 \mu\text{L}$, 1500 rpm) showing the fibres remain intact after spin-coating and the pristine P3HT web has increased in density.

micrographs of the active layer after spin-coating indicate that the fibres temporarily resist dissolution during spin-coating. Even so, some loss of donor polymer is expected.

Bedford et al. reported partial dissolution of electrospun P3HT:PCBM fibres following chloroform-based infiltration, but the remaining material maintained ‘structural coherence’ [61] Seidler and co-workers showed that self-assembled P3HT fibres were resistant to dissolution in chlorobenzene for ≤ 60 s, with 81% of the material retained versus

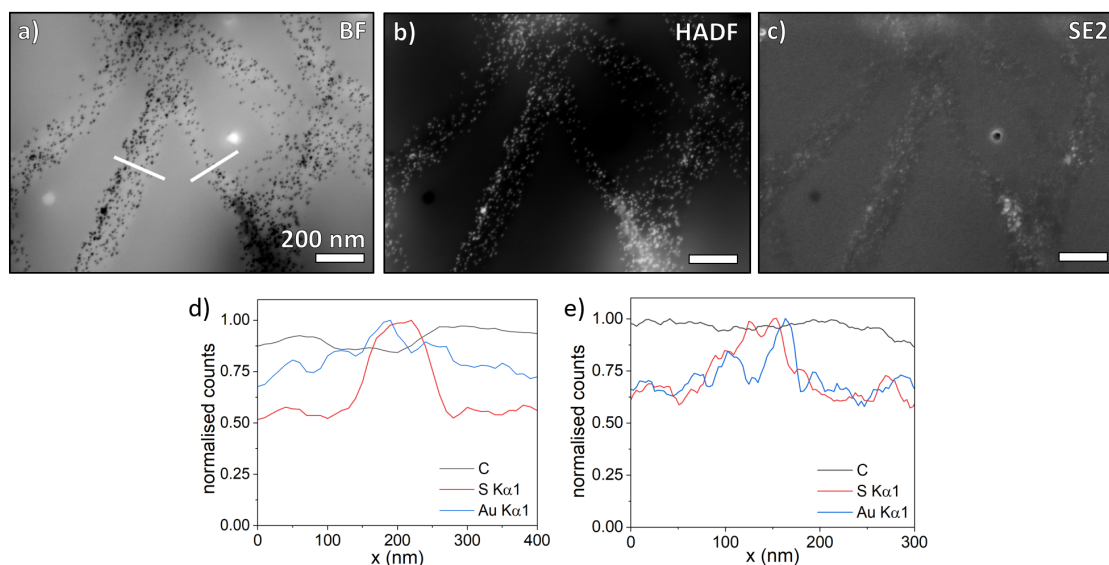


Figure 5.10: STEM-in-SEM (a) BF and (b) High ADF, and SEM (c) SE2 micrographs of a sparse nanofibrous active layer, and (d - e) EDX linescans across the nanoparticle pathways following PCBM infiltration, revealing the spatial distribution of P3HT, proportional to the sulfur count.

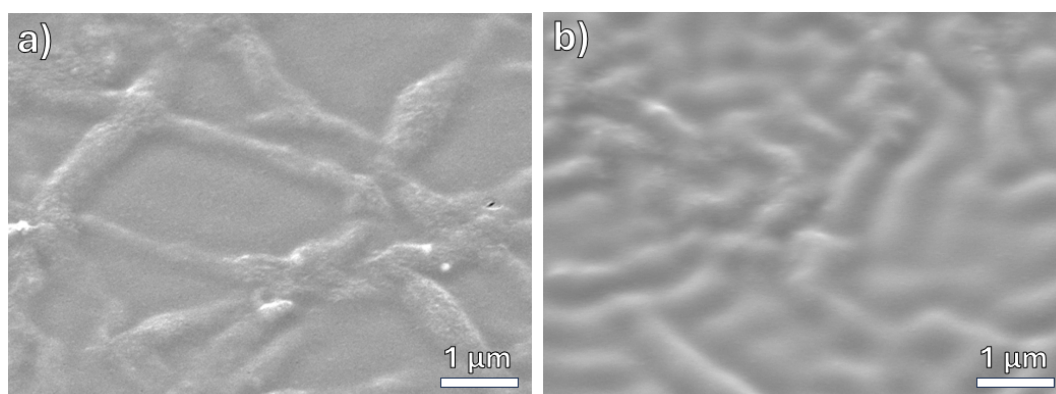


Figure 5.11: 45° tilted SEM micrographs of nanofibrous active layers achieved via electron acceptor infiltration from semi-orthogonal solvent systems of (a) 50:50 v/v DCM:chloroform and (b) DCM:chlorobenzene.

10% preservation of a thin-film. [296] Improvements were expected due to the slower solvent evaporation rates (higher boiling points) allowing for improved infiltration, improved wetting when using good solvents for P3HT, and enabling a higher PCBM concentration of 20 mg mL^{-1} in solution - saturating at 14 mg mL^{-1} in pure DCM. Indeed, the infiltration layers derived from semi-orthogonal solvents in Figure 5.11 do not feature pinholes/divots, and the layer deposited from DCM:chlorobenzene produces more complete fibre encapsulation.

5.5 Exciton Dissociation

5.5.1 Photoluminescence Quenching

To evaluate the ability of the nanofibrous active layer (PCBM layer deposited from DCM) to dissociate excitons generated following photo-absorption, PL emission of the nanoweb pre- and post-infiltration was measured. The experimental set-up is described in Section 2.2.2.4. Within the non-infiltrated electron donor fibres, many excitons undergo radiative charge recombination. However, upon backfilling the interstitial space with the electron acceptor, radiative recombination is quenched - indicative of electron transfer to the fullerene domains. Higher PL quenching efficiency is generally linked to greater eventual device performance in the absence of parasitic non-radiative decay pathways. [278, 279, 280]

Figure 5.12 and Table 5.2 show the ability of a 1:1 w/w P3HT:PCBM BHJ to quench 99.85% of radiative recombination measured within a pristine P3HT film (with half the thickness of the BHJ), suggesting that nearly 100% of excitons formed are dissociated. This indicates effective nanoscale phase separation of the donor and acceptor in the annealed BHJ, and the absence of large domains which would result in exciton recombination, and thus radiative emission.

Sample	PL without PCBM (counts ²)	PL with PCBM (counts ²)	Quenching Efficiency (%)
P3HT Film	133.64	0.197	99.85
P3HT NF	135.53	4.83	96.44
P3HT/PEO-red.AgNP NF (0 h)	141.29	6.93	95.10
P3HT/PEO-red.AgNP NF (24 h)	141.29	7.04	95.10
P3HT/PEO-red.AgNP NF (96 h)	141.87	7.12	94.99
P3HT/OA-AuNP NF (96 h)	141.17	4.58	96.74

Table 5.2: Integrated PL emission count of fibres before and after infiltration (normalized to (0-1) transition without PCBM). PL quenching efficiency, proportional to exciton dissociation in the active layers, is determined by the after/before ratio.

Kim et al. demonstrated that quenching drastically increased with reducing fibre diameter. [64, 67] However, Figure 5.12 shows that fluorescence quenching in fibrous active layers was independent of the fibre diameter, with a competitive rate of ~95 - 97 % radiative quenching compared to emission before infiltration. Fibres with larger

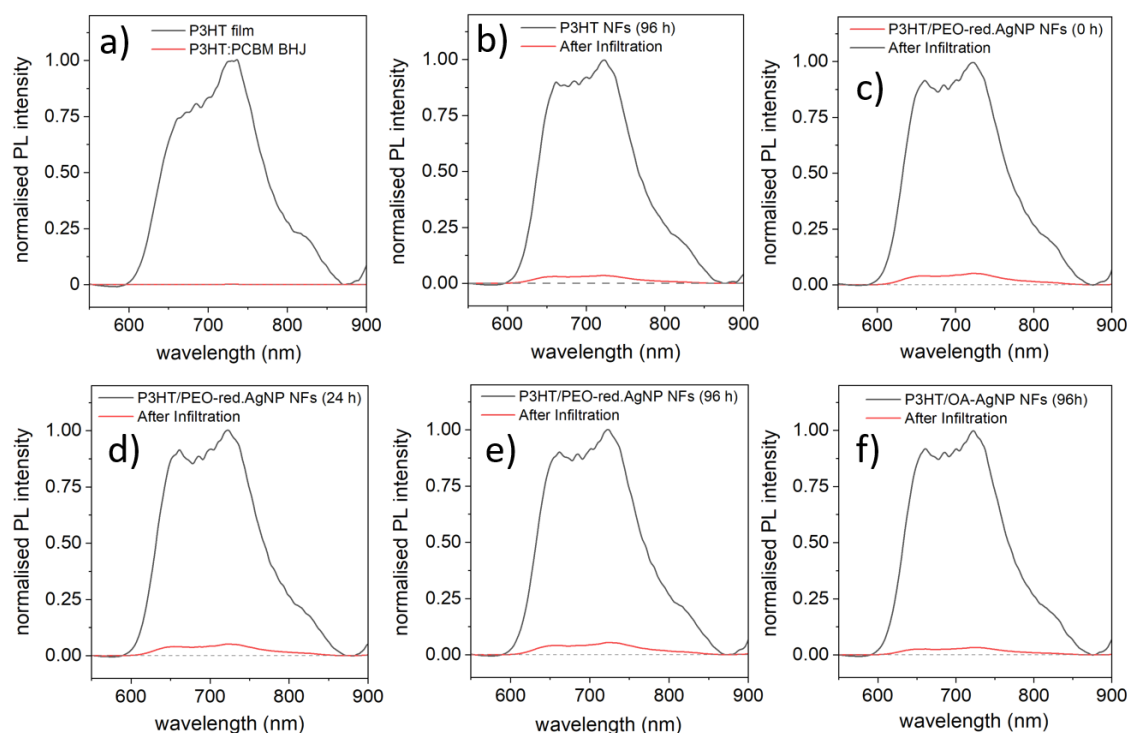


Figure 5.12: PL spectra of an annealed P3HT thin-film and P3HT:PCBM BHJ. (b-f) PL of pristine and NP-containing nanowebs normalised to the (0-1) transition intensity, and PL of the corresponding nanofibrous active layers after PCBM infiltration. Greater quenching upon acceptor addition indicates more effective exciton dissociation into free charge carriers. PL spectra were collected by Karim Elmetekawy.

diameters in Figure 5.12b - d outperformed expectations: Kim et al. reported that 290 nm P3HT fibres only offered $\sim 40\%$ quenching. [67] These findings provide evidence that PCBM diffuses long distances into the fibre reducing diffusion pathways and enabling higher levels of dissociation, despite the use of an orthogonal solvent.

Excitons formed in electrospun nanofibres may also possess longer diffusion lengths than those in films. Longer exciton lifetimes/diffusion lengths have been measured in electrospun poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) fibres. [297] As discussed in Chapter 4, these fibres also contain encapsulated self-assembled crystallites. Recently, self-assembled crystals have been demonstrated to offer diffusion lengths up to 300 nm along uninterrupted $\pi - \pi$ stacks. [245] Each fibrous architecture performed well, indicating the potential for good photovoltaic performance. Compounded with increased absorption reported in Section 5.3, it appears possible to translate these exciton populations into greater numbers of charges, provided quenching

proceeds via charge transfer to PCBM.

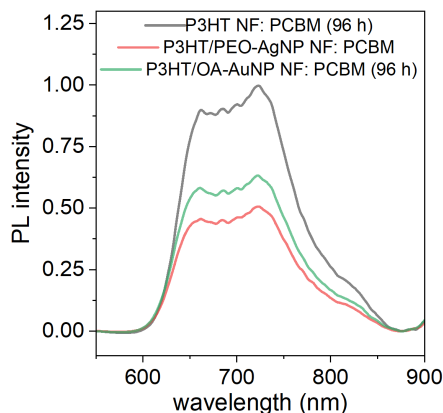


Figure 5.13: PL spectra of the P3HT nanowebs prior to infiltration relative to the pristine P3HT mat suggesting NPs reduce the intensity of radiative emission.

Fibres used in PL measurements were each electrospun for 120 s and therefore were of similar mass (differing due to changes in fibre coverage area). However, nanoparticle-containing fibres provide lower steady-state PL intensity than pristine fibres (47% lower for PEO-reduced AgNPs and 34% lower for OA-AuNPs in Figure 5.13) in the absence of PCBM. Although mass was not explicitly controlled, this suggests that the metal centres could act as non-radiative recombination centres or may provide additional exciton dissociation into charge carriers. With correct implementation, additional dissociation should prove advantageous, however in poorly-optimised devices, charges may remain trapped at the metal cores until recombination. [155, 289] If attributed to exciton dissociation, a lower initial PL emission would mean that the quoted quenching efficiencies in Table 5.2 would underestimate the initial exciton population, and therefore the dissociation probability.

5.5.2 Transient Absorption Spectroscopy

To further explore the dynamics of excitons, dissociation and resulting charges, fs-TAS measurements were conducted upon P3HT nanofibres and NF:PCBM active layers following backfill (using DCM). A detailed description of the instrument and sample preparation is provided in Section 2.2.2.3.

Use of a super-continuum pulse introduces a temporal dispersion in the probe light as the red portion arrives at the sample earlier. The chirp must be corrected by considering

the time delay for signal onset at several wavelength components. An example contour plot before and after chirp correction is displayed in Figure A.2.1. Finally, false colour contour plots were normalised to the most intense negative ΔmOD (assigned to -1.0). In Figure 5.14, signal differences between the fs-TAS contour plots before and after infiltration are distinct.

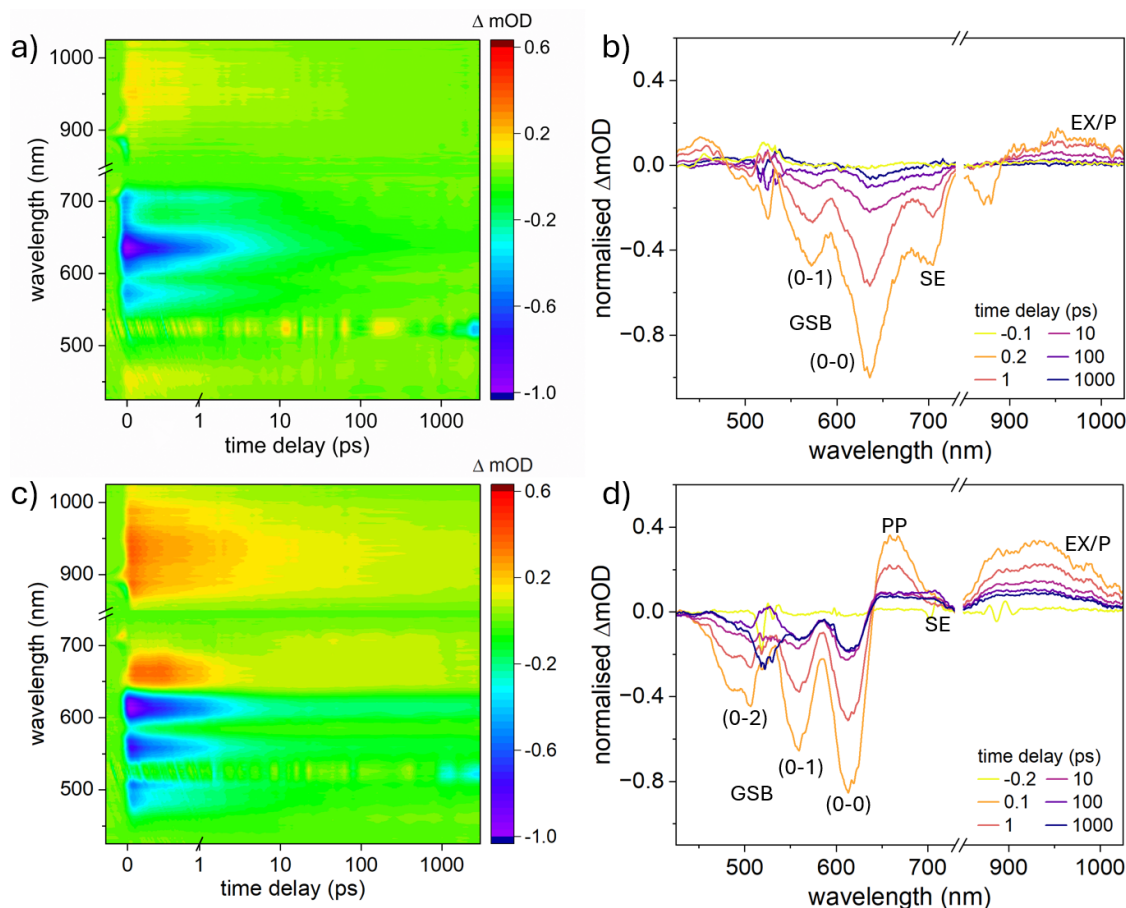


Figure 5.14: (a,c) fs-TAS contour plots and (b,d) transient absorption spectra at selected time delays of pristine P3HT fibres (a,b) before and (c,d) after PCBM infiltration (520 nm excitation pulse, -0.5 ps to 3 ns temporal range with 40 fs resolution). Plots were normalized to the most intense vibronic GSB signal. Measurements were conducted alongside Dr Jack Woolley at the Warwick Centre for Ultra-fast Spectroscopy.

First, the series of negative ΔmOD signals manifesting between ~ 450 and 650 nm are generated by the ground state bleach (GSB) following molecular photo-excitation by the pump pulse. In Figure 5.14a-b, the nanoweb generates vibronic peaks associated with the (0-0) and (0-1) transitions at ~ 635 and 570 nm, respectively. In the PCBM-infiltrated active layer, these peaks appear blue-shifted to 615 (0-0) and 560 nm (0-1), whilst the (0-2) vibronic transition bleach is also observable at ~ 495 nm. The fs-TAS spectra possess

greater red-shift and a larger (0-0)/(0-1) ratio than is measured by steady-state absorption in Section 4.4.1. Furthermore, the vibronic transition series is more ‘defined’. Blue-shift in the (0-0) transition and attenuation of (0-0)/(0-1) ratio after PCBM introduction may be a result of the evolution of a photoinduced absorption (PIA) peak at 660 nm.

The 660 nm PIA recorded in the nanofibrous active layer (Figure 5.14c-d) is generally assigned to polaron pairs (PP, an intermediate charge-transfer state between the coulombically-bound exciton and free polarons). [298, 31] However, sometimes it is ascribed to hole polarons (P, defined as free charges inclusive of distortion upon their surroundings) delocalised within crystalline P3HT. [155, 299, 300] Without PCBM present, there is no PIA signal at 660 nm revealing that PPs are not generated without acceptor molecules (Figure 5.14a-b).

Instead, a negative ΔmOD signal is recorded at 700 - 720 nm, associated with the stimulated emission (SE) of singlet excitons (consistent with PL measurements). Within the infiltrated active layer, SE appears as a negative ΔmOD inflection upon the more intense, positive ΔmOD signal at 660 nm. However, as demonstrated in the PL quenching study, emission is expected to be less intense in the presence of PCBM. In Figure 5.15a, the SE signal of the web prior to infiltration decays within 100 ps, consistent with studies on pristine P3HT films. [155] The cut-off between 740 - 850 nm originates from low flux of these wavelengths in the white light continuum (a filter is used to prevent detector saturation by the fundamental 800 nm laser).

Conventionally, a broad PIA signal centred at 1200 nm (spanning from ~ 800 nm to 1400 nm) is measured and assigned to singlet excitons in P3HT as its decay dynamics align with PL emission. [155, 245, 301] Dimitriev suggested it could be specifically attributed to those in amorphous domains. [299] Triplet excitons are not readily formed in RR-P3HT, unlike regiorandom (RRa)-P3HT and other poly(thiophenes). [31, 302] In RRa-P3HT, triplet excitons produce a positive signal at 800 nm, with a microsecond lifetime. [31]

Within tens of ps, excitons are separated in the presence of an electron acceptor [155], leaving behind a comparatively long-lived feature centred at 950 - 1000 nm [155] ascribed to P3HT polarons. [299] Due to the lack of pump wavelengths red of 1025 nm, fs-TAS

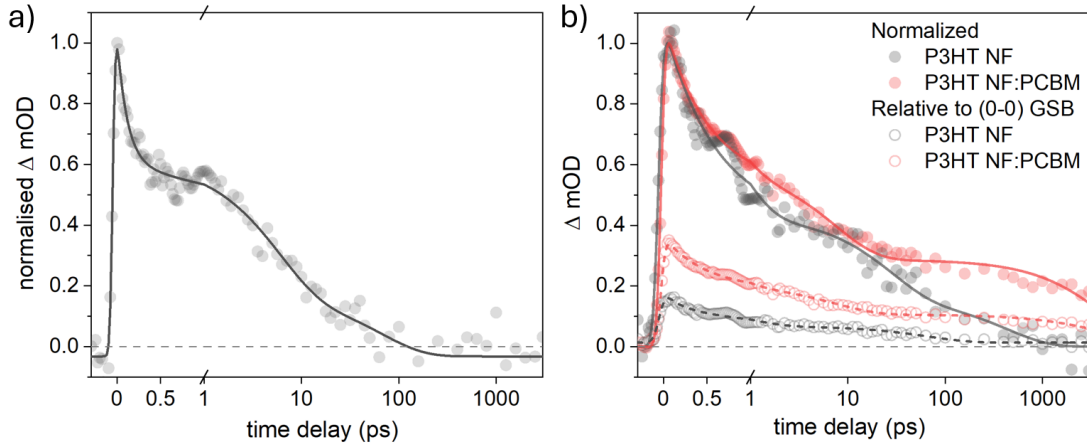


Figure 5.15: Normalised transient absorption decay of the (a) SE signal of singlet excitons in the P3HT web at 720 nm and (b) 950 nm signal decay, ascribed to a convolution from excitons and polarons, before and after infiltration. Decays were fitted using the tri-component exponential function in Equation 5.1. SE signal was also most appropriately fitted with a tri-component exponential decay due to the overlap with the GSB.

measurements in this work do not reveal the full exciton PIA, however the initial positive ΔmOD signal at >850 nm captures the shoulder of this broad peak.

As polarons are evolved from the dissociation of the excitons, the overall evolution of the signal magnitude is convoluted. However 1 ns after excitation, residual signal at this probe wavelength is attributed predominantly to polarons. Excitons quench within 100 ps in the nanoweb as demonstrated by SE decay, and one would expect faster depletion with PCBM.

Okhita et al. determined that the absorption coefficient of excitons at a probe wavelength of 950 nm is 41% of its maximum intensity at 1200 nm. At this pump wavelength, polarons possess a 1.97x larger coefficient than excitons, allowing comparison of their relative populations at a single wavelength. [31] Therefore, kinetics were fitted with the tri-component exponential decay function (Equation 5.1) and normalized between 0 (before pump) and 1 (maximum magnitude after photo-excitation).

$$x = y_0 + \sum_{n=1}^3 \left(A_n \exp \left(\frac{\left(\frac{G}{1.665109} \right)^2 - 4\tau_n(x - x_0)}{4\tau_n^2} \right) \times \left(1 - \operatorname{erf} \left(\frac{\left(\frac{G}{1.665109} \right)^2 - 2\tau_n(x - x_0)}{2 \left(\frac{G}{1.665109} \right) \tau_n} \right) \right) \right) \quad (5.1)$$

Where A_n is the amplitude and τ_n is the kinetic rate constant in ps of the n^{th} exponential decay component. G represents the instrument response time in ps, erf is an error function, x is the time delay, and x_0 and y_0 represent the initial signal magnitude and time delay, respectively.

Finally, the polaron population existing 1 ns after photo-excitation, relative to the initial exciton population, was estimated from the maximum signal magnitude at 950 nm (found 40 - 220 fs after excitation) versus the signal remaining 1 ns after the pump pulse (previously used by Wu et al. [155]) At 1 ns, the normalized signal of the infiltrated active layer in Figure 5.15b possesses a higher residual. The polaron population remaining at this time delay is roughly 11.6% of the initial exciton population, in comparison to 0.8% without PCBM, almost a 15-fold increase (Table 5.3). Until now, PL studies have shown that the excitons are effectively quenched via non-radiative mechanisms, but TAS provides evidence that this occurs via dissociation into free charges.

The fastest rate constant, τ_1 , has been attributed to singlet excitons in amorphous/intermixed regions, τ_2 to excitons in crystalline domains, and τ_3 to free polarons. [303] Comparing the amplitudes of the long-lived component in Table 5.3 offers alternative means to approximate polaron populations formed over the full temporal regime. In this case, the amplitude of the third component almost doubles and the time constant is 10x longer. The two exciton-associated time constants are reduced upon PCBM addition, indicative of exciton dissociation at the heterojunction.

Active Layer	A_1	$\tau_1(ps)$	A_2	$\tau_2(ps)$	A_3	$\tau_3(ps)$	ΔmOD ratio (1 ns/initial)	P population at 1 ns (% vs initial EX)
P3HT NF (SE, 720 nm)	0.31	0.12 ± 0.02	0.22	5.75 ± 1.21	0.10	67.9 ± 34.9	-	-
P3HT NF (EX/P, 950 nm)	0.35	0.59 ± 0.05	0.14	27.1 ± 10.1	0.07	430 ± 260	0.016	0.79
P3HT NF: PCBM	0.24	0.46 ± 0.04	0.14	7.48 ± 0.83	0.13	>3000 (4300 ± 600)	0.228	11.57

Table 5.3: Amplitude and time constants of exponential components fitted with Equation 5.1 to the signal relaxation at probe wavelength of 950 nm. G , the instrument response time, was ~ 100 fs, and y_0 and x_0 were ~ 0 ΔmOD . Exciton and polaron signals were estimated from the signal at 950 nm after initial photo-excitation and 1 ns, respectively, extracted from the fitted decays in Figure 5.15b. The polaron population at 1 ns, relative to the initial exciton population, is then determined using absorption coefficients proposed by Okhita et al. [31]

The initial signal at 950 nm, and therefore exciton populations, was larger in the active layer than the neat P3HT web. Whilst PCBM anions contribute toward this signal, it is not expected that PCBM is efficiently excited by the 520 nm excitation wavelength. [304] Overall, weak polaron/polaron pair signals produced by the P3HT fibres before infiltration suggests that in the absence of PCBM, intrinsic polaron formation is negligible. This is consistent with the well-defined SE peak and high radiative quenching rates measured with PL. Spontaneous charge formation in (RR-)P3HT reportedly occurs with a small driving force found at the crystalline/amorphous region interface, [305, 306] or via hot excitons [31] with an additional 0.7 eV energy above the band gap (not yet having undergone internal conversion) required to overcome the binding energy [307]. The 520 nm excitation pulse used here does not meet this requirement.

5.6 Polaron Generation and Dynamics

Figure 5.16 and 5.17 reveal that the BHJ and nanoparticle-containing nanofibrous active layers generate the same TAS signals to the pristine fibrous architecture presented in the previous section. The PEO-reduced AgNP-containing layer appears to have GSB and PP/SE characteristics between that of the BHJ and other fibre-based architectures. The SE emission inflection at 720 nm is less distinct in (a) and (c) compared to (b) and (d). This may be because the signal lies at the edge of the wavelength range. In Figure 5.17b and d, the GSB peaks are further red-shifted by 7 - 9 nm, and the corresponding blue-shift in SE translates this signal to higher-flux probe wavelengths.

Figure 5.18 presents the normalized relaxation kinetics of the (0-1) GSB, polaron pair (660 nm) and exciton/polaron (950 nm) signals for the BHJ and nanofibrous active layers extracted from the transient spectra. Overall, the signal decay measured in the P3HT:PCBM BHJ and the pristine nanofibre-based architecture are very similar. Additionally, upon first inspection, kinetics appear invariant of OA-AuNP addition. This is a promising result as bare and OA-capped AgNPs, were previously shown to impede free polaron formation, despite increasing exciton generation, attributed to fast charge trapping. [155, 288] In Figure 5.2, this manifested in the faster signal relaxation/shorter lifetimes. Here, the OA-AuNPs do not display the same tendencies within nanofibrous active layers.

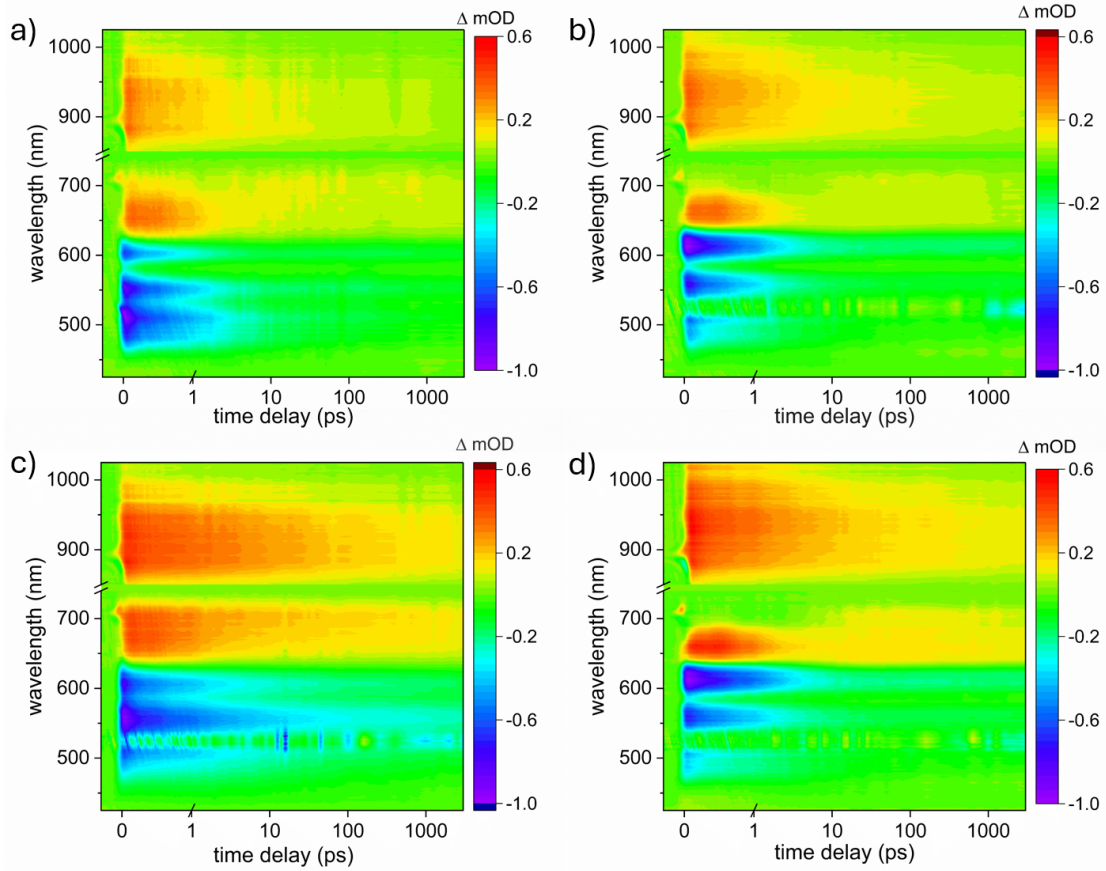


Figure 5.16: fs-TAS contour plots (520 nm excitation pulse) of the (a) conventional P3HT:PCBM BHJ and (b) pristine, (c) PEO-reduced AgNP-containing and (d) OA-AuNP-containing P3HT NF:PCBM active layers. For normalisation, the most intense GSB signal in each case was assigned ΔmOD of -1.0.

In Figure 5.18a-c, the decay transients of the GSB and photoinduced species' signals upon the introduction of PEO-reduced AgNPs (10 wt% $AgNO_3$ wrt PEO in solution) are significantly slower over the 4 temporal decades probed than presented by all other tested active layers. This is attributed to the nanoparticles, rather than any diameter reduction, due to the traces produced with OA-AuNPs. Additionally, incorporation of a low PEO-reduced AgNP concentration (1 wt% $AgNO_3$) produced a marginal/intermediate reduction in the signal decay rate (Figure 5.18d-f).

Bleaching signals are proportional to the population of excited molecules, and hence exciton and polaron populations. [31] Alongside the decay transient at 950 nm, slower relaxation suggests increased exciton/polaron lifetimes and/or a greater polaron generation rate which, possessing nanosecond lifetimes, slow signal decay. However, as one species

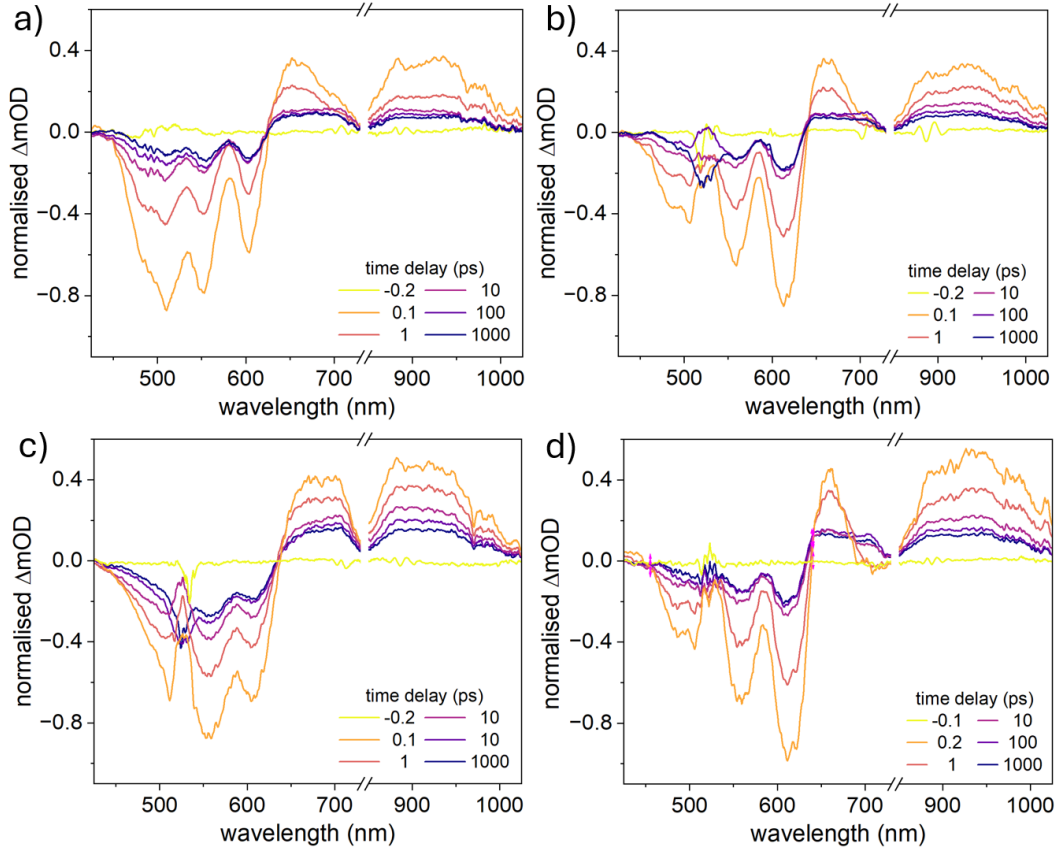


Figure 5.17: Change in optical density spectra of (a) the P3HT:PCBM BHJ and (b) pristine, (c) PEO-reduced AgNP-containing and (d) OA-AuNP-containing P3HT:PCBM nanofibrous active layers at select time delays.

dominates the signal at 660 nm, polaron pair lifetimes are conclusively extended in the presence of the PEO-reduced AgNPs.

In Table 5.4, the fitting parameters show that exciton/polaron lifetimes increase in the presence of both nanoparticle types. However, the amplitude of the polaron-associated component, A_3 , is only higher in the presence of the PEO-reduced AgNPs (0.21). Fitting suggests that OA-AuNPs may generate longer-lived species, but fewer polarons per exciton formed, whilst PEO-reduced AgNPs enhance both parameters. As the long-lived component extends beyond the temporal window, fitting the kinetics involves extrapolation, and so it is not entirely reliable.

Provided successful deconvolution, longer exciton lifetimes (τ_1 and τ_2) were also fitted to the metal-containing architectures, indicating either a reduced rate of exciton recombination, exciton dissociation or exciton-exciton annihilation. Firstly, worse dissociation by particle-containing layers is inconsistent with the steady-state PL quenching before

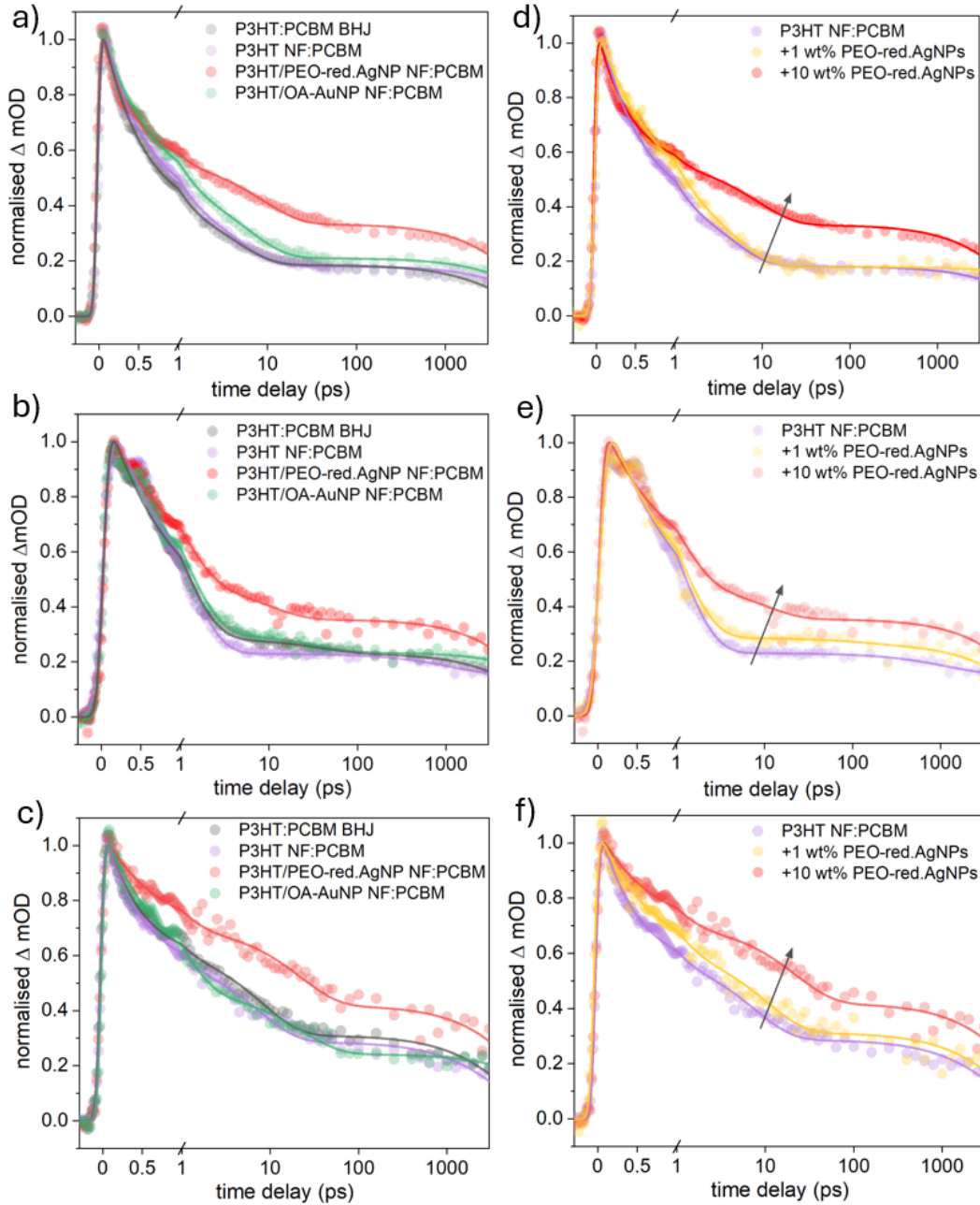


Figure 5.18: Normalised transient absorption decay of the (a,d) (0-1) GSB, (b,e) polaron pair (at 660 nm) (c,f) and exciton/polaron (950 nm) signals in (a,c,e) the BHJ and nanofibrous active layers, and (b,d,f) slower relaxation kinetics in the presence of low and high concentrations of PEO-reduced AgNPs. Decays were fitted using a tri-exponential component function (Equation 5.1).

and after infiltration. Regarding bimolecular annihilation, a relatively high flux of $74 \mu\text{J cm}^{-2}$ was used in these experiments to deliver good SNR. Therefore, a non-negligible bimolecular quenching rate is expected, however in Section 5.3, nanoparticles improve photon harvesting, which increases the exciton density and thus annihilation, not the

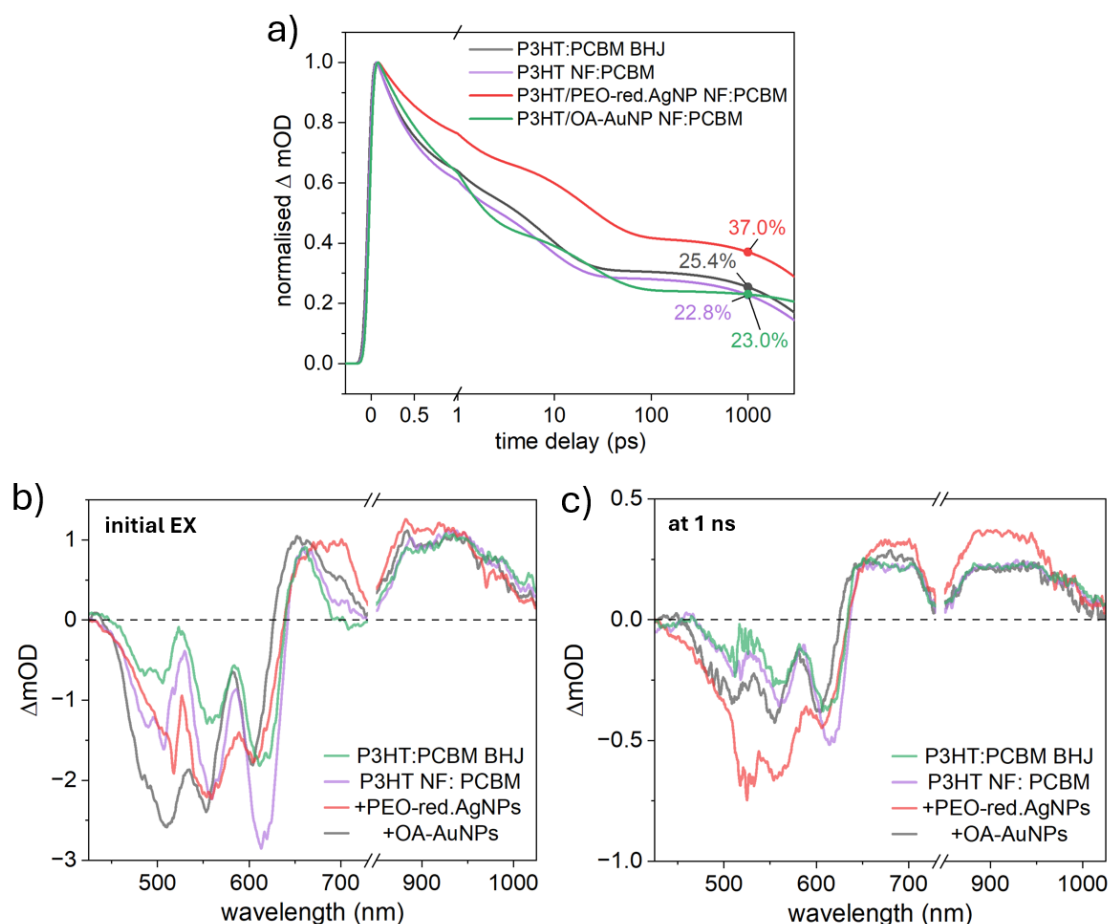


Figure 5.19: (a) Exponential decay fits of the exciton/polaron relaxation (950 nm probe wavelength) with annotated residual signal at 1 ns, used to estimate polaron populations. (b) TAS spectra of active layers normalised to the maximum signal intensity at 950 nm immediately after excitation, assigned to excitons, and (c) after 1 ns, when residual signal is now assigned to polarons.

opposite. Thus, these results seem to leave a reduced rate of exciton recombination as a possibility due to enhanced electric fields. [288] Likewise, longer polaron lifetimes suggest a reduced polaron recombination rate. The comparatively long polaron pair lifetime suggests further dissociation may occur at the ns time scale. Time-resolved PL measurements would be required to provide conclusive evidence of longer exciton lifetimes.

The method used in the previous section is once again employed to estimate the proportion of free polarons at 1 ns. A reminder, this figure is not representative of the full polaron population but those which exist at 1 ns relative to the exciton concentration formed - the total conversion rate will be higher. In Figure 5.19a and Table 5.5, approximately 9% fewer free polarons remain in the P3HT NF:PCBM layer versus the

Active Layer	A_1	$\tau_1(ps)$	A_2	$\tau_2(ps)$	A_3	$\tau_3(ps)$
P3HT:PCBM BHJ	0.22	0.44 ± 0.04	0.15	8.05 ± 0.81	0.15	5000 ± 600
P3HT NF:PCBM	0.24	0.46 ± 0.04	0.14	7.47 ± 0.83	0.13	4400 ± 600
P3HT/PEO-red.AgNP NF: PCBM	0.18	0.65 ± 0.06	0.14	21.90 ± 3.13	0.21	8000 ± 1600
P3HT/OA-AuNP NF: PCBM	0.28	0.81 ± 0.04	0.11	22.90 ± 3.45	0.11	18000 ± 11000

Table 5.4: EX/P (950 nm probe wavelength) relaxation amplitudes and time constants, extracted from the tri-component exponential decay function fitting (Equation 5.1) to the BHJ and nanofibrous active layers.

BHJ, which retains 11.35% of the possible polaron population at 1 ns. Upon PEO-reduced AgNP infusion, films contained $\sim 60\%$ more polarons at 1 ns relative to the BHJ. A_3 , proportional to the overall number of generated polarons, is 40% greater than the BHJ. Repeats show consistency between measurements on separately-fabricated BHJ and silver-containing composites (Figure A.5.4). In contrast, A_3 of the OA-AuNP containing layer is 27% lower relative to the BHJ, and its polaron population (per exciton) is 10% lower after 1 ns. Due to the longer polaron lifetimes, populations of charges in metal-containing architectures will increase relative to the pristine active layers at longer time delays.

To aid visualisation, the differential optical density spectrum of each layer was normalized in Figure 5.19b to the initial/maximum signal intensity at 950 nm, proportional to exciton generation. After scaling, PEO-reduced AgNPs clearly increase the number of free polarons existing at longer time scales in Figure 5.19c. By eye, polaron signal is largely invariant across the other architectures.

Given that nanoparticle infusion to fibres enables absorption of up to 58% more light than thin-films, these transient studies suggest that a plasmonically-enhanced exciton population would successfully translate into a corresponding increase in polarons, contrary to previous studies. In the case of PEO-reduced AgNPs, a further enhancement is compounded upon the harvesting improvement overall offering an approximate 135% increase in polarons versus the BHJ, measured at 1 ns in Table 5.5. Hence, nanoparticles within these active layers are not parasitic.

Active Layer	ΔmOD ratio (1 ns/initial)	P population at 1ns (% of initial EX)	Relative P Enhancement (%)	Compounded P Enhancement (%)
P3HT:PCBM BHJ	0.228 ± 0.001	12.89 ± 0.05	-	-
P3HT NF:PCBM	0.231	11.57	-10.2	2.3
P3HT/PEO-red. AgNP NF: PCBM	0.404 ± 0.047	20.51 ± 2.39	59.1	135.5
P3HT/OA-AuNP NF: PCBM	0.252	11.68	-9.4	43.2

Table 5.5: Determination of P3HT polaron populations at 1 ns relative to the initial exciton generation rate estimated from the decay profiles in Figure 5.19a. Initial ΔmOD signal is predominantly ascribed to excitons but 1 ns after excitation it is attributed to polarons. The relative populations were then determined using absorption coefficients proposed by Okhita et al. [31] Resultant polaron populations were compounded with absorption enhancements in Section 5.3 to estimate electrospinning/plasmon-enhanced charge carrier generation rates. TAS profiles of repeat/additional samples can be found in Figure A.5.4.

Insulating ligands such as oleylamine and PEO, if the AgNPs are indeed capped by the polymer, may be sufficient to electrically isolate the metal core from the active layer to prevent charge trapping. Oleylamine has previously been shown to be insufficient in this respect, however the particles prepared in Chapter 3 likely possess a denser capping layer due to their synthesis in neat oleylamine. LSPR may then extend beyond this capping layer and provide electric field enhancements, aiding in exciton dissociation or increasing photoinduced species' lifetimes. There is no evidence that the resultant polarons in these studies are trapped by the nanoparticles. [155, 289]

It is also possible that the selective encapsulation of nanoparticles within P3HT domains, reduces their interaction with fullerene molecules despite diffusion and may ameliorate previously reported issues. Studies have suggested that nanoparticle-associated recombination mechanisms occur at the P3HT:PCBM interface or involve PCBM. [155, 289] Despite PCBM diffusion, the sequential deposition of the plasmonic fibres and infiltration layer may reduce the detrimental fullerene-nanoparticle interaction.

5.7 Proof-of-Principle Photovoltaic Devices

5.7.1 J-V Characteristics

Numerous possible advantages of active layers based on electrospun fibres and plasmonic nanoparticles have been presented - enhanced photon absorption, unique crystallite orientation, competitive exciton dissociation, and greater polaron conversion and/or lifetimes.

OPVs with the inverted structure, ITO/AZO/active layer/MoO₃/Al, are presented to determine the efficiency of charge extraction from the active layer. These devices were fabricated over two iterations and therefore require considerable optimisation to unlock their ultimate potential, however this section provides an exploratory look into the material's photovoltaic promise. Alanood Aljaghwan provided assistance with the device fabrication and testing.

Active layers were built as in Section 5.4 upon a 40 nm AZO electron transport layer, where PCBM was deposited from DCM, DCM:chloroform or DCM:chlorobenzene. Full practical details of OPV fabrication is given in Section 2.1.3.

MoO₃ was chosen as the hole transport layer as it is deposited thermally under vacuum. As the active layer possesses uneven surface topology, evaporation was considered advantageous towards achieving a continuous, conformal layer. To promote this, deposition was limited to 0.1 - 0.2 Å s⁻¹. A relatively thick 9 nm was deposited to promote full coverage - considered the upper limit to prevent increased series resistance and voltage loss. [308, 309] The first 10 nm of Al deposited for the electrode was also limited to 0.3 Å s⁻¹.

In Figure 5.20, J-V performance (collection method and parameters described in Section 2.2.5.1) of the nanofibrous active layer (with a DCM-cast infiltration layer) was uncompetitive with the BHJ (Figure 5.22a). Inadequate performance arises from a degradation in J_{SC} , V_{OC} and FF. Low series and high shunt resistances lead to champion PCE of ~0.30% (Table 5.6). This performance may originate due to the poor infiltration layer morphology with many pinholes. In the inverted structure, holes are extracted from the P3HT domain through the MoO₃ layer and therefore the fibres must protrude from the active layer surface. Likewise, PCBM must make good contact with the underlying AZO layer for electron extraction requiring full infiltration of the casting solution.

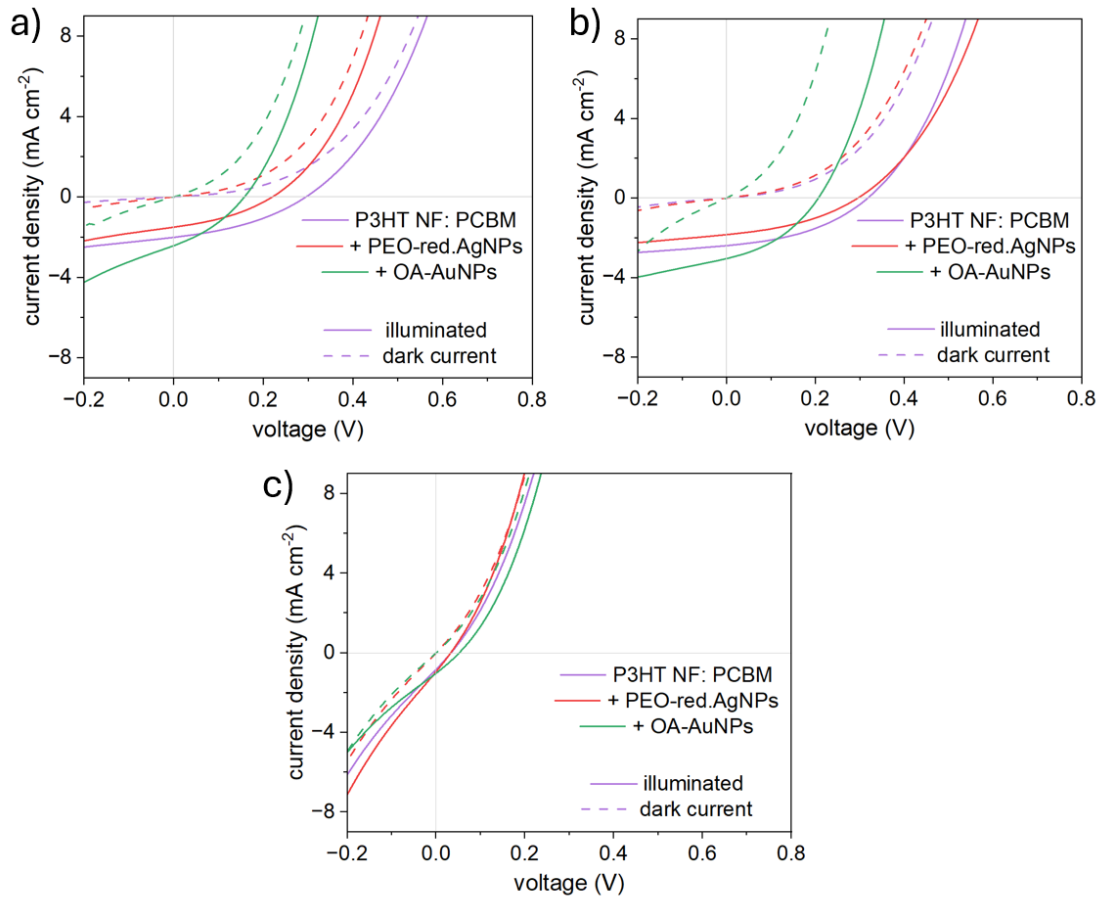


Figure 5.20: (a) Mean-average and (b) champion current density-voltage (J-V) characteristics of inverted structure OPV devices containing nanofibrous active layers and (c) device characteristics following annealing at 120 °C for 20 minutes. The electron acceptor was cast from 100% DCM. Averages are the mean behaviour of the greatest-performing 67% of pixels regarding PCE. Measurements were collected in the dark and under 1 Sun simulated solar irradiation with input power of 100 mW cm⁻².

Active Layer	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF	PCE (%)
P3HT NF:PCBM (As-cast)	2.27 ± 0.39	0.30 ± 0.01	0.38 ± 0.02	0.27 ± 0.06
Annealed	1.14 ± 0.27	0.02 ± 0.02	0.23 ± 0.03	0.00 ± 0.00
P3HT/PEO-red.AgNP NF: PCBM	1.70 ± 0.32	0.23 ± 0.04	0.36 ± 0.02	0.14 ± 0.04
Annealed	0.62 ± 0.29	0.03 ± 0.01	0.25 ± 0.01	0.01 ± 0.01
P3HT/OA-AuNP NF: PCBM	2.43 ± 0.38	0.16 ± 0.02	0.34 ± 0.02	0.13 ± 0.05
Annealed	1.00 ± 0.23	0.02 ± 0.02	0.34 ± 0.25	0.01 ± 0.01

Table 5.6: Key parameters extracted from the J-V characteristics of ITO/AZO/active layer/MoO₃/Al devices containing nanofibrous active layers before and after annealing (120 °C, 15 minutes), wherein the acceptor phase was cast from DCM.

Once annealed, performance degrades almost entirely, and in Figure 5.20c, the J-V curve shows near ohmic behaviour. Annealing may cause a contraction of the PCBM due to the prevalence of pinholes or gaps, deteriorating the contact and degrading all photovoltaic parameters. Additionally, heat treatment may accelerate molecular doping/oxidation of PCBM and P3HT by the 1 ppm O_2 and H_2O in the glove box. Pinholes allow these molecules to diffuse into the film, promoting degradation and out-competing benefits from donor/acceptor inter-mixing.

Next, active layers involving infiltration using the semi-orthogonal systems were tested. The DCM:chloroform-derived architectures in Figure 5.21 show significant improvement with a much greater V_{OC} of >0.41 V, and in some cases surpassing that of the reference (0.49 V). In Table 5.7, PEO-reduced AgNPs increases V_{OC} to 0.57 V.

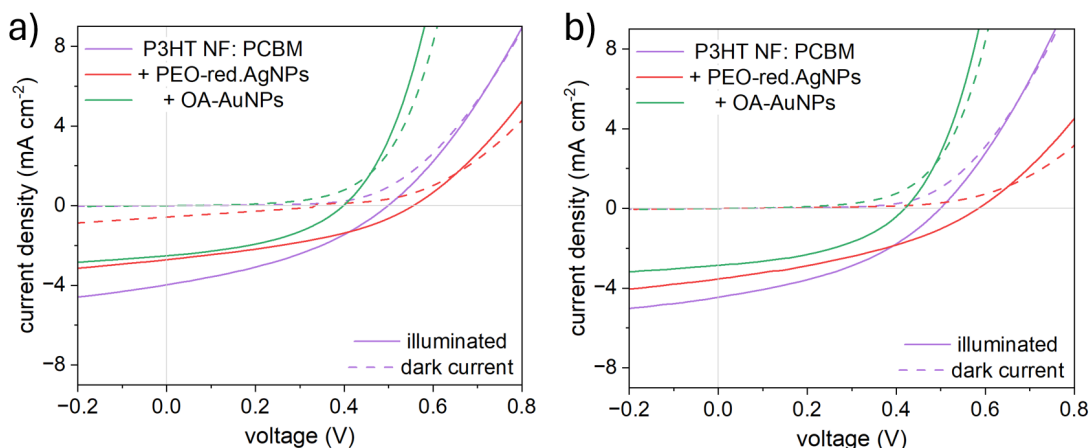


Figure 5.21: (a) Mean-average and (b) champion J-V characteristics of ITO/AZO/nanofibrous active layer/ MoO_3 /Al devices. Electron acceptor infiltration cast from the semi-orthogonal solvent system, 50:50 v/v DCM:chloroform.

However, FF is still comparable to levels achieved using neat DCM, and while J_{SC} undergoes slight improvement (up to $4.0 \mu J cm^{-2}$), owing to an improved morphology for charge extraction, it is still inferior to the BHJ ($7.8 \mu J cm^{-2}$).

The third system utilising DCM:chlorobenzene produced further PCE improvement, attributed mainly to increased FF (Figure Table 5.8). FF is reliant upon the series and shunt resistance in the device which would improve with better active-transport layer contact and pinhole removal. The champion devices with this backfill layer approach the PCE of the BHJ (1.72% vs 2.18%, Table 5.9). Its under-performance can be narrowed

Active Layer	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF	PCE (%)
P3HT NF:PCBM (As-cast)	3.97 ± 0.33	0.50 ± 0.01	0.36 ± 0.02	0.73 ± 0.09
P3HT/PEO-red.AgNP NF: PCBM	2.71 ± 0.76	0.57 ± 0.03	0.37 ± 0.06	0.57 ± 0.21
P3HT/OA-AuNP NF: PCBM	2.62 ± 0.19	0.41 ± 0.02	0.42 ± 0.01	0.45 ± 0.06

Table 5.7: Key parameters extracted from the ITO/AZO/active layer/MoO₃/Al devices incorporating BHJ and nanofibrous active layers. Nanofibrous active layer acceptor phase was cast from 50:50 DCM:chloroform.

down to inferior J_{SC} of 6.39 mA cm⁻², ~20% lower than the reference. J_{SC} is proportional to photon absorption and therefore was expected to increase due to polymer alignment and LSPR effects. However, it is also dependent on collection, [36] and therefore J_{SC} may be bottlenecked by poor extraction in the devices' current state. Furthermore, the active layer thickness/mass of P3HT fibre has not been optimised, which will have considerable influence on extraction. [36]

Again, V_{OC} improvements are noted with PEO-reduced AgNP addition. It has been proposed that this occurs due to reduction in electrical resistance, wherein Ag [281] or Au [310] nanoparticles may take part in carrier transport. The presence of silver may increase the built-in voltage, [311] which is related to the separation between donor HOMO and acceptor LUMO, and the magnitude of V_{OC} .

Active Layer	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF	PCE (%)
P3HT:PCBM BHJ (Annealed)	7.49 ± 0.34	0.49 ± 0.01	0.56 ± 0.02	2.09 ± 0.10
P3HT NF:PCBM (As-cast)	3.96 ± 0.51	0.51 ± 0.02	0.49 ± 0.02	0.98 ± 0.12
Annealed	2.54 ± 0.12	0.44 ± 0.01	0.52 ± 0.06	0.88 ± 0.28
P3HT/PEO-red.AgNP NF: PCBM	4.82 ± 0.71	0.57 ± 0.02	0.51 ± 0.05	1.37 ± 0.05
Annealed	1.99 ± 0.63	0.53 ± 0.04	0.50 ± 0.06	0.55 ± 0.26
P3HT/OA-AuNP NF: PCBM	2.90 ± 0.10	0.45 ± 0.02	0.41 ± 0.01	0.53 ± 0.02
Annealed	4.69 ± 1.35	0.47 ± 0.02	0.51 ± 0.03	1.15 ± 0.40

Table 5.8: Average J-V parameters extracted from the highest-performing 67% of fabricated ITO/AZO/active layer/MoO₃/Al devices incorporating BHJ and nanofibrous active layers. Nanofibrous active layer acceptor phase was cast from 50:50 DCM:chlorobenzene.

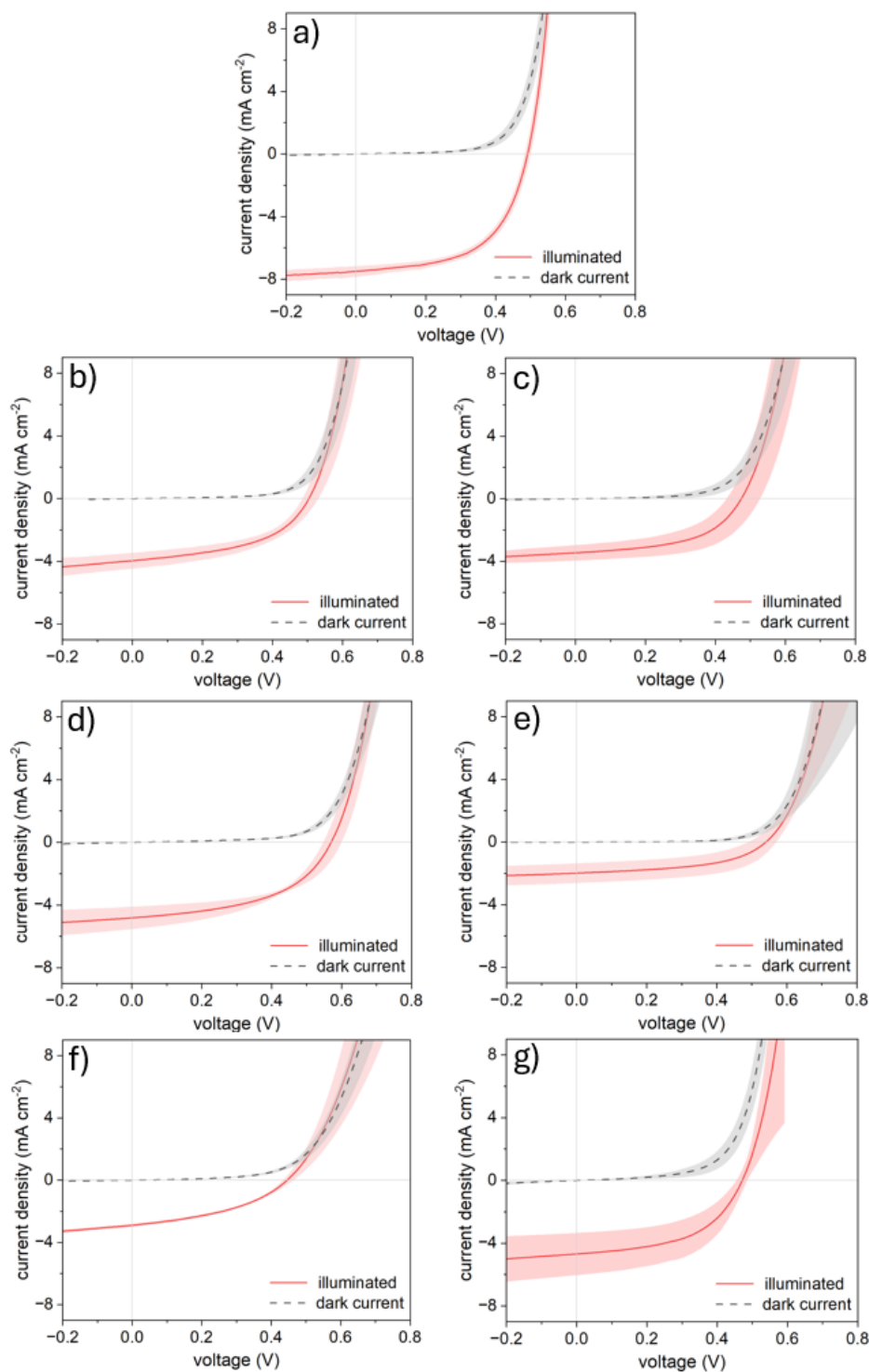


Figure 5.22: Standardised J-V characteristics of ITO/AZO/active layer/MoO₃/Al OPVs incorporating the (a) BHJ, (b, c) P3HT NF:PCBM nanofibrous active layer (acceptor cast from DCM:chlorobenzene), and those containing (d, e) PEO-reduced AgNPs and (c) OA-AuNPs, (c, e, g) before and (a, b, d, f) after annealing at 120 °C for 15 minutes. Shaded region represents the standard deviation.

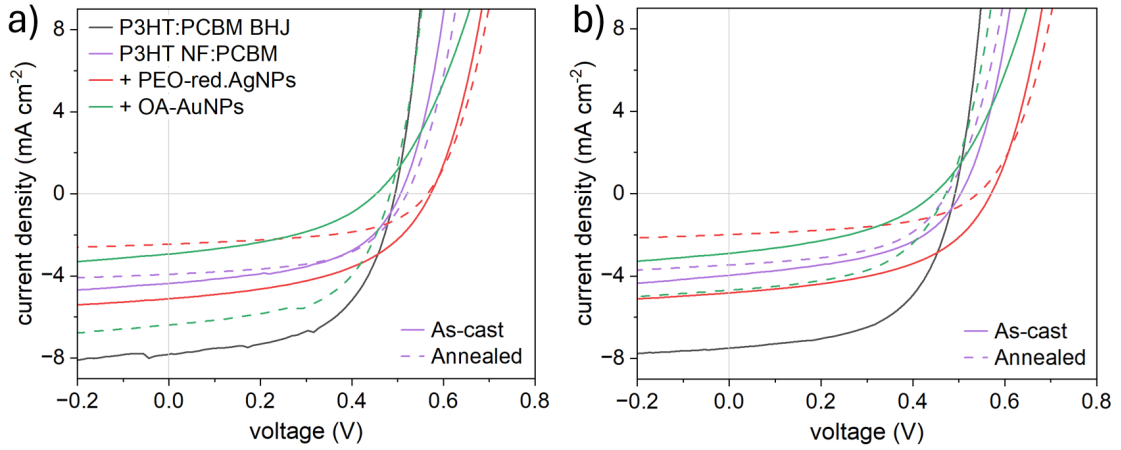


Figure 5.23: (a) Mean-average and (b) champion J-V characteristics of OPVs with BHJ and nanofibrous active layers measured with standard conditions under illumination and in the dark. Electron acceptor infiltration cast from the semi-orthogonal solvent system, 50:50 v/v DCM:chlorobenzene.

Active Layer	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF	PCE (%)
P3HT:PCBM BHJ (Annealed)	7.81	0.49	0.57	2.18
P3HT NF:PCBM (As-cast)	4.37	0.51	0.51	1.13
Annealed	3.92	0.52	0.56	1.14
P3HT/PEO-red.AgNP NF: PCBM	5.11	0.57	0.49	1.42
Annealed	2.69	0.56	0.58	0.89
P3HT/OA-AuNP NF: PCBM	2.93	0.45	0.42	0.55
Annealed	6.39	0.48	0.56	1.72

Table 5.9: Parameters extracted from champion J-V characteristics of OPVs with BHJ and nanofibrous active layers (acceptor cast from 50:50 v/v DCM:chlorobenzene).

There is no consistent trend across the backfill layers regarding the influence of nanoparticles/diameter reduction. Architectures without nanoparticles performed best for the DCM and DCM:chloroform-derived layers, yet this was not the case with DCM:chlorobenzene. Due to large variance in performance between nanofibrous active layer samples, and even pixels on the same device, further optimisation work is essential before plasmonic nanoparticles can be definitively evaluated as attractive or parasitic. Currently, morphological differences of the acceptor domain appear to have a greater influence than any impact of fibre diameter or nanoparticles.

Likewise, optimisation is needed to investigate the effect of annealing which Tables

5.8 and 5.9 show provides mixed results when using DCM:chlorobenzene. However, it is clear that solvent choice provides an opportunity to tune infiltration, and with just two iterations, the active layer designed within this thesis has produced efficiencies approaching that of the conventional system with competitive V_{OC} and FF.

5.7.2 External Quantum Efficiency

EQE was employed as in Section 2.2.5.2 in an attempt to elucidate the origin of under-performance - by determining the ratio of successful collected charge carriers to the number of incident photons at each wavelength. EQE at wavelengths above and below ~ 400 nm arises predominantly from P3HT and PCBM, respectively. Given evidence of effective charge generation, low EQE in the P3HT range would indicate poor hole extraction, or a low P3HT to PCBM ratio (optimal at $\sim 1:1$ in BHJ).

Poor EQE below 400 nm would suggest a low proportion of acceptor, poor dissociation of excitons formed in PCBM, and/or ineffectual extraction. This thesis has carefully controlled P3HT domain size, however PCBM domains have not been considered. Inspection of the interstitial space presented in SEM and AFM micrographs in Figure 4.9c and 5.9c, may suggest that backfilled fullerene domains are far larger than exciton diffusion lengths.

One might also expect a greater PCBM ratio, which given dissociation and collection would increase EQE sub-400 nm, but this is not observed. Whilst PCBM can diffuse into the P3HT fibres, Section 5.4 indicates P3HT does not significantly diffuse into PCBM regions, and therefore many excitons formed in PCBM domains quench before reaching the heterojunction.

In Figure 5.24, the as-cast fibrous architectures offer inferior EQE across the full wavelength range, with a similar EQE at P3HT and PCBM-associated wavelengths to the BHJ. As no component acts as a distinct bottleneck, this could indicate low collection efficiency arising from poor contacts or excessive active layer thickness. However, accurate interpretation of Figure 5.24 requires greater understanding of the nature of these contacts and determination of the P3HT:PCBM ratio.

The fibre's J-aggregate behaviour (enhanced (0-0)/(0-1) transition ratio) is not mirrored in the EQE, therefore, use of semi-orthogonal solvent systems may partially

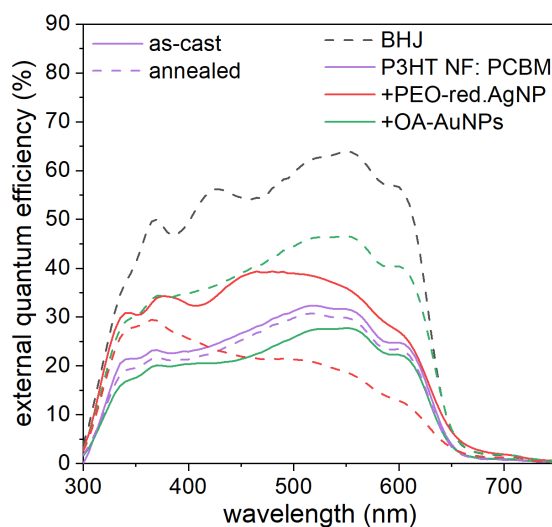


Figure 5.24: EQE of champion OPV devices presented in Figure 5.23b based upon the BHJ and nanofibrous active layers. Nanoweb acceptor infiltration was cast from the DCM:chlorobenzene.

dissolve the fibres or cause additional PCBM intermixing, disrupting intrachain order. Upon annealing the PEO-reduced AgNP-containing device, P3HT-associated EQE drops versus PCBM (below 400 nm). In this case, thermally-driven intermixing could deplete the MoO₃ interface of the donor polymer, attenuating hole extraction.

5.8 Conclusions

Until this chapter, the potential of aligned polymer and plasmonic particles towards greater photovoltaic performance has been discussed only theoretically. This chapter shows that light-harvesting ability by fibres increases following longer solution ageing time before it is electrospun. This occurs due to increasing LSPR intensity as the PEO-reduced AgNPs form, and to diameter reductions. Improvements to amorphous polymer chain (and crystallite) alignment in thinner fibres provide a greater proportion of polymer oriented in the substrate plane, and thus possess a more optimal orientation to absorb incumbent light. Thinner fibres provide additional scattering properties.

By preparing fibrous and spin-coated films with equal polymer mass, it is then evaluated that pristine P3HT fibres provide a 1.14x improvement in light-harvesting (integrated between 350 - 800 nm), suggesting that in-plane alignment surpasses that generated by spin-coating. Upon nanoparticle addition, significant broadband enhancements are recorded with PEO-reduced AgNPs (1.48x) and OA-AuNPs (1.58x), meanwhile absorption

was invariant of OA-AgNPs (1.04x). FDTD simulation offers a possible explanation as the LSPR of OA-AgNPs, and therefore electric field enhancements, have worse spectral overlap with P3HT. The discrepancy in harvesting enhancement between OA-AuNP-containing films (1.17x) and fibres (1.58x) can be attributed to polymer chain alignment. The almost 60% improvement is greater than the sum of the plasmonic effect (1.17x) and the spinning enhancement (1.14x) with the difference ascribed to the greater extent of alignment upon fibre diameter reduction.

The difficulty in producing high-quality PCBM infiltration layers is then discussed, and the use of semi-orthogonal solvent systems is proposed to ameliorate pinhole issues seen using pure DCM. SEM, AFM, STEM-in-SEM and EDX are employed to show that the fibre structure is resistant to the solvent exposure.

PL quenching efficiency provides evidence that the increased exciton populations may be effectively dissociated. Here, a competitive 95 - 97% of the fibre PL emission is quenched after acceptor introduction. Assuming no change to other non-radiative processes, this indicates good dissociation and charge transfer to the PCBM domain, and confirms that the fibres are of a suitable size for OPVs. Interestingly, quenching efficiency was independent of the fibre diameter, probably due to significant PCBM diffusion and possibly longer exciton diffusion lengths. Lower steady-state PL of particle-containing samples suggests that nanoparticles may aid exciton dissociation or introduce parasitic non-radiative quenching mechanisms.

To confirm that quenching proceeds via exciton dissociation and results in free charge carriers, ultra-fast transient optical studies were conducted before and after infiltration of a pristine P3HT web. Here, the post-infiltration evolution of a polaron pair PIA signal at 660 nm, attenuation of exciton emission, and a greater long-lived component at 950 nm (arising from polarons) confirm the hallmarks of dissociation and successful charge formation. Normalized to the initial exciton concentration, polaron populations estimated at 1 ns time delay are 15x times greater upon PCBM backfill. TAS measurements of the BHJ and pristine nanofibrous layer show nearly identical signal relaxation dynamics of photoinduced species.

fs-TAS confirms nanoparticles do not induce parasitic charge trapping/recombination. Instead, signal relaxation shows that PEO-reduced AgNPs slow the decay rate. Analysis of polaron populations at 1 ns, and the kinetic rate constants fitted by a tri-component exponential function, reveals PEO-reduced AgNP-containing active layers contain 60% more polarons than the BHJ at 1 ns per exciton formed. Polaron lifetimes were also estimated to be $\sim 60\%$ longer. OA-AuNPs did not enhance relative polaron populations but fitted lifetimes were $>3\times$ longer than the BHJ. These findings are very promising for the ultimate PCE potential of plasmonic, nanofibrous active layers.

Finally, proof-of-principle inverted structure OPVs were synthesised using three backfill solvent systems. The semi-orthogonal mixtures outperformed the purely DCM solution owing to an improvement in infiltration layer morphology, however the performance of champion cells (up to 1.72%) was inferior to the BHJ (2.18%), ascribed to lower J_{SC} . EQE revealed that under-performance was not down to just one component, therefore perhaps carrier collection is low due to poor contact with the charge transport layers. It is hoped that further optimisation of infiltration, thickness, nanoparticle concentration etc., will unlock the theoretical potential of this active layer. One promising outcome was the increase in V_{OC} , from 0.49 V to 0.57 V, upon silver addition.

6

Conclusions and Future Work

Photovoltaic conversion is a cornerstone technology for providing inexpensive and renewable energy at the point-of-use. Third-generation PVs, including organic solar cells, provide distinct advantages over silicon archetypes, such as flexibility, low weight and minimal energy processing. To date, the performance of organic technologies is hampered by poor carrier extraction at active layer thickness required for total light harvesting.

Photovoltaic operation can be simplified to three processes: (1) exciton generation following photo-excitation, (2) dissociation into free charge carriers, and (3) charge transport and extraction. If just one of these processes acts as a bottleneck, overall performance becomes rate-limited. This thesis presents novel fibre/nanoparticle composites which produce enhancements to the first and second processes, however further research must be conducted to offer competitive charge extraction, and ultimately unlock the potential of this novel architecture: the plasmonic, nanofibrous active layer.

6.1 Advantages of Lower Diameter Semiconductor Fibres

Uni-axial elongation during electrospinning generates an intriguing structure, wherein polymer chains involved in amorphous domains are axially-aligned along the forming fibre backbone. Simultaneously, anisotropic crystallites assembled in the spinning solution become oriented along the fibre axis under the same driving force. There, polymer chains are oriented orthogonal to the fibre due to the preference of P3HT to crystallise along

the $\pi - \pi$ direction. Orthogonally-oriented backbones in crystalline polymer has been reported with P3HT fibres, however the origin for its formation was unknown. The diameter reduction mechanism, whereby plasmonic Ag or Au NPs induce a spinning solution viscosity reduction, can improve the extent of this alignment, in particular with amorphous phases. Providing understanding of how internal fibre morphology forms allows researchers to tune nanostructure to achieve desired properties for an intended application.

These alignment effects enhance the light-harvesting capabilities of lower diameter fibres - absorbing additional photons by generating a polymer orientation following fibre collection which offers a better overlap with the electric field vector of incident light. Given that this method has produced ultra-thin fibres with record low diameters, one may expect that the greatest degree of polymer alignment, and thus photon harvesting capability, could be obtained using nanoparticle-induced viscosity reductions. Versus conventional spin-coated thin-films, composite fibres absorb up to 60% more light, as electrospinning delivers a larger proportion of amorphous polymer chains oriented in the substrate plane.

Simultaneously, long-range lateral crystallite alignment may offer efficient hole transport along $\pi - \pi$ stacks with persistence lengths up to 80 nm. Furthermore, higher prevalence of ‘end-on’ crystallites provides a mechanism for vertical transport in the direction of fastest transport (along the backbone), not generally found in thin-films.

Nanoparticle-driven diameter reduction produces unparalleled diameters of P3HT (and PEO) fibres and has been directly translated to other semiconducting polymers under identical conditions. The lack of apparent interaction between the photoactive polymer and nanoparticle provides an advantage over the previous state-of-the-art strategy of polar co-solvent addition. Here, the non-solvent induces precipitation and limits further diameter reduction varying upon the material.

Previous studies have demonstrated strong correlation between electrospun donor fibre diameter and exciton dissociation. However in this work, PL quenching was independent of the nanofibre diameter over the range tested; large diameter fibres outperformed expectations, likely owing to significant PCBM diffusion, although this may change with alternative donor:acceptor systems or the solvent used for infiltration.

In conducting this work, related research questions or additional topics were envisaged as areas worthy of further study. For example, the application of this platform to other organic semiconductors which exhibit superior performance to P3HT, which retains relevance due its high relative stability. In Section 3.6, this adaptability is demonstrated with PCE12 and PM6. This method could also be applied to polymeric electron acceptors.

Regarding nanoparticles, ≤ 10 nm AgNPs and AuNPs have been shown to deliver viscosity reductions in PEO solutions, however the effect of size has not been elucidated. Larger diameter particles could impart beneficial light scattering effects, but at some critical point, it is expected that Einsteinian behaviour would lead to viscosity increases. Furthermore, is viscosity modulation unique to noble metals, or can it be replicated with inexpensive plasmonic nanoparticles of copper or aluminium, or even non-metallic particles? Likewise, can nanoparticles change the viscosity of other ‘electrospinnable’ solutions of PCL, PMMA or PVAc - all used previously as auxiliary polymer for P3HT electrospinning? Ultimately, the replacement of chloroform with green solvents in the spinning solution is essential.

This thesis has focussed solely on controlling the diameter and morphology of donor domains to enable dissociation of the enhanced exciton populations into useful charge carriers. However, PCBM domains have yet to be considered. Research to increase the density of electrospun nanofibres should be investigated e.g. using rotating collectors or post-processing by spin-coating which was shown to compact the web. PCBM produces low exciton concentrations relative to P3HT, however other molecular acceptors possess comparable absorption coefficients, and hence optimisation of acceptor domains would be essential. This issue could be partially relieved through the use of NFAs which possess longer diffusion lengths and some self-dissociation ability.

Furthermore, the influence of crystallite alignment has only been discussed theoretically. Direct measurement of the fibres’ ability to transport charges laterally and vertically should be conducted to provide understanding of its potential within OPVs and other organic electronics such as OFETs (where lateral transport is paramount). Whilst the extent of crystallinity has not been explicitly investigated, the evidence suggests that the fibres contain a lower degree of crystallinity than thin-films due to quicker solvent evaporation.

However, the alignment of amorphous chains may help to offset this, aiding the transfer of charges between J-aggregate crystals, which represents the rate-limiting step in transport.

Finally, the concept of developing a PV fabric by combining this technology with a multi-axial spinneret, to layer device components concentrically is raised. Whilst an ambitious project, the realisation of a truly flexible, lightweight, colourful, and substrate-free solar cloth would be distinctly advantageous versus conventional planar devices regarding integration into clothing or furnishings.

6.2 Plasmonic Particles in Nanofibrous Active Layers: Attractive or Parasitic?

As the plasmonic nanoparticles remain in the material following solvent evaporation, they must provide a positive benefit towards the photovoltaic application. The success of nanoparticle addition to active layers has been highly-debated, considering their expense in a system of otherwise Earth-abundant elements. LSPR and/or light scattering enhancements are reliably recorded upon noble metal particle addition, however influence on eventual device efficiency is mixed due to nanoparticle-associated recombination mechanisms.

Herein, strong broadband enhancements in light absorption were recorded upon particle infusion to P3HT fibres, synergistic with the electrospinning effects. This was attributed to LSPR as their size (≤ 10 nm) renders them ineffectual scatterers. Furthermore, the active layer fabrication method allows for selective delivery of nanoparticles to P3HT domains, thereby the primary light-harvesting component is located at the area of highest electric field strength. This ability is unique to sequentially deposited systems such as the bilayer and the nanofibrous heterojunction described herein. In NFA blends, preferential delivery may not provide as much of an advantage.

PL quenching and ultra-fast transient studies of photo-induced dynamics over 4 temporal decades reveal no evidence of charge trapping. Contrary to prior reports, nanoparticles capped only by organic ligands induce longer polaron lifetimes and/or deliver greater polaron populations for a given initial exciton population. Compounded with the increased exciton generation, particle-containing nanofibrous active layers present an architecture with a very high ultimate potential.

This represents a significant finding and may help to elucidate the origins of parasitic recombination. It is proposed that the difference between this system and previous devices, is either a denser/thicker capping layer providing electrical isolation, or that the metal centres are overwhelmingly in contact with P3HT, thereby ameliorating detrimental interactions with PCBM. Whilst further research is required, these findings help researchers to design robust plasmonic OPVs with particles located within the active layer - the most desirable location as plasmon resonance decays exponentially with distance.

To consolidate the dynamics of excitons and polarons in the presence of nanoparticles, future work should focus on measuring time-resolved PL of plasmonic active layers to reveal the true influence on exciton lifetimes. Additionally, select delivery of nanoparticles to the fullerene region in bilayers and nanofibrous active layers, may help to elucidate whether nanoparticle-associated recombination proceeds via interaction with the PCBM molecules.

6.3 Potential and Current Limitations of the Plasmonic, Nanofibrous Active Layer

95 - 97% of the enhanced exciton generation in the nanofibrous active layer is dissociated and successfully converted into higher concentrations of charge carriers. In the presence of PEO-reduced AgNPs, the free carrier population is estimated to be 135% greater than the conventional BHJ, 1 ns after photo-excitation. Considering the stage (1) and (2) of photovoltaic operation are extremely promising, the architecture appears to justify its more complex fabrication versus films. However, the current morphology of the infiltration layer presents a significant impediment to the final charge extraction step, degrading the performance of OPV devices based upon these active layers.

Proof-of-principle devices presented a champion PCE of 1.72%, ~20% lower than the BHJ. This was attributed to difficulty in producing high-quality infiltration layers leading to ineffective contacts between P3HT/MoO₃ and PCBM/AZO. However, PEO-reduced AgNP addition induced an improvement in V_{OC} . If extraction can be improved in a well-optimised nanofibre-based device, voltage gains and photon-harvesting improvements could allow efficiency to surpass the BHJ. Extensive device optimisation is required

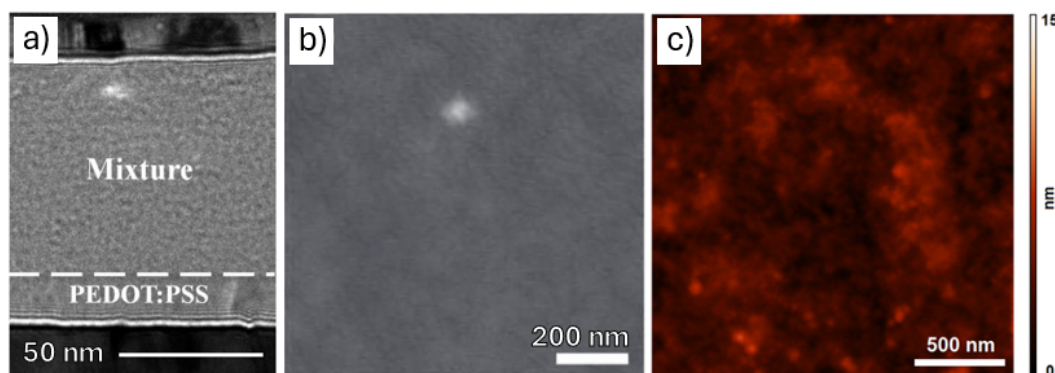


Figure 6.1: Previous reports of high-quality continuous, encapsulation layers achieved by infiltration of (a) PCDTBT fibres with PCBM cast from DCM analysed by cross-sectional TEM, or backfill of (b) CoP(3DDT)-(C₆₀HT) and (c) P3HT:PCBM fibres with BHJ blends cast with chloroform, characterised by AFM topographic micrographs. Reprinted with permission from references [64], [61] and [63], respectively. Copyright 2014 The Royal Society of Chemistry, Copyright 2012 WILEY-VCH Verlag GmbH Co. KGaA, Weinheim, Copyright 2017 American Chemical Society.

to determine the ideal active layer thickness, P3HT:PCBM ratio, backfill host solvent, nanoparticle type and concentration, etc.

In prior reports, fibre-based devices with a conventional structure (ITO/PEDOT:PSS/active layer/AZO/Al) have presented greater PCE than BHJ references, [64, 65] revealing that good infiltration is achievable as reproduced in Figure 6.1. The conventional structure likely has a higher ultimate potential than the inverted structure used here. The order of sequential deposition produces a graded active layer logical for conventional carrier extraction - electrospinning P3HT directly onto the hole transport layer would make better contact. However, as the overlying AZO layer must be annealed, the effect of annealing on the active layer must be further understood to implement this structure.

To transition to the conventional structure, electron transport layers, such as N,N'-Bis(N,N-dimethyl propan-1-amine oxide) perylene-3,4,9,10-tetracarboxylic diimide (PDINO), could be investigated which do not require high temperature annealing. Should effective infiltration of PCBM remain elusive, alternative electron acceptors including (5Z,5'Z)-5,5'-((7,7'-(4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl) bis(benzo[c][1,2,5] thia diazole-7,4-diyl))bis(methanylylidene))bis(3-ethyl-2-thioxo thiazolidin-4-one) (IDTBR) [79] could be investigated to unlock this active layer's potential. Akin to other reports, a BHJ blend could be used for infiltration [61, 63], but is likely to disrupt the fibres' internal nanostructure. Bedford et al. devised a strategy involving the dispersion of

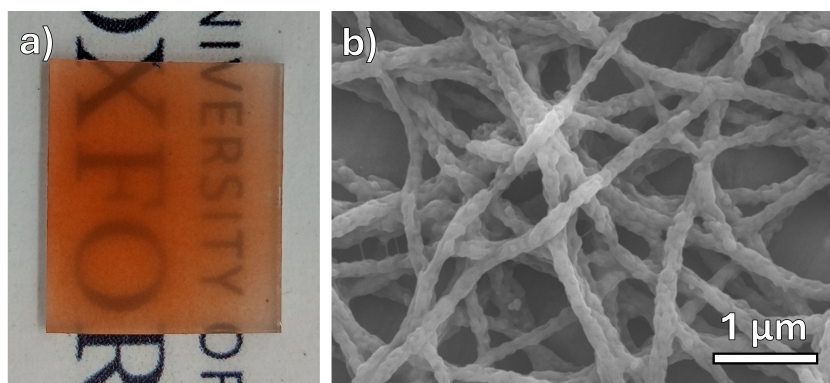


Figure 6.2: (a) Digital photograph and (b) SEM micrograph of electrospun fibres prepared from a thiophene co-polymer containing carboxylic acid-derived moieties used in nano-textured glucose sensors. This co-polymer was synthesised by Harry Potter.

P3HT:PCBM electrospun fibres within cyclopentanone, which was subsequently deposited by spin-coating. These approaches also warrant further study.

6.4 Beyond Photovoltaics

Besides photovoltaic applications, electrospun conjugated polymer fibres have been demonstrated to be suitable for use in other electronic and energy applications, including organic light-emitting diodes (OLEDs), [312] field-effect transistors [313, 314, 315] including strain, [316] pressure, [317] and photo-sensors, [318] optoelectronic synapses [319] and triboelectric nanogenerators. [320]

OLEDs could benefit from the fibres' diffuse light scattering and/or polarized emission generated by the polymer chain alignment, enhanced via diameter reductions. Fibre-based OFETs frequently provide greater mobility and/or enhanced on/off current ratios versus thin-films, [313, 314, 315] with mobility linked to polymer alignment and fibre diameter. [277, 321, 322] Further, the finding that crystallites in organic semiconductor fibres predominantly arise during pre-aggregation, offers an additional strategy to enhancing charge mobility by optimizing the extent of crystallinity.

I have also demonstrated that thiophene co-polymers containing monomers with carboxylic-acid derived side-chains may be electrospun under identical conditions to P3HT (Figure 6.2). Fibres provide additional surface area for the covalent immobilization of enzymes for sensing applications versus films. The addition of nanoparticles may enhance charge mobility and surface area via diameter reductions.



Appendices

Table A.1.1: Details of electrospun photoactive nanofibres reported in literature and their photovoltaic advantages

Nanofibre	Spinning Solution	Diameter (nm)	$\eta(\%)$	J_{SC} (mA cm ⁻¹)	Enhancement/degradation versus BHJ (%)	V_{OC} (V)	Advantages	Ref.	Year
P3HT Fibres									
P3HT	P3HT/PEO (CF)	500+	-	-	-	-	Conductivity	[323]	2007
P3HT	P3HT (CF)	800	-	-	-	-		[105]	2010
P3HT	P3HT/PEO (CF; DMF; Acetic Acid)	80	-	-	-	-	Red-shift Higher crystallinity	[67]	2011
F8BT	F8BT/PEO (CF; DMF; Acetic Acid)	180	-	-	-	-			
P3HT	P3HT/PEO (CF) (CF; DMF :Acetic Acid)	81 ± 16 (No Beads) 64 ± 12 (130) 50 ± 9 (191) 38 ± 4 (251)	2.12 1.26 0.75 0.30	7.00 5.12 4.01 2.19	50.2 45 37.7 30.9	0.604 0.546 0.497 0.439	Red-shift Beads leads to recombination	[64]	2014
P3HT	P3HT/PEO (CF)	1400 - 2800	-	-	-	-		[106]	2015
P3HT	Core: P3HT (CF) Sheath: PMMA (CB)	414 (2° Field) 144	-	-	-	-	Enhanced charge transport	[227]	2015
P3DDT	Core: P3DDT (CF) Sheath: PMMA (CB)	-	-	-	-	-	Lower mobility improvement (longer side chains)		
P3HT	P3HT (CF) Core: P3HT (CF) Sheath: CF	500+ 500	-	-	-	-	Enhanced charge transport	[116]	2015
P3HT	Core: P3HT (CF) Sheath: PCL (CF)	250	-	-	-	-			
P3HT:CdS	P3HT:CdS /PEO (CF)	1000+	-	-	-	-	Enhanced photoluminescence Red-shift	[107]	2017
P3HT	P3HT/PEO (CF; DMF; Acetic Acid)	655 ± 86 448 ± 52 315 ± 45	1.26 - -	4.74 - -	44 - -	0.60 - 0.52	Thicker fibres provide favourable face-on orientation with PCBM	[66]	2018

Table A.1.1: Continued...

Nanofibre	Spinning Solution	Diameter (nm)	Characteristic (Enhancement/degradation versus BHJ (%))				Advantages	Ref.	Year
			η (%)	J_{SC} (mA cm ⁻¹)	FF (%)	V_{OC} (V)			
P3HT	Core: P3HT (CF) Sheath: PMMA (CB)	1000 - 2000	-	-	-	-	Enhanced charge transport	[228]	2019
P3HT	P3HT/PEO (CF + Aged)	500 - 2000	-	-	-	-	Enhanced charge transport	[112]	2022
P3HT	P3HT/PEO (CB)	~1000	-	-	-	-		[114]	2022
P3HT	P3HT/PEO (CF)	~2000+	-	-	-	-	Increased photoconductance	[115]	2022
P3HT:PCBM Fibres									
P3HT:PCBM	Core: P3HT:PCBM (CF:toluene) Sheath: PVP (CF: Ethanol)	940 ± 180	8.7E-8	3.2E-6	22.1	0.12	Red-shift	[109]	2010
P3HT:PCBM	Core: P3HT:PCBM Sheath: PVP (Chloroform: DMF)	500 ± 100 (Annealed)	2.00 (-13) 3.20 (+39)	6.80 (-43) 9.7 (+11)	44 (-4) 55 (+20)	0.65 (+12) 0.59 (+2)	Enhanced absorption Charge transport	[61]	2012
P3HT:PCBM	Core: P3HT:PCBM (CF) Sheath: PEG (CF:DMF)	150 - 160	4.84 (+42)	11.09 (+30)	73.2 (+12)	0.60 (-2)	Greater absorption	[62]	2018
P3HT:PTB7 :PCBM	Core: P3HT:PTB7 :PCBM (CF) Sheath: PEG (CF:DMF)	150 - 160	5.68 (+39)	14.74 (+39)	63.55 (-10)	0.61 (0)	Charge transport		

Table A.1.1: Continued...

Nanofibre	Spinning Solution	Diameter (nm)	Characteristic η (%)	Enhancement/degradation versus BHJ (%)	J_{SC} (mA cm ⁻¹)	FF (%)	V_{OC} (V)	Advantages	Ref.	Year
Alternative donor:acceptor systems										
P3DDT	P3DDT/PEO (CF)	1000	-	-	-	-	-		[324]	2007
P(NDI2OD-T2)	P(NDI2OD-T2)/PEO (CB)	1180	-	-	-	-	-	Enhanced charge transport	[325]	2007
BEH-PPV	BEH-PPV (CF; Methanol)	100 - 300	-	-	-	-	-	Red-shift	[326]	2009
BEH-PPV:PCBM	BEH-PPV:PCBM (CF; Methanol)	120	-	-	-	-	-	Enhanced charge transport		
MEH-PPV:PCBM	Core: MEH-PPV; :PCBM (CB) Sheath: PVP (Ethanol; Water)	800	7.92E-10 (-100)	2.73E-6	0.43	0.11		Red-shift	[108]	2013
MEH-PPV	MEH-PPV (CF; DMF)	207 ± 63 wide 115 ± 57 high	-	-	-	-	-	Enhanced charge transport	[113]	2016
CoP-(3PPT)-(C ₆₀ HT)	CoP../PEO (CF; DMF)	500 ± 100 (Annealed)	3.76 (+8) 5.58 (+61)	11.4 (+7) 13.3 (+39)	55 (0) 62 (+13)	0.60 (+2) 0.61 (0)		Red-shift; Better overlap with solar emission	[63]	2017

Table A.1.2: Details of nanoparticle-containing OPV devices reported in literature and their enhancement mechanism

Photoactive Layer	Nanoparticle	Efficiency (%)	Change ($\pm$ (%))	Mechanism	Ref.	Year
Addition to Active Layer						
P3OT-C ₆₀	6 nm AuNPs	1.90	+73	Charge transport	[132]	2005
	5 nm AgNPs	1.65	50			
P3HT:PCBM	4 nm AuNPs	1.50	-67	Exciton quenching	[283]	2009
PCDTBT:PC ₇₀ BM	70 nm AuNPs	7.10	+13	Light scattering	[327]	2011
P3HT:PC ₇₀ BM	20 nm AgNPs	2.06	+96	LSPR effect and light scattering	[129]	2011
P3HT:PCBM	110 nm AgNWs	3.91	+18	LSPR effect and light scattering	[126]	2011
PCDTBT:PC ₇₀ BM	40 nm AgNPs	6.45	+16	LSPR effect and	[310]	2011
P3HT:PC ₇₀ BM		4.36	+23	Charge transport		
PCDTBT:PC ₇₁ BM	15 nm AuNPs	6.10	+9	LSPR effect and	[130]	2011
	15 nm Au-WS ₂ NPs	6.30	+13	energy level matching		
P3HT:PC ₇₀ BM	5 - 15 nm AgNPs	3.30	-3	Charge recombination	[282]	2011
P3HT:PC ₇₁ BM	40 nm Ag NPs	4.00	+25	LSPR effect and	[127]	2012
PCDTBT:PCBM		6.4	+8	light scattering		
P3HT:PC ₇₁ BM	200 - 500 nm	4.40	+37			
PCDTBT:PCBM	Ag Nanoplates	6.60	+12			
PBDTTT-C-T:PC ₇₀ BM	20 nm AuNPs	7.83	+3	LSPR Effect,	[328]	2012
	50 nm AuNPs	8.11	+7	Charge balancing and lower series resistance		
PCDTBT:PC ₇₁ BM	100 nm Au Arrowhead Nanorods	7.40	+29	LSPR effect and charge transport	[311]	2013
P3HT:PCBM	20 by 80 nm Au/SiO ₂	3.90	+7	Light scattering	[329]	2013
PBDTT:PCBM	Nanorods	5.64	+14			
P3HT:PCBM	25 nm Ag nanoprisms	2.60	-16	LSPR effect and recombination	[155]	2013
P3HT:PCBM	2 - 15 nm AuNPs	3.71	+14	LSPR effect	[330]	2014
P3HT:PCBM	35 nm Au dodecahedra	4.14	+20	LSPR effect	[331]	2015
P3HT:PCBM	15 nm Ag/P3HT NPs	3.65	+37	LSPR effect and	[332]	2015
PTB7:PC ₇₁ BM	75 nm Au Nanodisks	9.29	+21	light scattering		
:n-MWCNTs				LSPR effect and	[333]	2015
PCDTBT:PC ₇₁ BM	15 nm by 60 nm Au Nanorods	6.83	+19	light scattering	[334]	2015
				LSPR effect, light scattering and charge transport		
P3HT:PCBM nanoprisms	1 by 20 nm Ag/TiO ₂	4.03	+30	LSPR effect and reduced recombination	[335]	2015
PFSDCN:PCBM	18 nm AgNPs	2.17	+32	LSPR effect	[336]	2018

Table A.1.2: Continued...

Photoactive Layer	Nanoparticle	Efficiency (%)	Change ($\pm$ (%))	Mechanism	Ref.	Year
Addition to Charge Transport Layers						
P3HT:PCBM	30 - 40 nm Au NPs	4.19	+20	LSPR Effect	[337]	2009
P3HT:PCBM	45 nm Au NPs	4.24	+19	LSPR Effect	[338]	2011
P3HT:PCBM	18 nm Au NPs	3.51	+13	LSPR Effect	[339]	2011
P3HT:PCBM	60 nm Ag NPs	2.75	+64	LSPR Effect	[340]	2011
MEH-PPV:PCBM	15 nm Au NSs	2.36	+19	LSPR Effect	[341]	2011
PIDT-PhanQ:	70 nm (HTL)/	7.50	+13	Light Trapping	[342]	2013
PC ₇₁ BM	50 nm (ETL) Au NPs					
PIDTT-DFBT:	40 nm (HTL)/	9.02	+18	Light Trapping	[343]	2014
PC ₇₁ BM	20 nm (ETL) Ag prisms					
P3HT:ICBA	18 nm Au/GO NPs	5.05	+26	LSPR Effect	[344]	2014
CTL-Active Layer Interface						
P3HT:PCBM	7-9 nm Au NWs	2.72	+12	Light Scattering	[345]	2012
P3HT:PCBM	12.5 nm Ag NPs	2.82	+17	Light Scattering	[346]	2012
P3HT:PCBM	5-10 nm Au NPs	3.36	-8	Recombination	[284]	2012
P3HT:PCBM	22 nm Au/GO Nanocomposites	4.66	+26	LSPR Effect and Dielectric Enhancement	[347]	2013
PTB7:PC ₇₀ BM	60 nm Ag@SiO ₂ NPs	8.49	+17	LSPR Effect and Light Scattering	[348]	2015

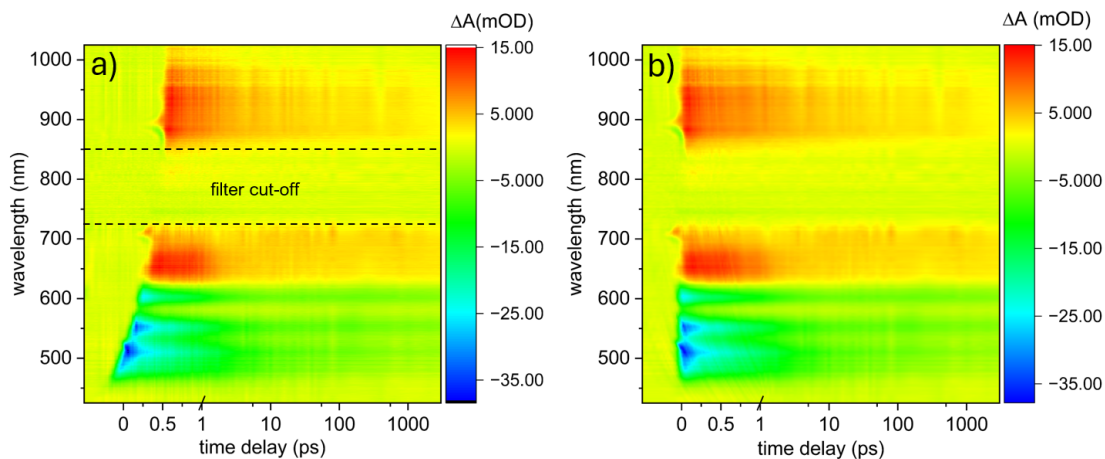


Figure A.2.1: 2D TAS image of the P3HT:PCBM BHJ thin-film (a) before and (b) after chirp correction of the temporal dispersion of the different wavelengths in the super-continuum pulse using the software *KOALA*. Wavelengths between 725 - 850 nm are attenuated by the filter used to prevent detector saturation/damage, as shown in (a).

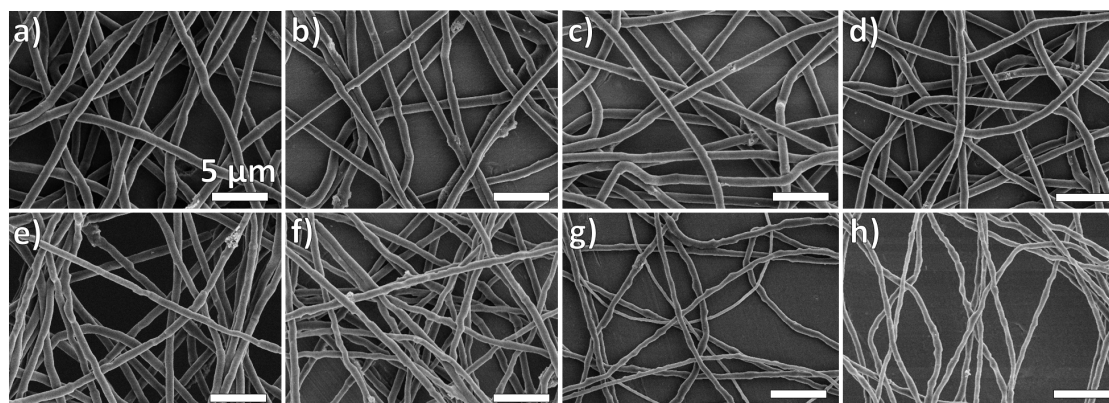


Figure A.3.1: SEM micrographs of nanofibres electrosun from 1.5 wt% PEO solutions in 92: 8 w/w chloroform: DMF with OA-capped AgNP doping levels of (a) 0, (b) 0.05, (c) 0.1, (d) 0.2, (e) 0.5, (f) 1, (g) 2 and (h) 5 wt% AgNO₃ wrt PEO.

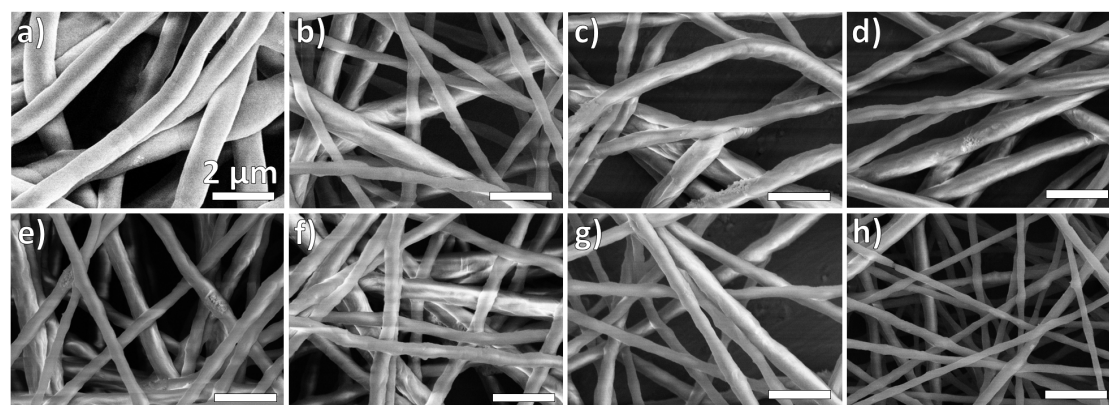


Figure A.3.2: SEM micrographs of nanofibres electrosun from 1.5 wt% PEO solutions in 92: 8 w/w chloroform: DMF with OA-capped AuNP doping levels of (a) 0, (b) 0.05, (c) 0.1, (d) 0.2, (e) 0.5, (f) 1, (g) 2 and (h) 5 wt% AgNO₃ wrt PEO.

Material	Weight Loss Range (°C)	Maximum Loss Rate (°C (% min ⁻¹))	Weight Loss Range (°C)	Maximum Loss Rate (°C (% min ⁻¹))
Oleylamine	286 - 314	305 (-6.0)	353 - 403	378 (-4.0)
AgNO ₃	439 - 485	478 (-11.8)	-	-
OA-capped Ag-NPs	250 - 451	363 (-1.0)	511 - 659	565 (-0.6)
OA-capped AuNPs	158 - 264	224 (-0.4)	442 - 536	484 (-0.4)

Table A.3.1: Analysis of TGA traces revealing the range and rate of weight loss of AgNO₃ and OA-capped NPs.

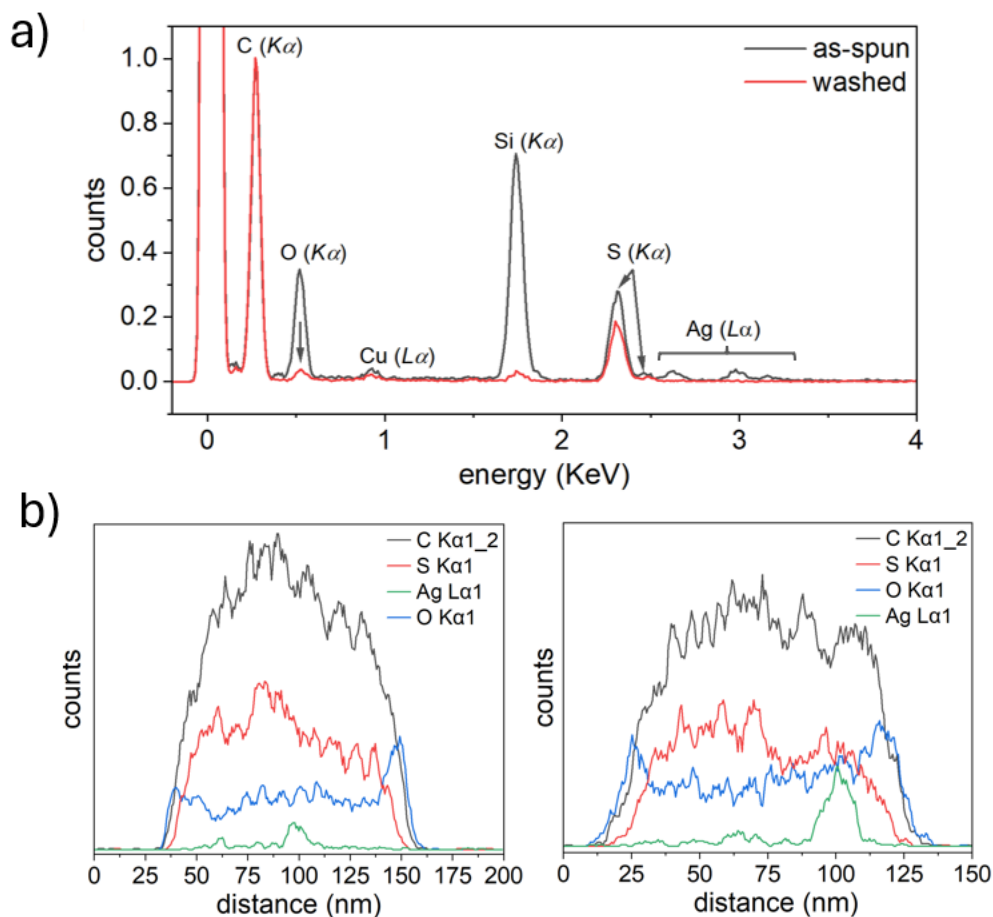


Figure A.4.1: (a) EDX spectrum of the as-spun nanoparticle-containing P3HT/PEO and washed P3HT fibre featured in the linescan in Figure 4.4b-e. (b) Examples of EDX linescans across the width of P3HT/PEO showing the polymer core-sheath phase separation and confirming the presence of silver nanoparticles.

Sample	Dispersion (°)	Amount (nm)	Goodness
P3HT NF	8.54 ± 0.57	0.81 ± 0.04	0.97 ± 0.02
P3HT/PEO-reduced AgNP NF (0 h)	11.54 ± 1.66	0.77 ± 0.09	0.91 ± 0.07
P3HT/PEO-reduced AgNP NF (24 h)	8.98 ± 0.79	0.74 ± 0.02	0.96 ± 0.02
P3HT/PEO-reduced AgNP NF (96 h)	10.60 ± 1.35	0.73 ± 0.02	0.94 ± 0.04
P3HT/ OA-capped AuNP NF (96 h)	9.18 ± 1.48	0.76 ± 0.04	0.92 ± 0.02

Table A.4.2: The extent of fibre-to-fibre alignment generated with different nanofibres collected using a rotating collector, determined using the *Directionality* plugin within *ImageJ*. 'Dispersion' represents the standard deviation of the Gaussian distribution fitted to the orientation angle histogram (Lower = better aligned). 'Amount' constitutes the proportion of fibres from centre - standard deviation to centre + standard deviation (Higher = better aligned). 'Goodness' reports the quality of the fit to the orientation histogram. (Higher = better aligned).

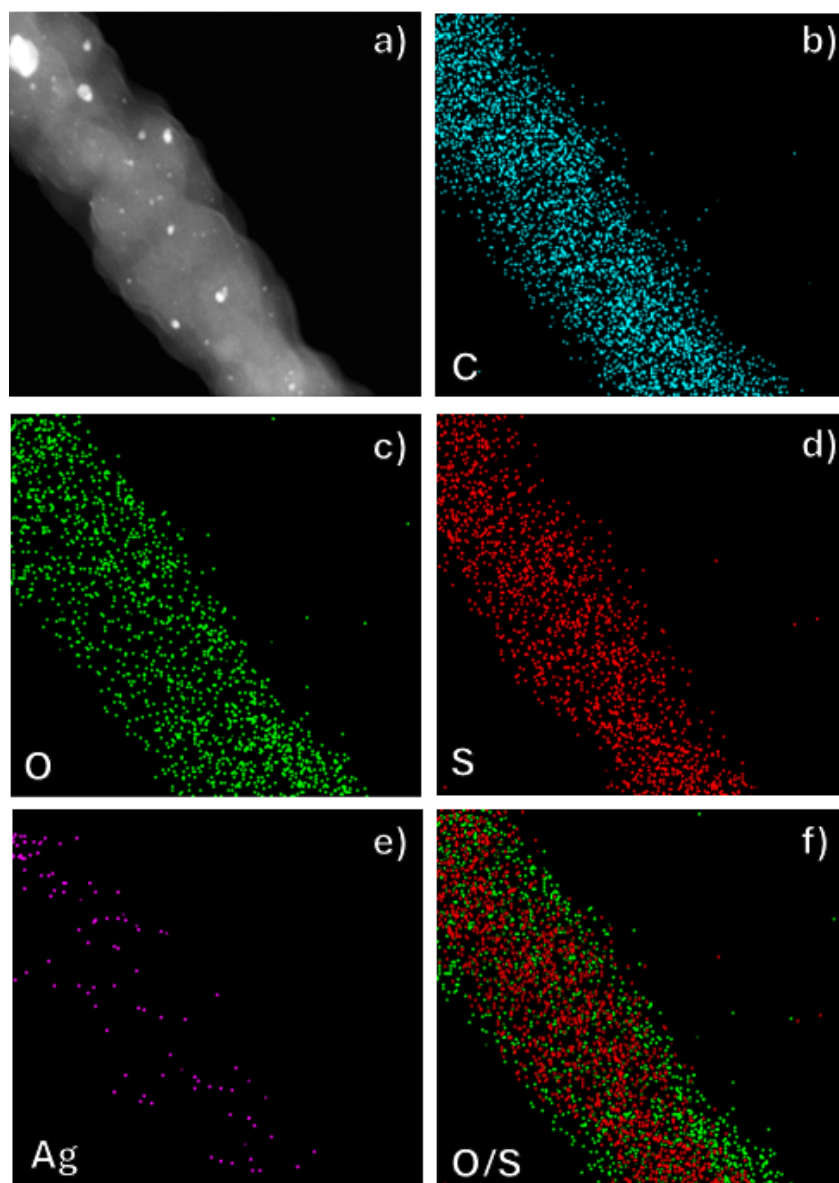


Figure A.4.2: (a) STEM-ADF micrograph of the PEO-reduced AgNP-containing P3HT/PEO nanofibers in Figure 4.4 with EDX elemental mapping of K-series (b) carbon, (c) oxygen, (d) sulfur, and L-series (e) silver. (f) Overlay of the sulfur (red) and oxygen (green) elemental mapping showing the sheathing of P3HT with higher viscosity PEO.

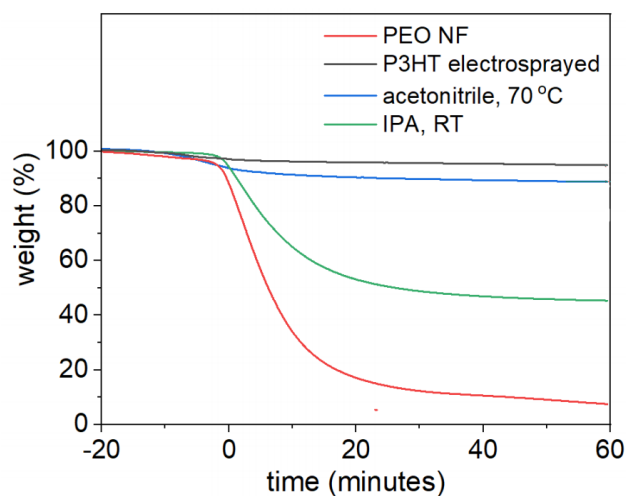


Figure A.4.3: (a) 370 °C isothermal gravimetric analysis of P3HT/PEO fibres washed in acetonitrile at 70 °C and IPA at RT. Negative times represent ramping from room temperature at 10 °C min⁻¹ to 370 °C (reached at 0 minutes).

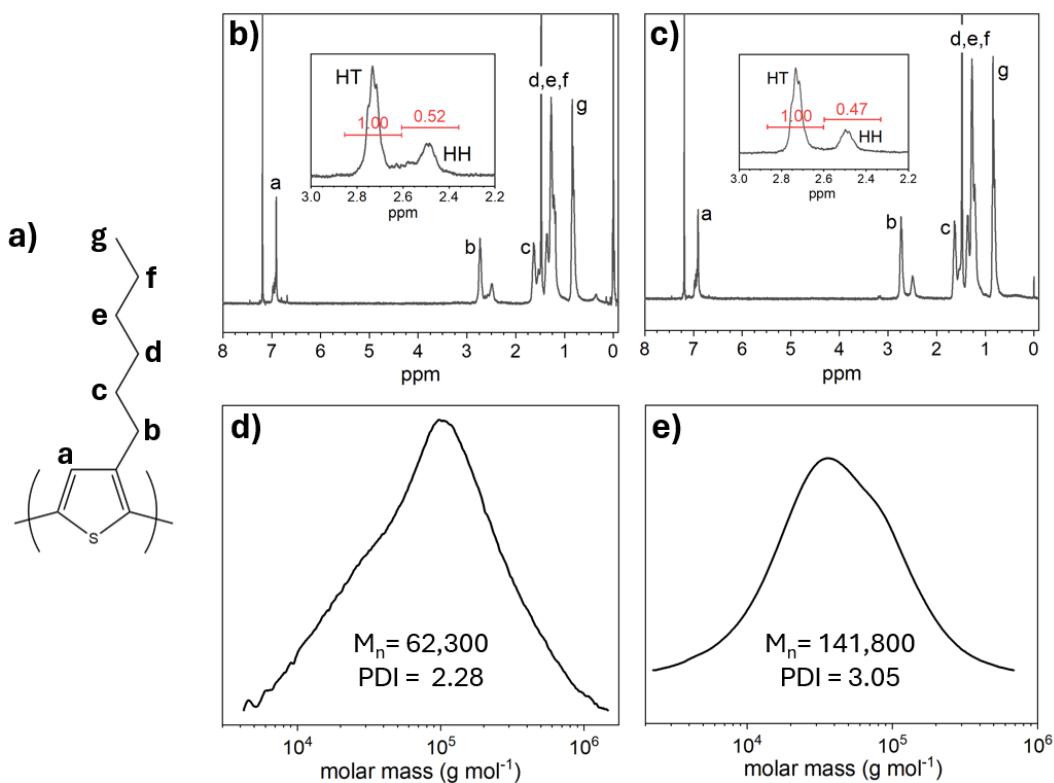


Figure A.4.4: (a) Molecular structure of P3HT labelled with the unique hydrogen environments. ¹H-NMR spectra of P3HT prepared by oxidative addition in the presence of a FeCl₃ catalyst using a reaction solvent of (b) chloroform and (c) acetonitrile producing a RR of 66% and 68%. Gel Permeation Chromatography (GPC) traces of the polymer synthesized in (d) chloroform and (e) acetonitrile.

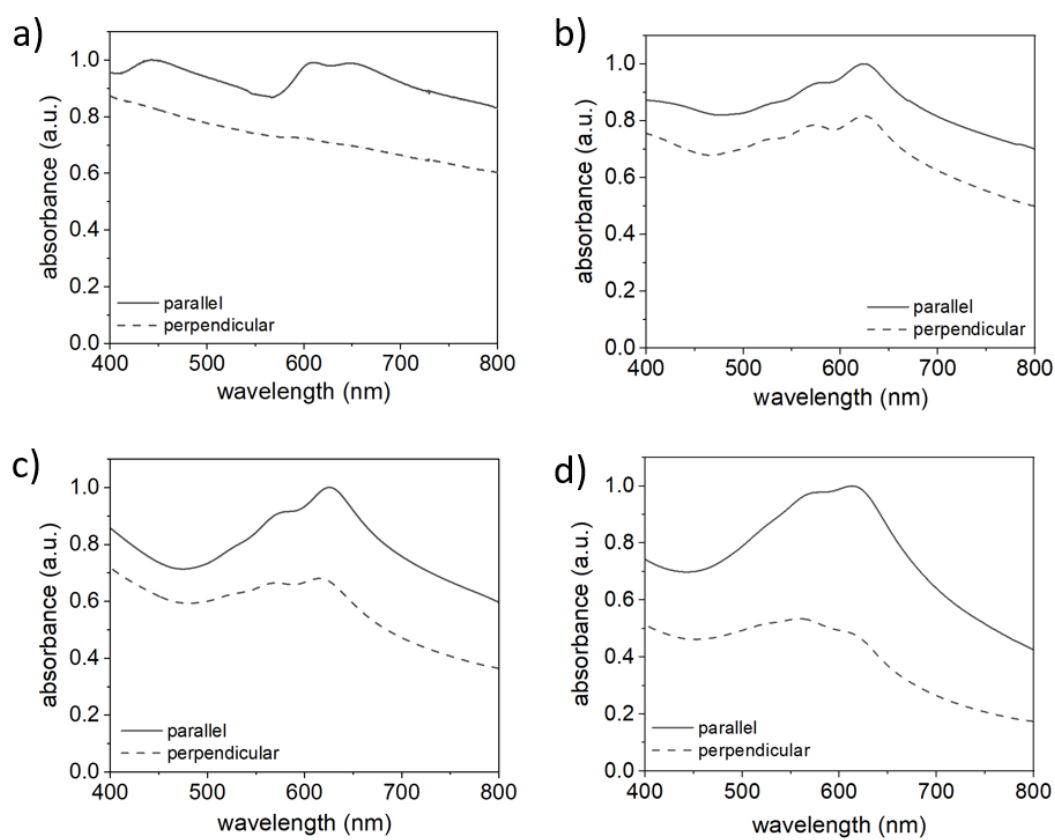


Figure A.4.5: Polarized UV-visible absorption spectra of (a) PEO nanofibres, (b) pristine P3HT nanofibres and PEO-reduced AgNP-containing P3HT fibres spun after (c) 24 h and (d) 96 h of solution ageing deposited on ITO substrates measured in linear transmission mode. Scattering is greater when light is polarized parallel to the fibre axis versus perpendicular to.

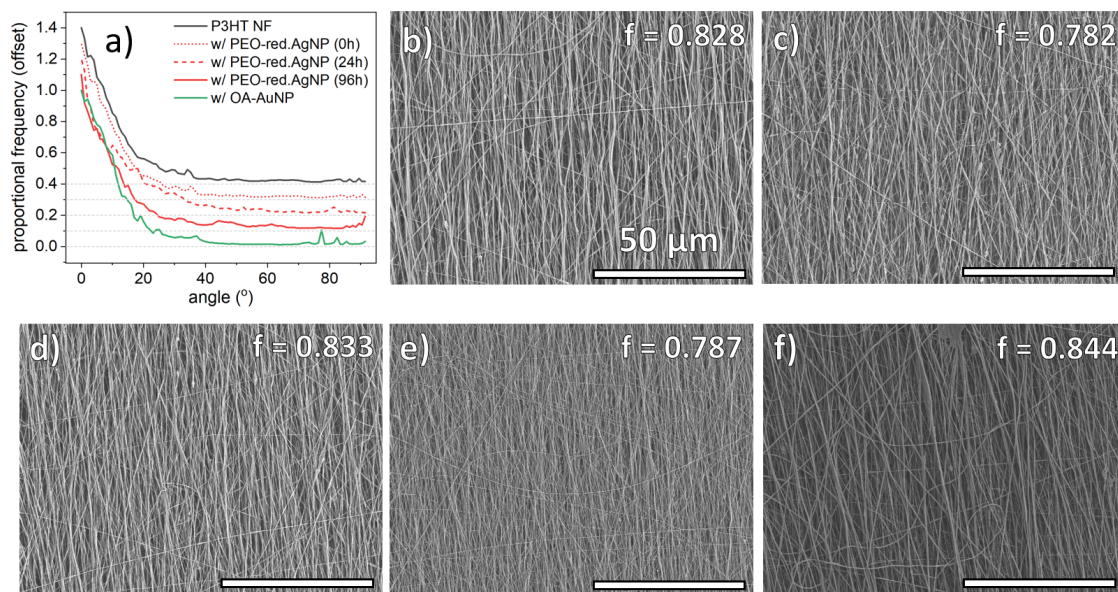


Figure A.4.6: Angular frequency histogram of the aligned nanoweb produced from the micrographs in (b - f) using the ImageJ plugin, Directionality (the common direction is set to 0°). SEM micrographs of as-spun (b) pristine P3HT/PEO nanofibres, and those containing PEO-reduced AgNPs spun after (c) 0 h, (d) 24 h and (e) 96 h ageing, and (f) OA-capped AuNPs spun after 96 h. In all cases, a similar level of fibre-to-fibre alignment is generated.

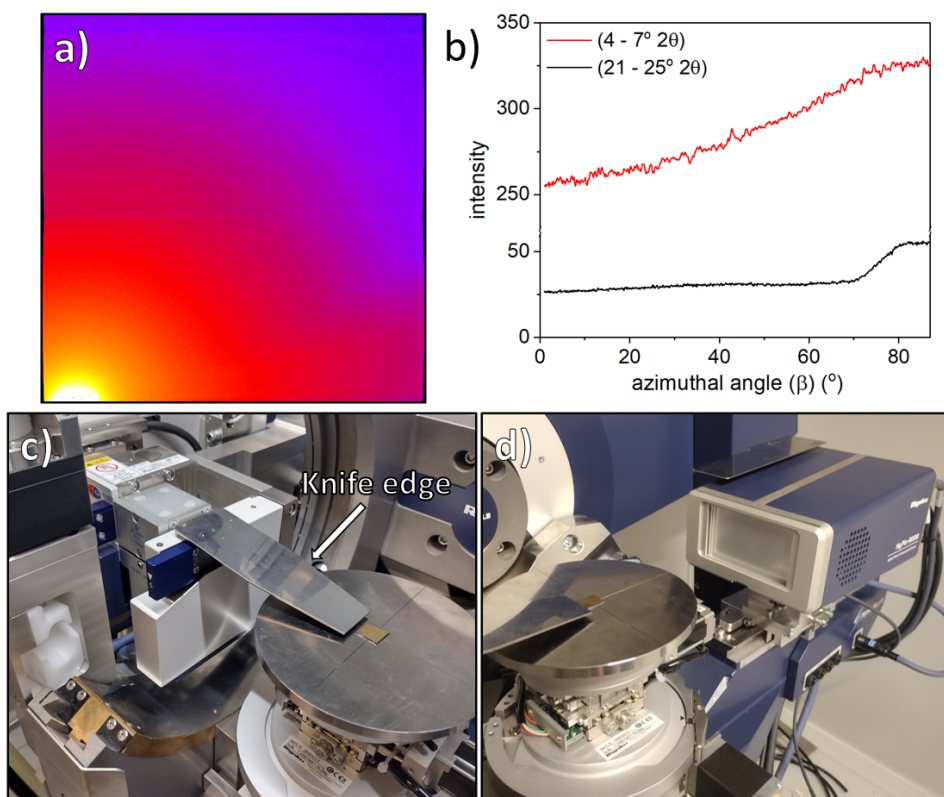


Figure A.4.7: 2D GI-XRD raw detector image of a (a) pristine silicon wafer substrate and extracted 1D azimuthal profiles over the (100) and (020) scattering regions presenting the high IP background scattering. Digital photographs of (c) incident end optics and knife edge, and (d) receiving optics including the Hypix 2D area detector.

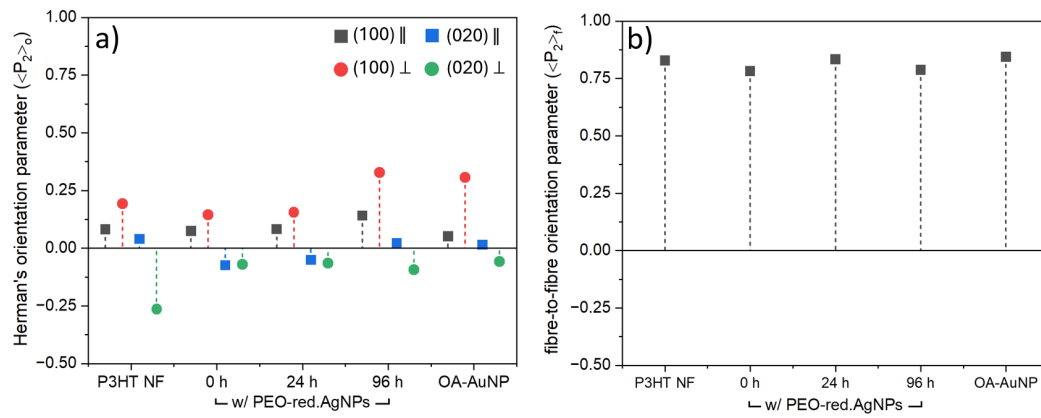


Figure A.4.8: (a) Overall crystallite orientation factors ($\langle P_2 \rangle_o = \langle P_2 \rangle_c * \langle P_2 \rangle_f$) from the (100) and (020) azimuths of pristine and nanoparticle-containing fibres. (b) The fibre-to-fibre orientation factor determined from SEM micrographs in Figure A.4.6.

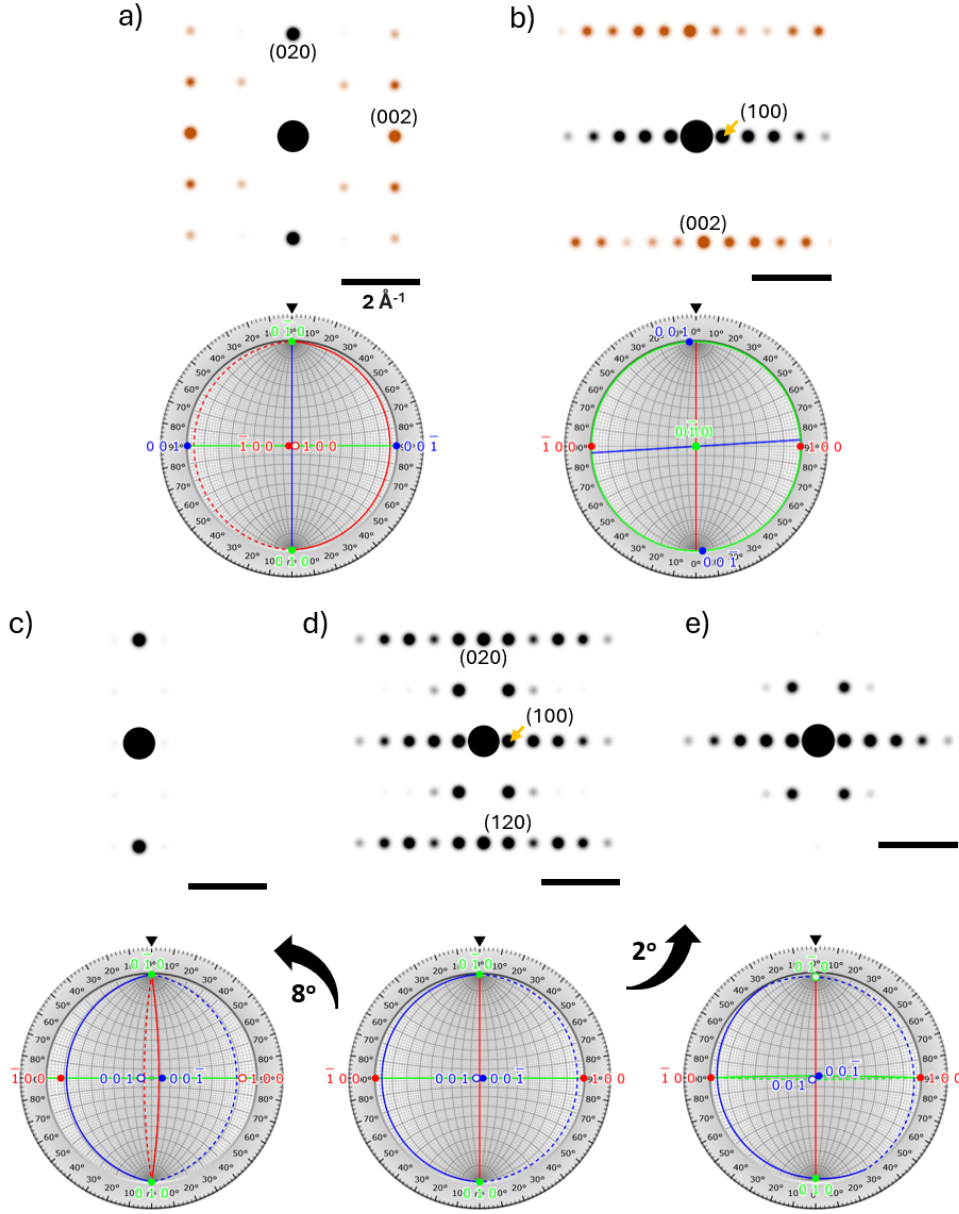


Figure A.4.9: Expected electron diffraction patterns generated when the beam is incident along the (a) (h00), (b) (0k0), and (c) (00l) axes. Orange colours are spots only produced given order in the (001) direction. The attenuation of (100) and (020) spots upon tilting a crystallite viewed initially down the (00l) axis upon (d) an 8° rotation about the (0k0) axis and (e) 2° rotation about the (h00) axis simulated in *Crystallmaker/SingleCrystal* software.

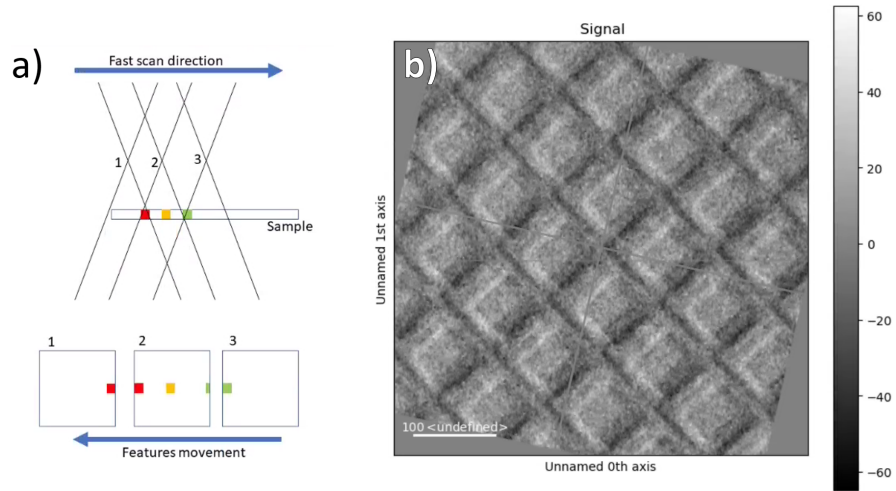


Figure A.4.10: (a) In the correct rotation, features move in the opposing direction of the fast scan. (b) Corrected rotation of Au standard cross-grating where features move horizontally from right to left.

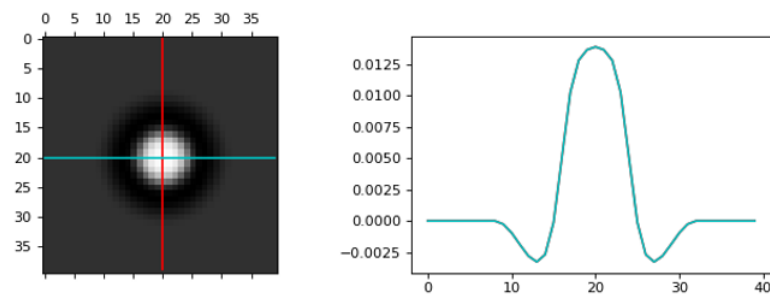


Figure A.4.11: The synthetic probe, a flat disc with an edge that decays sigmoidally to zero, which allows for precise control to tune Bragg disc detection via a cross-correlation approach.

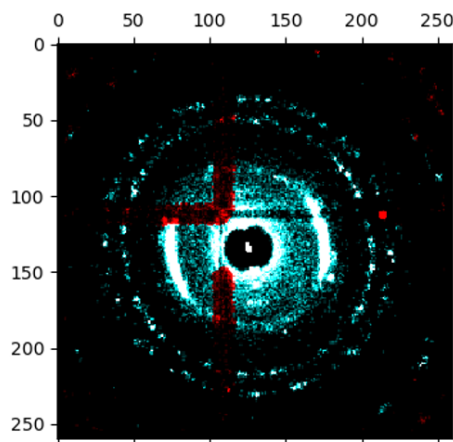


Figure A.4.12: A mask is applied to the Bragg vector map to prevent the gap between the detector chips forming false positives, generated using the beamstop mask protocol.

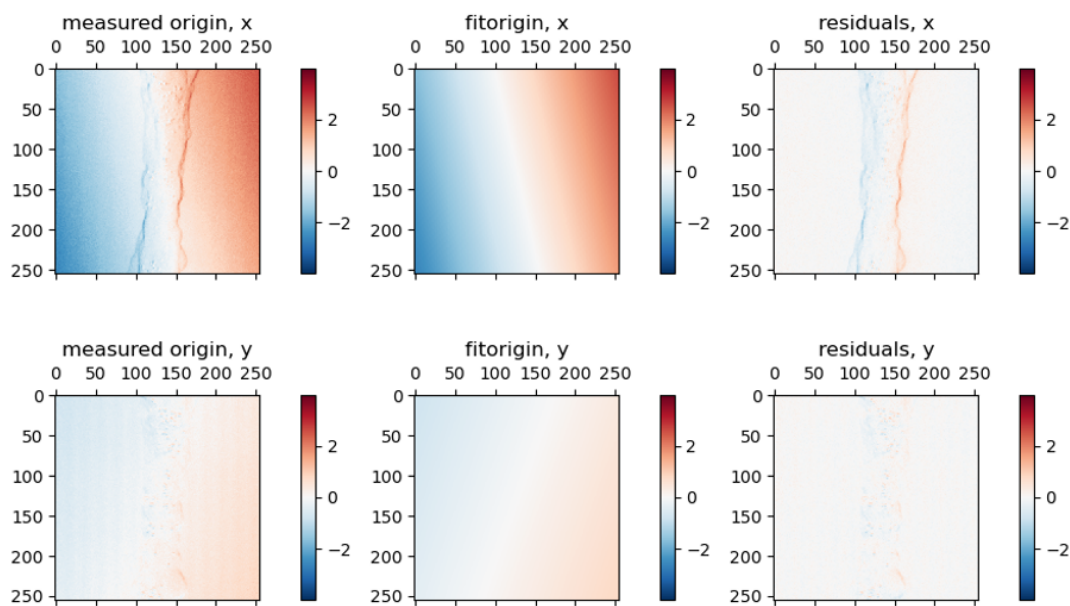


Figure A.4.13: Measurement of the diffraction pattern's central disc and the effect of its translation in real space, generally amounting to < 2 pixels.

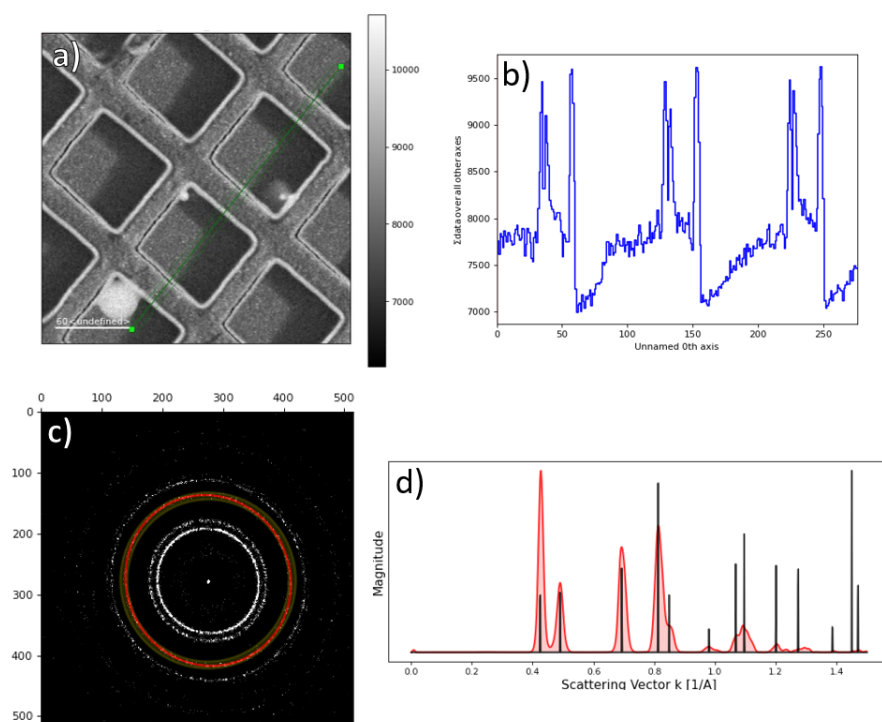


Figure A.4.14: (a) vDF of the gold cross-grating standard with a grating pitch of 500 nm used to (b) calibrate the real-space pixel size at each magnification. (c) The BVM of the Au cross-grating is used to produce an affine transformation to correct for elliptical distortions and (d) calibration of the reciprocal-space pixel size using the expected diffraction lengths of the gold standard.

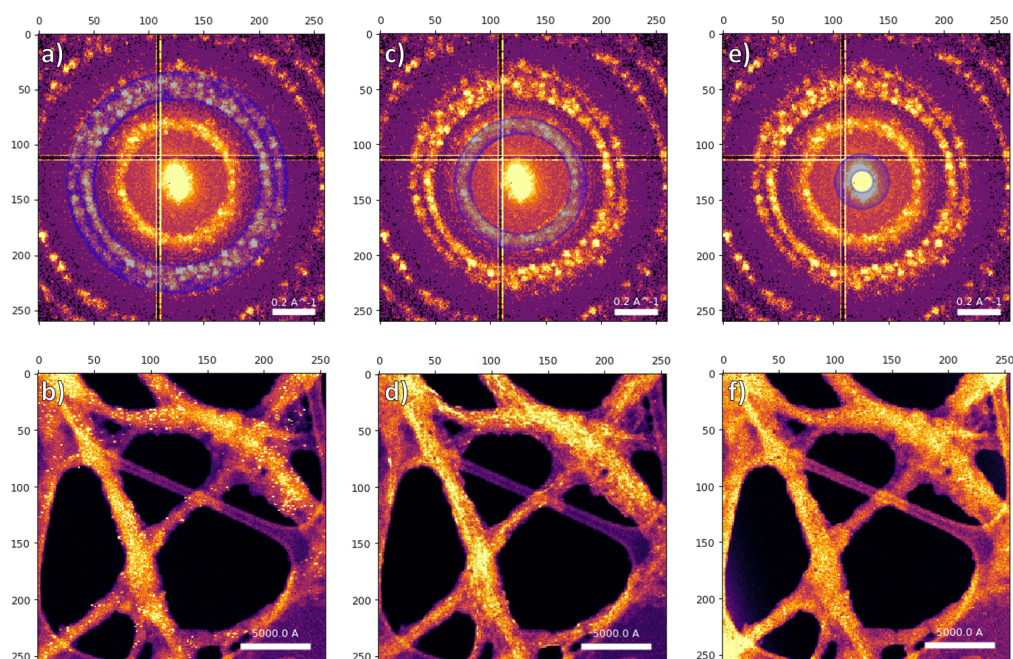


Figure A.4.15: (a, c, e) Annular masks applied to the max diffraction pattern and (b, d, f) vDF images showing the location of features giving rise to the (a, b) (111) and (200) reflection of AuNPs and the (c, d) (020) and (e, f) (100) P3HT reflections.

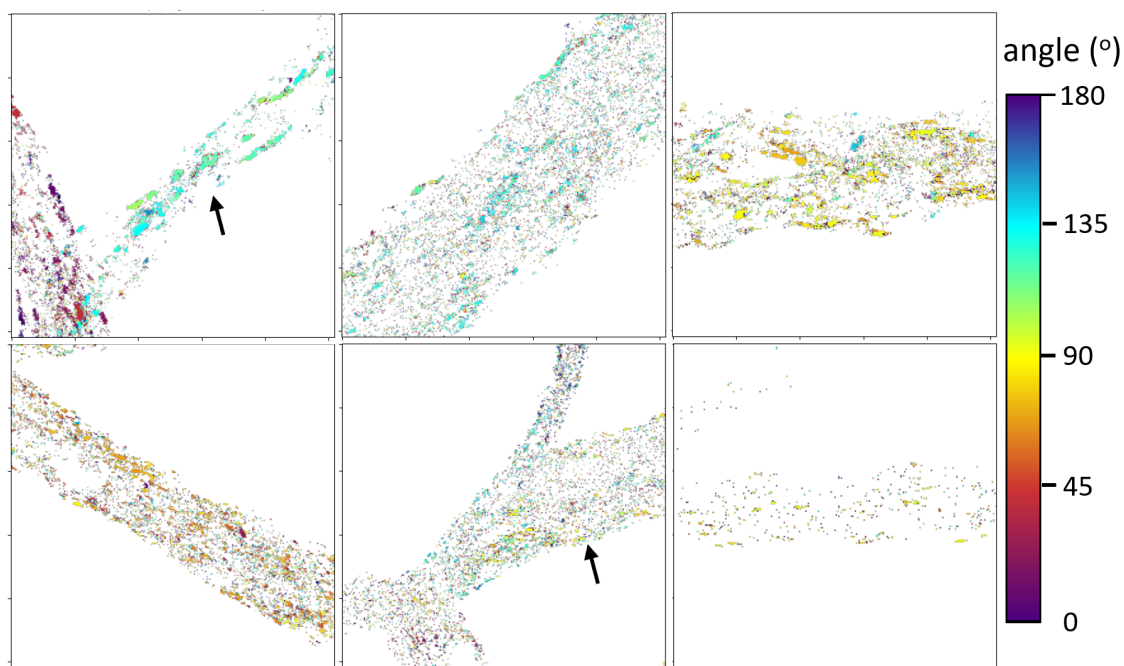


Figure A.4.16: Intensity-weighted orientation maps of (020) reflection of several electrospun nanofibres normalised to the maximum intensity of the individual fibre.

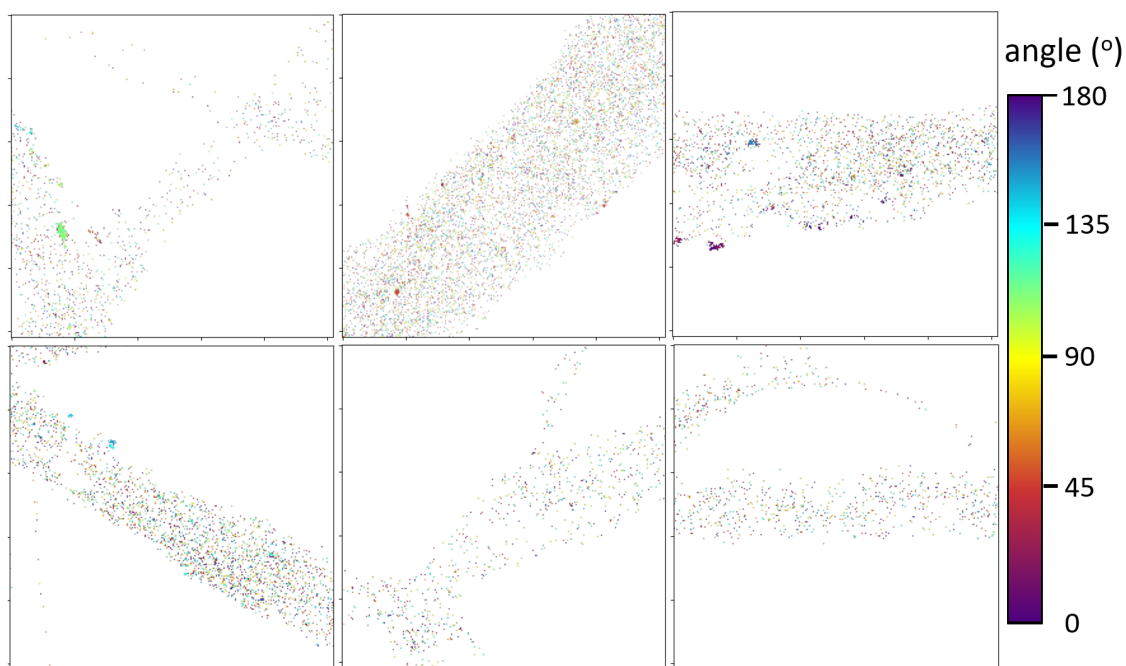


Figure A.4.17: Intensity-weighted orientation maps of (100) reflection of several electrospun nanofibres normalised to the maximum intensity of the individual fibre.

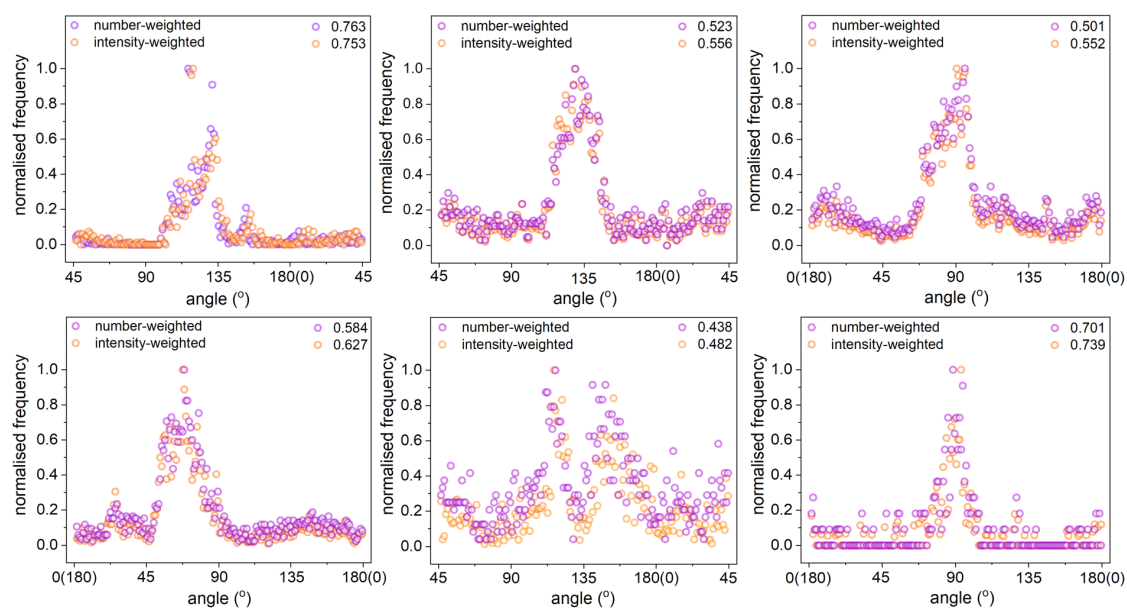


Figure A.4.18: Pixel number- and intensity-weighted 2D histograms of the (020) orientation maps of the corresponding fibres displayed in Figure A.4.13.

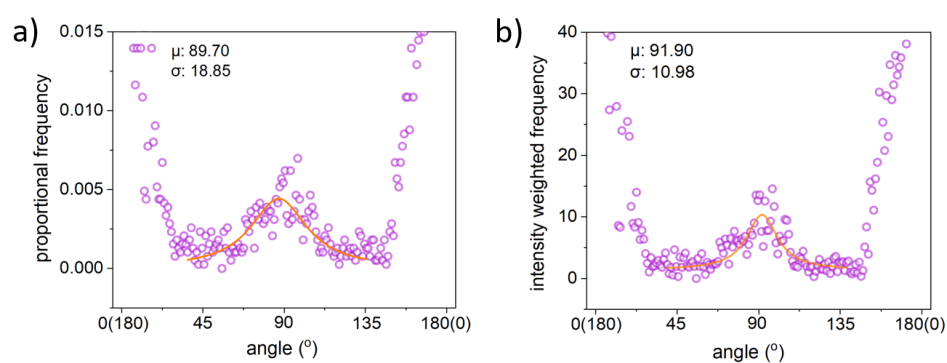


Figure A.4.19: (a) Pixel number-weighted and (b) intensity-weighted 2D histograms of the orientation maps in Figure 3.38 and 4.39, centred about the sub-peak found 90° azimuthal rotation to the primary (020) scattered intensity.

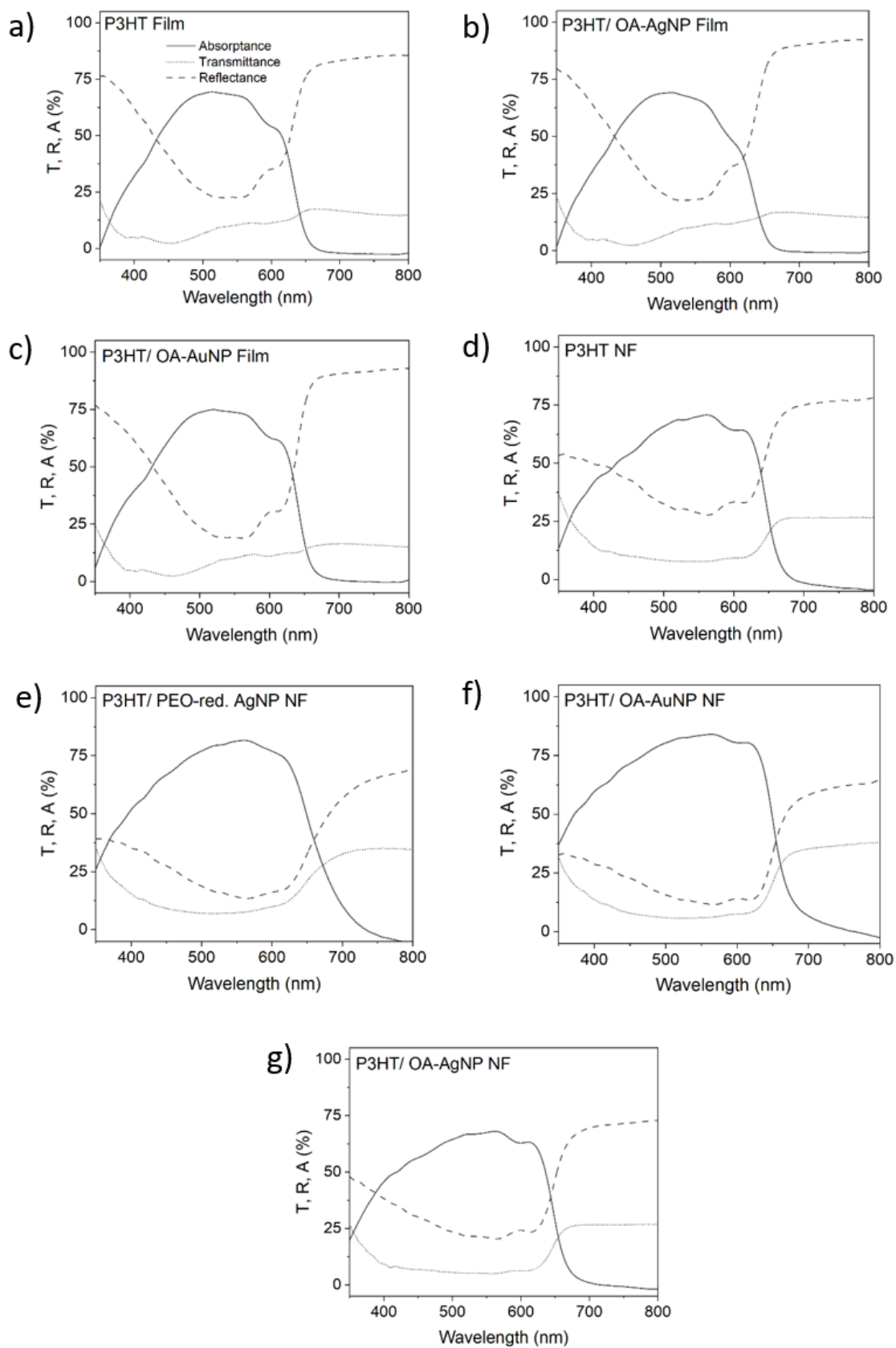


Figure A.5.1: Total reflectance, transmittance and absorptance spectra of P3HT thin-films and nanofibres in Figure 5.4.

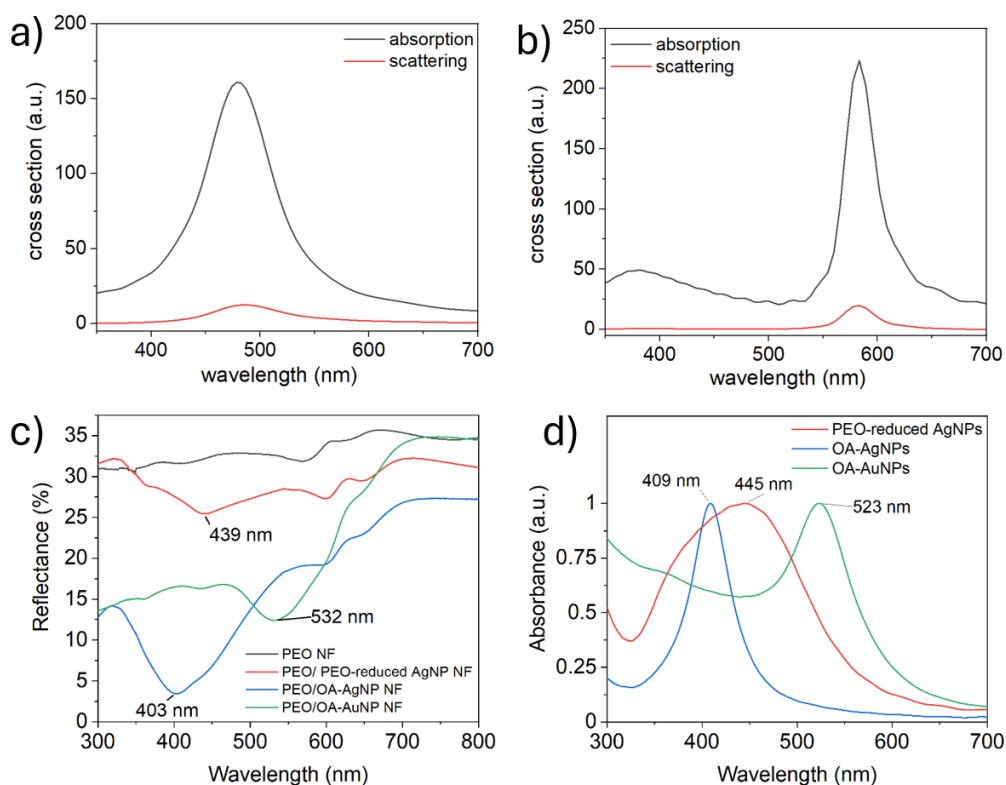


Figure A.5.2: FDTD-simulated absorption and scattering spectra of 10 nm (a) Ag and (b) AuNPs suspended in a medium with a refractive index of 1.95. (c) Diffuse reflectance spectra of nanoparticle-containing PEO nanofibres demonstrating the preservation of plasmonic resonance and (d) experimental absorbance spectra of nanoparticles dispersed in chloroform, presenting a ca. 40 nm red-shift of PEO-reduced AgNPs versus OA-AgNPs.

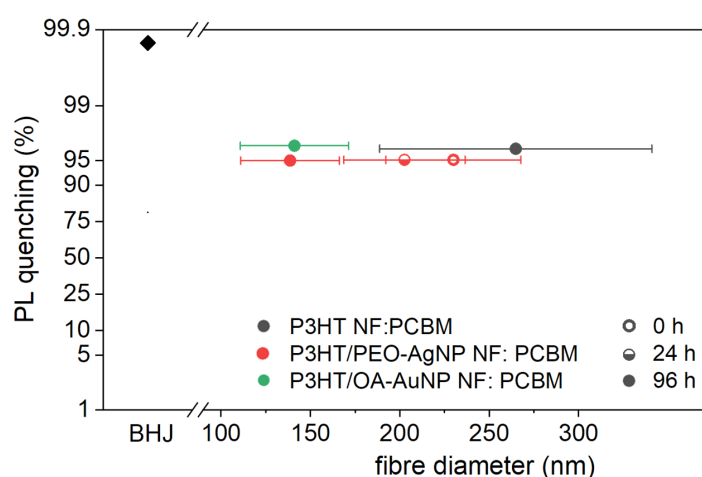


Figure A.5.3: Integrated PL quenching of BHJ and nanofibrous active layer architectures showing impressive dissociation rates and independence upon the diameter of the P3HT/PEO-based fibres prior to washing.

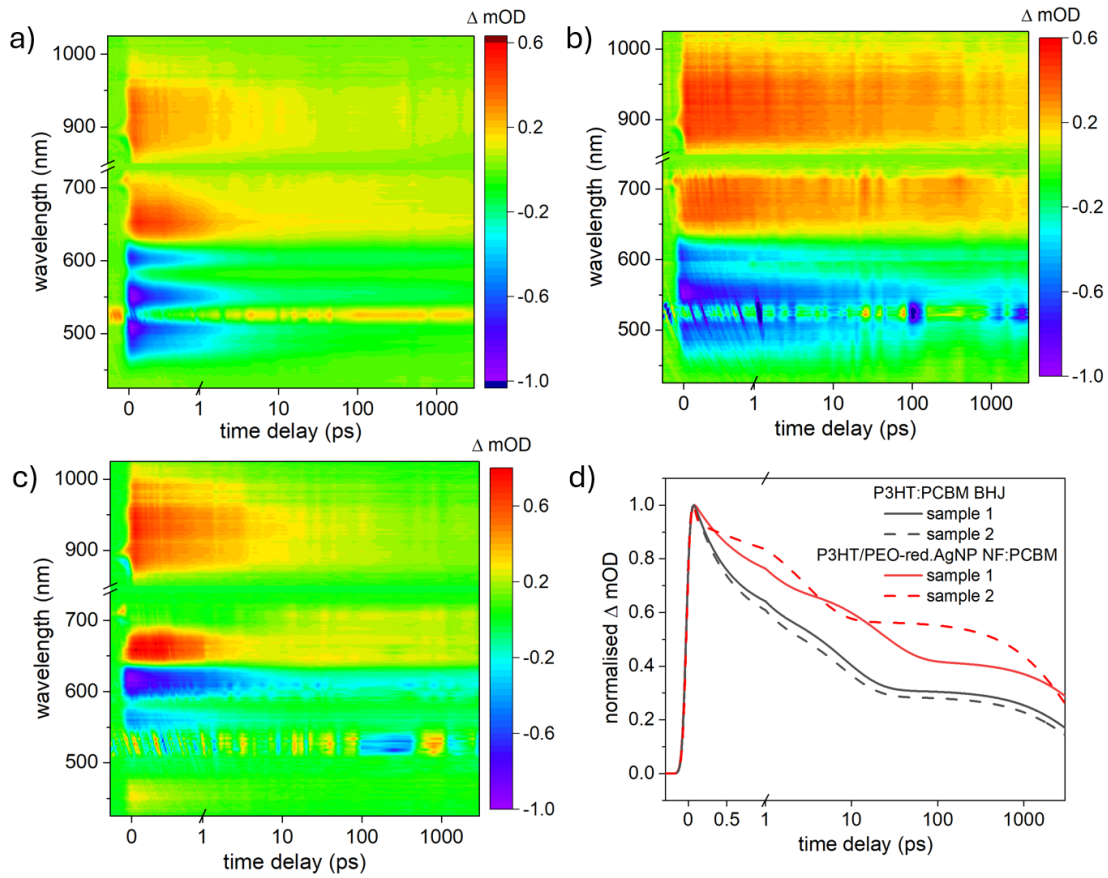


Figure A.5.4: TAS contour plots of (a) a repeat P3HT:PCBM BHJ, (b) repeat PEO-reduced AgNPs (10 wt% $AgNO_3$ addition wrt PEO in solution) nanofibrous active layer and (c) 1 wt% PEO-reduced AgNP-containing nanofibrous active layer. (d) 950 nm signal decay kinetics of repeat BHJ and P3HT/PEO-reduced AgNP NF:PCBM active layers. Artefacts around 520 nm originates from imperfect subtraction of the excitation pulse.

Bibliography

- [1] Energy Institute. Statistical Review of World Energy. <https://www.energyinst.org/statistical-review>, 2023.
- [2] International Renewable Energy Agency (IRENA). *Renewable Power Generation Costs in 2020*. eBook, Abu Dhabi, 2022.
- [3] LAZARD. 2023 Levelized Cost of Energy⁺. <https://www.lazard.com/research-insights/2023-levelized-cost-of-energyplus/>, 2023.
- [4] J. Christians, R. Fung, and P. Kamat. An Inorganic Hole Conductor for Organo-Lead Halide Perovskite Solar Cells. Improved Hole Conductivity with Copper Iodide. *J. Am. Chem. Soc.*, 136:758–764, 2014.
- [5] C. W. Tang. Two-layer organic photovoltaic cell. *Appl. Phys. Lett.*, 48:183–185, 1986.
- [6] R. L. Z. Hoyer et al. Roadmap on Photovoltaic Absorber Materials for Sustainable Energy conversion. *arXiv preprint arXiv:2310.19430*, 2023.
- [7] F. C. Krebs, N. Espinosa, M. Hosel, R. R. Sondergaard, and M. Jorgensen. 25th Anniversary Article: Rise to Power – OPV-Based Solar Parks. *Adv. Mater.*, 26:29–39, 2014.
- [8] I. Burgues-Cebellos, L. Lucera, P. Tiwana, K. Ocytko, L. W. Tan, S. Kowalski, J. Snow, A. Pron, H. Burkstummer, N. Blouin, , and G. Morse. Transparent Organic Photovoltaics: A Strategic Niche to Advance Commercialization. *Joule*, 5:2261–2272, 2021.
- [9] S. Y. Park, C. Labanti, J. Luke, Y.-C. Chin, and J.-S. Kim. Organic Bilayer Photovoltaics for Efficient Indoor Light Harvesting. *Adv. Energy. Mater.*, 12:2103237, 2021.
- [10] W. Song, J. Ge, L. Xie, Z. Chen, Q. Ye, D. Sun, J. Shi, X. Tong, X. Zhang, and Z. Ge. Semi-transparent organic photovoltaics for agrivoltaic applications. *J. Phys. Chem. C*, 116:108805, 2023.
- [11] P. Su, Y. Liu, J. Zhang, C. Chen, B. Yang, C. Zhang, , and X. Zhao. Pb-Based Perovskite Solar Cells and the Underlying Pollution behind Clean Energy: Dynamic Leaching of Toxic Substances from Discarded Perovskite Solar Cells. *J. Phys. Chem. Lett.*, 11:2812–2817, 2020.
- [12] S. Muller and S. Kube. Statistical Review of World Energy. <https://www.heliatek.com/en/technology/sustainability/>, 2023.
- [13] J. Fu, P. W. K. Fong, H. Liu, C.-S. Huang, X. Lu, S. Lu, M. Abdelsamie, T. Kodalle, C. M. Sutter-Fella, Y. Yang, and G. Li. 19.31% binary organic solar cell and low nonradiative recombination enabled by nonmonotonic intermediate state transition. *Nat. Commun.*, 4:1760, 2023.
- [14] A. Armin, W. Li, O. J. Sandberg, Z. Wuo, L. Ding, J. Nelson, D. Neher, K. Vandewal, S. Shaoaee, T. Wang, H. Ade, T. Heumuller, C. Brabec, and P. Meredith. A History and Perspective of Non-Fullerene Electron Acceptors for Organic Solar Cells. *Adv. Energy Mater.*, 11(15):2003570, 2021.
- [15] Q. Burlingame, X. Huang, X. Liu, C. Jeong, C. Coburn, and S. R. Forrest. Intrinsically stable organic solar cells under high-intensity illumination. *Nature*, 573:394–397, 2019.

- [16] W. R. Mateker, I. T. Sachs-Quintana, G. F. Burkhard, R. Cheacharoen, and M. D. McGehee. Minimal Long-Term Intrinsic Degradation Observed in a Polymer Solar Cell Illuminated in an Oxygen-Free Environment. *Chem. Mater.*, 27(2):404–407, 2015.
- [17] Y. Han, H. Dong, W. Pan, B. Liu, X. Chen, Z. Li R. Huang, F. Li, Q. Luo, J. Zhang, Z. Wei, and C.-Q. Ma. An Efficiency of 16.46PM6:Y6 Inverted Organic Solar Cells Enabled by Surface Acid Treatment of the Zinc Oxide Electron Transporting Layer. *ACS Appl. Mater. Inter.*, 13(15):17869–17881, 2021.
- [18] D. Corzo, D. Rosas-Villalva, A. G. Tastado-Blazquez, E. B. Alexandre, L. H. Herndandez, J. Han, H. Xu, M. Babics, S. De Wolf, and D. Baran. Semi-transparent organic photovoltaics for agrivoltaic applications. *Nat. Energy*, 8:62–73, 2023.
- [19] J. Clayden, N. Greeves, and S. Warren. Structure of molecules. In J. Clayden, N. Greeves, and S. Warren, editors, *Polymer Science: A Comprehensive Reference*, pages 80–106. Oxford University Press, Oxford, UK, 2012.
- [20] A. Köhler and H. Bässler. The electronic structure of organic semiconductors. In A. Köhler and H. Bässler, editors, *Electronic Processes in Organic Semiconductors*, pages 1–81. Wiley-VCH, Weinheim, Germany, 2015.
- [21] O. Mikhnenko, P. W. M. Blom, and T.-Q. Nguyen. Exciton diffusion in organic semiconductors. *Energy Environ. Sci.*, 8:1867, 2015.
- [22] A. Jablonskit. Efficiency of Anti-Stokes Fluorescence in Dyes. *Nature*, 131:839–840, 1933.
- [23] P. Atkins and J. de Paula. *Atkins’ Physical Chemistry 10th Edition*. Oxford University Press, Oxford, 2014.
- [24] J. Frenkel. On the transformation of light into heat in solids. ii. *Phys. Rev.*, 37:1276, 1931.
- [25] F. Arabpour Roghabadi, N. Ahmadi, V. Ahmadi, A. Di Carlo, K. Oniy Aghmiuni, A. Shokrolahzadeh Tehrani, F. S. Ghoreishi, M. Payandeh, and N. Mansour Rezaei Fumani. Bulk heterojunction polymer solar cell and perovskite solar cell: Concepts, materials, current status, and opto-electronic properties. *Sol. Energy*, 173:407, 2018.
- [26] M. Pope and C.E. Swenberg. *Electronic Processes in Organic Crystals and Polymers*. Oxford University Press, UK, 1990.
- [27] A. Köhler and H. Bässler. Triplet states in organic semiconductors. *Mater. Sci. Eng. R: Rep.*, 66(4-6):71–109, 2009.
- [28] O. P. Dimitriev. Dynamics of Excitons in Conjugated Molecules and Organic Semiconductor Systems. *Chem. Rev.*, 122(9):8487–8593, 2022.
- [29] J. R. Lakowicz. Introduction to fluorescence. In J. R. Lakowicz, editor, *Principles of Fluorescence Spectroscopy, Third Edition*, pages 1–25. Springer, New York, US, 2006.
- [30] O. V. Mikhnenko, P. W. M. Blom, and T.-Q. Nguyen. Exciton diffusion in organic semiconductors. *Energy Environ. Sci.*, 7:1867–1888, 2015.
- [31] J. Guo, H. Ohkito, H. Bente, and S. Ito. Near-IR Femtosecond Transient Absorption Spectroscopy of Ultrafast Polaron and Triplet Exciton Formation in Polythiophene Films with Different Regioregularities. *J Am. Chem. Soc.*, 131(46):16869–16880, 2015.
- [32] I. Glowacki, J. Jung, J. Ulanski, and A. Rybak. Conductivity measurements. In Krzysztof Matyjaszewski and Martin Möller, editors, *Polymer Science: A Comprehensive Reference*, pages 847–877. Elsevier, Amsterdam, The Netherlands, 2012.
- [33] A. Köhler and H. Bässler. *Electronic Processes in Organic Semiconductors*. Wiley-VCH, Germany, 2015.
- [34] G. Yu, J. Gao, J. C. Hummelen, and A. J. Heeger. Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions. *Science*, 270(5243):1789–1791, 2015.

- [35] S. van Bavel, E. Sourty, G. de With, K. Frolic, and J. Loos. Relation between Photoactive Layer Thickness, 3D Morphology, and Device Performance in P3HT/PCBM Bulk-Heterojunction Solar Cells. *Macromolecules*, 42:7396–7403, 2009.
- [36] M. Lenes, L. J. A. Koster, V. D. Mihailetschi, and P. W. M. Blom. Thickness dependence of the efficiency of polymer:fullerene bulk heterojunction solar cells. *Appl. Phys. Lett.*, 88:243502, 2006.
- [37] S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, and J. C. Hummelen. 2.5% efficient organic plastic solar cells. *Appl. Phys. Lett.*, 78:841–843, 2001.
- [38] J. Roncali. Molecular Bulk Heterojunctions: An Emerging Approach to Organic Solar Cells. *Acc. Chem. Res.*, 42:1719–1730, 2009.
- [39] A. Solanki, B. Wu, T. Salim, Y. M. Lam, and T. C. Sum. Correlation between blend morphology and recombination dynamics in additive-added P3HT:PCBM solar cells. *Phys. Chem. Chem. Phys.*, 17:26111–26120, 2015.
- [40] V. D. Mihailetschi, H. X. Xie, B. de Boer, L. J. A. Koster, and P. W. H. Blom. Charge transport and photocurrent generation in Poly(3-hexylthiophene):Methanofullerene Bulk-heterojunction solar cells. *Adv. Funct. Mater.*, 16:699–708, 2006.
- [41] W. Ma, C. Yang, X. Gong, K. Lee, and A. J. Heeger. Thermally Stable, Efficient Polymer Solar Cells with Nanoscale Control of the Interpenetrating Network Morphology. *Adv. Funct. Mater.*, 15:1617–1622, 2005.
- [42] Y. Kim, S. A. Choulis, J. Nelson, D. D. C. Bradley, S. Cook, , and J. R. Durrant. Device annealing effect in organic solar cells with blends of regioregular poly(3-hexylthiophene) and soluble fullerene). *Appl. Phys. Lett.*, 86:063502, 2005.
- [43] G. Li, Y. Yao, H. Yang H, V. Shrotriya, G. Yang, and Y. Yang. “solvent Annealing” Effect in Polar Solar Cells Based on Poly(3-hexylthiophene) and Methanofullerenes. *Adv. Funct. Mater.*, 17:1636–1644, 2007.
- [44] J. H. Park, J. S. Kim, J. H. Lee, W. H. Lee, and K. Cho. Effect of Annealing Solvent Solubility on the Performance of Poly(3-hexylthiophene)/Methanofullerene Solar Cells. *J. Phys. Chem.*, 113:17579–17584, 2009.
- [45] J. Jo, S.-I. Na, S.-S. Kim, T.-W. Lee, Y. Chung, S.-J. Kang, D. Vak, and D.-Y. Kim. Three-Dimensional Bulk Heterojunction Morphology for Achieving High Internal Quantum Efficiency in Polymer Solar Cells. *Adv. Funct. Mater.*, 19:2398–2406, 2009.
- [46] X. Yang, J. K. van Duren, R. A. J. Janssen, M. A. J. Michels, and J. Loos. Morphology and Thermal Stability of the Active Layer in Poly(p-phenylenevinylene)/Methanofullerene Plastic Photovoltaic Devices. *Macromolecules*, 37(6):2151–2158, 2004.
- [47] National Renewable Energy Laboratory. Best Research-Cell Efficiency Chart. <https://www.nrel.gov/pv/cell-efficiency.html>, 2023.
- [48] Y. Tamai. What’s Next for Organic Solar Cells? The Frontiers and Challenges. *Adv. Energy. Sust. Res.*, 4(1):2200149, 2022.
- [49] B. Ehrler, E. Alarcon-Llado, S. W. Tabernig, T. Veeken an E. C. Garnett, and A. Polman. Photovoltaics Reaching for the Shockley–Queisser Limit. *ACS Energy Lett.*, 5(9):3029–3033, 2020.
- [50] J. Kirkpatrick, C. B. Nielsen, W. Zhang, H. Bronstein, R. S. Ashraf, M. Heeney, and I. McCulloch. A Systematic Approach to the Design Optimization of Light Absorbing Indenofluorene. *Adv. Energy Mater.*, 2(2):260–265, 2012.
- [51] Q. Zhao, Y. Shan, H. Zhou, G. Zhang, and W. Liu. Machine learning-assisted performance prediction and molecular design of all-small-molecule organic solar cells based on the Y6 acceptor. *Sol. Energy*, 265:112115, 2023.

- [52] P. Kaienburg, H. Bristow, A. Jungbluth, I. Habib, I. McCullough, and M. Riede. Vacuum-Deposited Donors for Low-Voltage-Loss Nonfullerene Organic Solar Cells. *ACS Appl. Mater. Interfaces*, 15(26):31684–31691, 2023.
- [53] H. Gao, Y. Sun, L. Meng, C. Han, X. Wan, and Y. Chen. Recent Progress in All-Small-Molecule Organic Solar Cells. *Small*, 19(3):2205594, 2022.
- [54] A. Ventateswarareo and K.-T. Wong. Small Molecules for Vacuum-Processed Organic Photovoltaics: Past, Current Status, and Prospect. *Bull. Chem. Soc. Jpn.*, 94(3):812–838, 2021.
- [55] M. Riede, D. Spoltore, and K. Leto. Organic Solar Cells—The Path to Commercial Success. *Adv. Energy. Mater.*, 11(1):2002653, 2020.
- [56] J. Xue, T. Wu, Y. Dai, and Y. Xia. Electrospinning and Electrospun Nanofibers: Methods, Materials, and Applications. *Chem. Rev.*, 119(8):5298–5415, 2019.
- [57] A. L. Yarin and E. Zussman. Upward needleless electrospinning of multiple nanofibers. *Polymer*, 45:2977–2980, 2004.
- [58] D. Lukas, A. Sakar, and P. Pokorný. Self-organization of jets in electrospinning from free liquid surface: A generalized approach. *J. Appl. Phys.*, 103:084309, 2008.
- [59] G. I. Taylor. Disintegration of water drops in an electric field. *Proc. Roy. Soc. A*, 280:383–397, 1964.
- [60] J. Fernandez de la Mora. The fluid dynamics of taylor cones. *Annu. Rev. Fluid Mech.*, 39:217–243, 2007.
- [61] N. M. Bedford, M. B Dickerson, L. F. Drummy, H. Koerner, K. M. Singh, M. C. Vasudev, M. F. Durstock, R. R. Naik, and A.J. Steckl. Nanofiber-Based Bulk-Heterojunction Organic Solar Cells Using Coaxial Electrospinning. *Adv. Energy Mater.*, 2:11363, 2012.
- [62] H.J n. Huang, H. R. Nan, Y. G. Yang, X. Y. Gao, F. Chen, and Z.-K. Chen. Improved Performance of Thick Films Based Binary and Ternary Bulk Heterojunction Organics Photovoltaic Devices Incorporated with Electrospinning Processed Nanofibers. *Adv. Mater. Interfaces.*, 5:1800914, 2018.
- [63] F. Pierini, M. Lanzi, P. Nakielski, S. Pawlowska, O. Urbanek, K. Zembrzycki, and T.A. Kowalewski. Single-Material Organic Solar Cells Based on Electrospun Fullerene-Grafted Polythiophene Nanofibers. *J. Mater. Chem.*, 21:14231–14239, 2017.
- [64] T. Kim, S. J. Yang, S. K. Kim, H. S. Choi, and C. R. Park. Preparation of PCDTBT nanofibers with a diameter of 20 nm and their application to air-processed organic solar cells. *Nanoscale*, 6:2847–2854, 2014.
- [65] T. Kim, S. J. Yang, S. J. Sung, Y. S Kim, M. S. Chang, H. Jung, and C. R. Park. Highly Reproducible Thermocontrolled Electrospun Fiber Based Organic Photovoltaic Devices. *ACS Appl. Mater. Interfaces*, 7:4481–4487, 2015.
- [66] S. Yoon, Y. Han, and I. Hwang. Probing Molecular Orientation of P3HT Nanofibers in Fiber-Based Organic Solar Cells. *Electron. Mater. Lett.*, 14:46–51, 2018.
- [67] T. Kim, J. H. Im, H. S. Choi, S. J. Yang, S. W. Kim, and C. R. Park. Preparation and photoluminescence (PL) performance of a nanoweb of P3HT nanofibers with diameters below 100 nm. *J. Mater. Chem.*, 21:14231–14239, 2011.
- [68] T. Erb, S. Raleva, U. Zhokhavets, G. Gobsch, B. Stühn, M. Spode, and O. Ambacher. Structural and optical properties of both pure poly(3-octylthiophene) and P3OT/fullerene films. *Thin Film Solids*, 450:97–100, 2004.
- [69] M. C. Gurau, D. M. Delongchamp, B. M. Vogel, E. K. Lin, D. A. Fischer, S. Sambasivan, and L. J. Richter. Measuring Molecular Order in Poly(3-alkylthiophene) Thin Films with Polarizing Spectroscopies. *Langmuir*, 23(2):834–842, 2007.

- [70] K. Gu and Y.-L. Loo. The Polymer Physics of Multiscale Charge Transport in Conjugated Systems. *J. Polym. Sci. B Polym. Phys.*, 57(23):1559–1571, 2019.
- [71] D. E. Johnston, K. G. Yager, H. Hlaing, X. Lu, B. M. Ocko, and C. T. Black. Nanostructures Surfaces Frustrate Polymer Semiconductor Molecular Orientation. *ACS Nano*, 8:243–249, 2014.
- [72] R. Noriega, J. Rivnay, K. Vandewal, F. P. V. Koch, N. Stingelin, P. Smith, M. F. Toney, and A. Salleo. A general relationship between disorder, aggregation and charge transport in conjugated polymers. *Nat. Mater.*, 12:1038–1044, 2013.
- [73] A. Troisi C. Poelking, K. Daoulas and D. Andrienko. *Morphology and Charge Transport in P3HT: A Theorist’s Perspective*. In S. Ludwigs, editor, *P3HT Revisited - From Molecular Scale to Solar Cell Devices. Advances in Polymer Science, vol 265.*, chapter 12, pages 139–180. Springer, Berlin, Heidelberg, Germany, 2014.
- [74] H. Wang, Y. Xu, X. Yu, R. Xing, J. Liu, and Y. Han. Structure and Morphology Control in Thin Films of Conjugated Polymers for an Improved Charge Transport. *Polymers*, 5(4):1272–1324, 2013.
- [75] F. Liu, Y. Gu, J. W. Jung, W. H. Jo, and T. P. Russell. On the morphology of polymer-based photovoltaics. *J. Polym. Sci. Part B: Polym. Phys.*, 50(15):1018–1044, 2012.
- [76] A. Smets, K. Jager, O. Isabella, R. van Swaaij, and M. Zeman. *Solar Energy: The Physics and Engineering of Photovoltaic Conversion Technologies and Systems*. UIT Cambridge, Cambridge, UK, 2016.
- [77] PV Education. Short-Circuit Current. <https://www.pveducation.org/pvcdrom/solar-cell-operation/short-circuit-current>, 2023.
- [78] Ossila. Fill Factor of Solar Cells. <https://www.https://www.ossila.com/pages/fill-factor-solar-cells>, 2023.
- [79] S. Holliday, R. Shahid Ashraf, A. Wadsworth, D. Baran, S. Amber Yousaf, C. B. Nielsen, C.-H. Tan, S. D. Dimitrov, Z. Shang, N. Gasparini, M. Alamoudi, F. Laquai, C. J. Brabec, A. Salleo, J. R. Durrant, and I. McCulloch. High-efficiency and air-stable P3HT-based polymer solar cells with a new non-fullerene acceptor. *Nat. Commun.*, 7:11585, 2016.
- [80] C. D. Saquing, J. L. Manasco, and S. A. Khan. Electrospun Nanoparticle-Nanofiber Composites via a One-Step Synthesis. *Small*, 5:944–951, 2009.
- [81] L. D. Tijing, M. T. G. Ruelo, A. Amarjargal, H. R. Pant, C.-H. Park, and C. S. Kim. One-step fabrication of antibacterials (silver nanoparticles/poly(ethylene oxide)) – Polyurethane bicomponent hybrid nanofibrous mat by dual-spinneret electrospinning. *Mater. Chem. Phys.*, 118:557–561, 2013.
- [82] A. T. Haedler, K. Kreger, A. Issac, B. Wittman, M. Kivala, N. Hammer, J. Kohler, H.-W. Schmidt, and R. Hildner. SERS-active silver colloids prepared by reduction of silver nitrate with short-chain polyethylene glycol. *Nano Express*, 8:47, 2013.
- [83] H. Hiramatsu and F. E. Osterloh. A Simple Large-Scale Synthesis of Nearly Monodisperse Gold and Silver Nanoparticles with Adjustable Sizes and with Exchangeable Surfactants. *Chem. Mater.*, 16:2509–2511, 2004.
- [84] B. H. Savitzky, S. E. Zeltmann, L. A. Hughes, H. G. Brown, S. Zao, P. M. Pelz, T. C. Pekin, E. S. Bernard, J. Donohue, J. Donohue, L. R. DaCosta, E. Kennedy, Y. Xie, M. T. Janish, M. M. Schneider, P. Herring, C. Gopal, A. Anapolsky, R. Dhall, K. C. Bustillo, P. Ercius, M. C. Scott, J. Ciston, A. M. Minor, and C. Ophus. py4DSTEM: A Software Package for Four-Dimensional Scanning Transmissiob Electron Microscopy Data Analysis. *Microscopy and Microanalysis*, 27(4):712–743, 2021.
- [85] B. H. Savitzky and C. Ophus. py4dstem. <https://github.com/py4DSTEM/py4DSTEM>, 2023.

- [86] International Union of Pure and Applied Chemistry (IUPAC). '*Green Book*' or *Quantities, Units and Symbols in Physical Chemistry*. Blackwell Science Ltd, Oxford, UK, 1988.
- [87] A. Hope. *Diffuse Reflectance and Transmittance*. In T. A. Germer, J. C. Zwinkels, and B. K. Tsai, editors, *Spectrophotometry*, chapter 6, pages 179–219. Academic Press, Cambridge, USA, 2014.
- [88] N. Sheppard, H. A. Willis, and J. C. Rigg. Names, symbols, definitions and units of quantities in optical spectroscopy (Recommendations 1984). *Pure Appl. Chem.*, 57(1):105–120, 1985.
- [89] E. W. Thulstrup and J. Michl. *Elementary Polarization Spectroscopy*. John Wiley Sons, 1989.
- [90] E. W. Thulstrup and P. W. Thulstrup. Polarization Spectroscopic Studies of Ordered Samples. *Acta Chim. Slov.*, 52, 2005.
- [91] S. Srivastava, S. Ranjan, L. Yadav, T. Sharma, S. Choudhary, D. Agarwal, A. Sigh, S. Satapathi, R. Kumar Gupta, A. Garg, and K. S. Lalwa. Advanced spectroscopic techniques for characterizing defects in perovskite solar cells. *Commun. Mater.*, 4:52, 2023.
- [92] J. M. Woolley, M. Staniforth, M. D. Horbury, G. W. Richings, M. Wills, and V. G. Stavros. Unravelling the Photoprotection Properties of Mycosporine AminoAcid Motifs. *J. Phys. Chem. Lett.*, 9:3043–3048, 2018.
- [93] National Insistute of Standards and Technology. Nist/epa gas-phase infrared database. <https://webbook.nist.gov/cgi/inchi?ID=C124389&Type=IR-SPEC&Index=0>, 2023.
- [94] Inc. Brookfield Engineering Laboratories. *Brookfield DV2T Viscometer Operating Instructions*. Pure Appl. Chem., Middlebro, USA.
- [95] J. M. Andreas, E. A. Hauser, and W. B. Tucker. Boundary Tension by Pendant Drops. *J. Phys. Chem.*, 42(8):1001–1019, 1938.
- [96] E. Y. Arashiro and N. R. Demarquette. Use of the Pendant Drop Method to Measure Interfacial Tension between Molten Polymers. *Mater. Res.*, 2(1):23–32, 1999.
- [97] W. H. Bragg and W. L. Bragg. The reflection of X-rays by crystals. *Proc. Math. Phys. Eng. Sci.*, 88(605):428–438, 1913.
- [98] J. R. H. Ross. *Catalyst Characterisation*. In J. H. R. Ross, editor, *Comtemporary Catalysis: Fundamentals and Current Applications*, chapter 5, pages 121–132. Elsevier, Amsterdam, The Netherlands, 2019.
- [99] D. H. Reneker and A. L. Yarin. Electrospinning jets and polymer nanofibers. *Polymer*, 49:2387–2425, 2008.
- [100] T. Yasuda, H. Meguro, S. Okamoto, and L. Han. Bulk-heterojunction organic photovoltaic cells fabricated using a high-viscosity solution of poly(3-hexylthiophene) with extremely high molecular weight. *Funct. Polym.*, 45:129–132, 2013.
- [101] Y. S. Silva and M. V. Marques. Organic Solar Cells with Nanofibers in the Active Layer Obtained by Coaxial Electrospinning. *Adv. Energy Convers. Mater.*, 4(2):96–120, 2023.
- [102] D. Joly, J.-W. Jung, I.-D. Kim, and R. Demadrille. Electrospun materials for solar energy conversion: innovations and trends. *J. Mater. Chem. C*, 4:10173–10197, 2016.
- [103] N. Amarieri, L. R. Manea, A. P. Berteau, A Berteau, and A. Popa. The Influence of Polymer Solution on the Properties of Electrospun 3D Nanostructures. *IOP Conf. Ser.: Mater. Sci. Eng.*, 209:012092, 2017.
- [104] S. Lee, G. D. Moon, and U. Jeong. Continuous production of uniform poly(3-hexylthiophene) (P3HT) nanofibers by electrospinning and their electrical properties. *J. Mater. Chem.*, 19:743–748, 2009.

- [105] K. H. K. Chan, T. Yamao, M. Kotaki, and S. Hotta. Unique spectral features and electrical properties of electrospun conjugated polymer poly(3-hexylthiophene) (P3HT) fibers. *Synth. Met.*, 160:2587–2595, 2010.
- [106] D. Hernandez-Martinez, C. Martinez-Alonso, M. M. Castillo-Ortega, M. C. Arenas-Arrocena, and M. E. Nicho. Preparation and characterization of electrospun fibers containing poly(3-hexylthiophene) and poly (3-hexylthiophene)/CdS. *Synth. Met.*, 209:496–501, 2015.
- [107] D. Hernandez-martinez, M. E. Nicho, H. Hu, U. Leon-Silva, M. C. Arenas-Arrocena, and C. H. Garcia-Escobar. Electrospinning of P3HT-PEO-CdS fibers by solution method and their properties. *Mater. Sci. Semicond. Process*, 61:50–56, 2017.
- [108] S. Nagata, G. M. Atkinson, D. Pestov, G. C. Tepper, and J. T. Mcleskey. Electrospun Polymer-Fiber Solar Cell. *Adv. Mater. Sci. Eng*, page 975947, 2013.
- [109] S. Sundarrajan, R. Murugan, A. S. Nair, and S. Ramakrishna. Fabrication of P3HT/PCBM solar cloth by electrospinning technique. *Mater. Lett.*, 64(21):2369–2372, 2010.
- [110] Z. Yang, M. Moffa na fY. Liu, H. Li, L. Persano, A. Camposeo, R. Saija, M. A. Iati, O. M. Marago, D. Pisigano, C.-Y. Nam, E. Zussman, and M. Rafailovich. Electrospun Conjugated Polymer/Fullerene Hybrid Fibers: Photoactive Blends, Conductivity through Tunneling-AFM, Light Scattering, and Perspective for Their Use in Bulk-Heterojunction Organic Solar Cells. *J. Phys. Chem. C. Nanomater. Interfaces.*, 122(5):3058–3067, 2018.
- [111] A. Fotia, A. Malara, E. Paone, L. Bonaccorsi, P. Frontera, G. Serrano, and A. Caneschi. Self Standing Mats of Blended Polyaniline Produced by Electrospinning. *Nanomaterials*, 11(5):1269, 2021.
- [112] H. Ahmad, S. Zhang, C.-T. Liu, G. Ma, J. D. Azoulay, X. Gu, M. K. Gangishetty, and S. Kundu. Effects of poly(3-hexylthiophene) molecular weight and the aging of spinning solution on the electrospun fiber properties. *ACS Appl. Polym. Mater.*, 4:8812–8824, 2022.
- [113] S. Yoon, S. Ji, Y. Yoo, J.-E. Jeong, J. Kim, H. Y. Woo, B. Park, and I. Hwang. Enhanced Polarization Ratio of Electrospun Nanofibers with Increased Intrachain Order by Postsolvent Treatments. *J. Phys. Chem. B*, 120(50):12981–12987, 2016.
- [114] A. Arrigoni, L. Brambilla, C. Castiglioni, and C. Bertarelli. Conducting Electrospun Nanofibers: Monitoring of Iodine Doping of P3HT though Infrared (IRAV) and Raman (RaAM) Polaron Spectroscopic Features. *Nanomaterials*, 12:4308, 2022.
- [115] G. Papaparaskeva, P. Papagiogis, G. Itskos, and T.Krasia-Christoforou. Highly Aligned Electrospun Polymer Fibers Produced Using a Corrugated Static Collector. *ACS. Appl. Polym. Mater.*, 4:586–597, 2022.
- [116] C. Dillard, R. Singhal, and V. Kalra. Hierarchical self-assembly in mooaxially electropsun P3HT/PCBM Nanofibers. *Macromol. Mater. Eng.*, 300(3):320–327, 2015.
- [117] Unversity of Washington. Dielectric Constant of Common Solvents. https://depts.washington.edu/eo optic/linkfiles/dielectric_chart%5B1%5D.pdf, 2023.
- [118] N. D. Treat, M. A. Brady, G. Smith, M. F. Toney, E. J. Kramer, C. J. Hawker, and M. L. Chabinyc. Interdiffusion of PCBM and P3HT Reveals Miscibility in a Photovoltaically Active Blend. *Adv. Energy Mater.*, 1:82–89, 2011.
- [119] H. Flugge, M. Pfannmoller, G. Benner, I. Wacker, H. Schmidt, T. Rabe, R. R. Schroder, and W. Kowalsky. Heterogeneous nanoscale morphology in cross-sections of bulk heterojunction polymer solar cells visualized by analytical electron microscopy. *Energy Procedia*, 31:46–59, 2012.
- [120] X. Lin, J. Seok, T. Kim, B. Kim, and K. Kim. Morphological investigation of P3HT/PCBM heterojunction and its effects on the performance of bilayer organic solar cells. *Synth. Met.*, 196:145–150, 2014.

- [121] D. H. Wang, D.-G. Choi, and O. O. Park J. H. Park. Solution-processable polymer based photovoltaic devices with concentration graded bilayers made via composition control of a poly(3-hexylthiophene)/[6,6]-phenyl-C⁶¹-butyric acid methyl ester. *Synth. Met.*, 20:4910–4915, 2010.
- [122] A. L. Ayzner, C. J. Tassone, S. H. Tolbert, and B. J. Schwartz. Reappraising the Need for Bulk Heterojunctions in Polymer-Fullerene Photovoltaics: The Role of Carrier Transport in All-Solution-Processed P3HT/PCBM Bilayer Solar Cells. *J. Phys. Chem. C*, 113:20050–20060, 2009.
- [123] R. Zhou, W. Chen, X. Jiang, S. Wang, and Q. Gong. Enhanced exciton migration in electrospun poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene]/poly(vinyl pyrrolidone) nanofibers. *Appl. Phys. Lett.*, 96:133309, 2010.
- [124] X.-H. Jin, M. B. Price, J. R. Finnegan, C. E. Boott, J. M. Richter, A. Rao, S. M. Menke, R. H. Friend, G. R. Whittell, and I. Manners. Long-range exciton transport in conjugated polymer nanofibers prepared by seeded growth. *Science*, 360(6391):897–900, 2018.
- [125] A. T. Haedler, K. Kreger, A. Issac, B. Wittman, M. Kivala, N. Hammer, J. Kohler, H.-W. Schmidt, and R. Hildner. Long-range energy transport in single supramolecular nanofibres at room temperature. *Nature*, 523:196–199, 2015.
- [126] C.-H. Kim, S.-H. Cha, M. SONG, J. Lee, W. S. Shin, S.-J. Moon, J. H. Bahng, N. A. Hotov, and D.-H. Jin. Silver Nanowire Embedded in P3HT:PCBM for High-Efficiency Hybrid Photovoltaic Device Applications. *ACS Nano*, 5:3319–3325, 2011.
- [127] D. H. Wang, J. K. Kim, G.-H. Lim, K. H. Park, O. O. Park, B. Lim, and J. H. Park. Enhanced light harvesting in bulk heterojunction photovoltaic devices with shape-controlled Ag nanomaterials: Ag nanoparticles versus Ag nanoplates. *RSC Adv.*, 2:7268–7272, 2011.
- [128] Y. H. Jang, Y. J. Jang, S. Kim, L. N. Quan, K. CHung, and D. H. Kim. Plasmonic Solar Cells: From Rational Design to Mechanism Overview. *Che. Rev.*, 116(24):14982–15034, 2016.
- [129] B. Paci, G. D. Spyropoulos, A. Generosi, D. Pailo, V. R. Albertini, E. Stratakis, and E. Kymakis. Enhanced Structural Stability and Performance Durability of Bulk Heterojunction Photovoltaic Devices Incorporating Metallic Nanoparticles. *Adv. Funct. Mater.*, 21(18):3573–3582, 2011.
- [130] M. Xue, L. Li, B. J. Termolet de Villers, H. Shen, J. Zhu, Z. Yu, A. Z. Stieg, Q. Pei, B. J. Schwartz, and K. L. Wang. Charge-carrier dynamics in hybrid plasmonic organic solar cells with ag nanoparticles. *Appl. Phys. Lett.*, page 253302, 2011.
- [131] E. Stratakis and E. Kymakis. Nanoparticle-based plasmonic organic photovoltaic devices. *Mater. Today*, 16(4):133–146, 2013.
- [132] K. Kim and D. L. Carroll. Roles of Au and Ag nanoparticles in efficiency enhancement of poly(3-octylthiophene)/C₆₀ bulk heterojunction photovoltaic devices. *Appl. Phys. Lett.*, 87(24):203113, 2005.
- [133] B. Paci, G. D. Spyropoulos, A. Generosi, D. Bailo, V. R. Albertini, E. Stratakis, and E. Kymakis. Enhanced Structural Stability and Performance Durability of Bulk Heterojunction Photovoltaic Devices Incorporating Metallic Nanoparticles. *Adv. Funct. Mater.*, 21(18):3573–3582, 2011.
- [134] K. Topp, H. Borchart, F. Johnen, A. V. Tunc, M. Knipper, E. von Hauff, J. Parisi, and K. Al-Shamery. Surface Plasmonic Effects of Metallic Nanoparticles on the Performance of Polymer Bulk Heterojunction Solar Cells. *J. Phys. Chem. A*, 114(11):3981–3989, 2010.
- [135] J.-L. Wu, F.-C. Chen, Y.-S. Hsiao, F.-C. CHien, P. Chen, C.-H. Kuo, M. H. Huang, and C.-S. Hsu. Surface Plasmonic Effects of Metallic Nanoparticles on the Performance of Polymer Bulk Heterojunction Solar Cells. *ACS Nano*, 5(2):959–967, 2011.

- [136] R. M. Hofer and R. Shubert. The influence of Einstein's effective viscosity on sedimentation at very small particle volume fraction. *Ann. Inst. Henri Poincaré (C) Anal. Non Linéaire*, 38:1897–1927, 2021.
- [137] M. Duenrinckx and A. Gloria. On einstein's effective viscosity formula. *arXiv preprint arXiv:2008.03837*, 2022.
- [138] M. Hlaing, B. Bebear-Eigzabher, A. Roa, A. Marcano, D. Radu, and C.-Y. Lai. Absorption and scattering cross-section extinction values of silver nanoparticles. *Opt. Mater.*, 58:439–444, 2016.
- [139] A. Warshawsky, R. Kalir, A. Deshe, H. Perkovitz, and A. Patchornik. Polymeric pseudocrown ethers. 1. Synthesis and complexation with transition metal anions. *J. Am. Chem. Soc.*, 101(15):4249–4258, 1979.
- [140] L. Longenberger and G. Mills. Formation of Metal Particles in Aqueous Solutions by Reactions of Metal Complexes with Polymers. *J. Phys. Chem.*, 99(2):475–478, 1995.
- [141] I. Pastoriza-Santos and L. M. Liz-Marzan. Binary cooperative complementary nanoscale interfacial materials. Reduction of silver nanoparticles in DMF. Formation of monolayers and stable colloids. *Pure Appl. Chem*, 72(1):83–90, 2000.
- [142] I. Pastoriza-Santos, C. Serra-Rodriguez, and L. M. Liz-Marzan. Self-Assembly of Silver Particle Monolayers on Glass from Ag^+ Solutions in DMF. *J. Colloid Interface Sci.*, 221:236, 2000.
- [143] S. Kedenburg, M. Vieweg, T. Gissibl, and H. Giessen. Linear refractive index and absorption measurements of nonlinear optical liquids in the visible and near-infrared spectral region. *Opt. Mat. Express*, 2:1588–1611, 2012.
- [144] Scientific Polymer Products Inc. Refractive index of polymers by index. <https://www.energyinst.org/statistical-review>, 2023.
- [145] V. Allizond, G. Banche, M. Salvoni, M. Malandrino, C. Ceccone, A. M. Cuffini, and P. Bracco. Facile One-Step Electrospinning Process to Prepare AgNPs-Loaded PLA and PLA/PEO Mats with Antibacterial Activity. *Polymers*, 15(6):1470, 2023.
- [146] R. A. Hamouda, M. H. Hussein, and R. A. Abo elmagd anf S. S. Bawair. Synthesis and biological characterization of silver nanoparticles derived from the cyanobacterium *Oscillatoria limnetica*. *Sci. Rep.*, 9:13071, 2019.
- [147] F. Bensebaa. *Biomedical*. In F. Bensebaa, editor, *Nanoparticle Technologies*, chapter 6, pages 385–427. Elsevier, Amsterdam, The Netherlands, 2013.
- [148] H. Wang. Plasmonic refractive index sensing using strongly coupled metal nanoantennas: nonlocal limitations. *Sci. Rep.*, 8:9589, 2018.
- [149] L. Catanzaro, V. Scardaci, M. Scuderi, M. Condorelli, L. D'Urso, and G. Compagnini. Surface plasmon resonance of gold nanoparticle aggregates induced by halide ions. *Mater. Chem. Phys.*, 308:128245, 2023.
- [150] V. Ershov, N. Tarsova, and B. Ershov. Evolution of Electronic State and Properties of Silver Nanoparticles during Their Formation in Aqueous Solution. *Int. J. Mol. Sci.*, 22(19):10673, 2021.
- [151] M. Abbas, A. Leitgeb, J. Kienberger, and C. Slugocov. Solvent-free synthesis of silver-nanoparticles and their use as additive in poly(decyclopentadiene). *J. Chem. Soc. Pak.*, 35:359–362, 2013.
- [152] D. Piché, I. Tavernaro, J. Fleddermann, J. G. Lozano, A. Varambhia, M. L. Maguire, M. Koch, T. Ukai, L. Jones A. J. Hernández Rodríguez, F. Dillon, I. Reyes Molina, M. Mitzutani, E. R. González Dalmau, T. Maekawa, P. D. Nellist, A. Kraegeloh, and N. Grobert. Targeted T_1 Magnetic Resonance Imaging Contrast Enhancement with Extraordinarily Small CoFe_2O_4 Nanoparticles. *ACS Appl. Mater. Inter.*, 11(7):6724–6740, 2019.

- [153] D. Maity, S.-G. Choo, J. Yi, J. Ding, and J. M. Xue. Synthesis of magnetite nanoparticles via a solvent-free thermal decomposition route. *J. Magn. Magn. Mater.*, 321:1256–1259, 2009.
- [154] M. Chen, Y.-G. Feng, X. Wang, T.-C. Li, J.-Y. Zhang, and D.-J. Qian. Silver Nanoparticles Capped by Oleylamine: Formation, Growth, and Self-Organization. *Langmuir*, 23(10):5296–5304, 2007.
- [155] B. Wu, X. Wu, C. Guan, K. F. Tai, E. K. L. Yeow, H. J. Fan, N. Matthews, and T. C. Sum. Uncovering loss mechanisms in silver nanoparticle-blended plasmonic organic solar cells. *Nat. Commun.*, 4:2004, 2013.
- [156] M. S. Islam, B. C. Ang, A. Andriyana, and A. M. Affi. A review on fabrication of nanofibers via electrospinning and their applications. *SN Appl. Sci.*, 1:1248, 2019.
- [157] L. Wannatong, A. Sirivat, and P. Supaphol. Effects of solvents on electrospun polymeric fibers: preliminary study on polystyrene. *Polym. Int.*, 53(11):1851–1859, 2004.
- [158] W. K. Son, J. H. Youk, T. S. Lee, and W. H. Park. The effects of solution properties and polyelectrolyte on electrospinning of ultrafine poly(ethylene oxide) fibers. *Polymer*, 45(9):2959–2966, 2004.
- [159] S. Nagata, G. M. Atkinson, D. Pestov, G. C. Tepper, and J. T. Mcleskey. Eco-friendly fabrication of organic solar cells: electrostatic stabilization of surfactant-free organic nanoparticle dispersions by illumination. *Nanoscale*, 14:5569–5578, 2022.
- [160] W. K. Son, J. H. Youk, T. S. Lee, and W. H. Park. The effects of solution properties and polyelectrolyte on electrospinning of ultrafine poly(ethylene oxide) fibers. *Polymer*, 45(9):2959–2966, 2004.
- [161] Y. Xu, L. Zou, and T. Kang. Effect of different solvent systems on PHBV/PEO electrospun fibers. *RSC Adv.*, 7:4000–4010, 2017.
- [162] A. K. Hagni and M. Akbari. Trends in electrospinning of natural nanofibers. *RSC Adv.*, 204(6):1830–1834, 2007.
- [163] N. Bhardwaj and S. C. Kundu. Electrospinning: a fascinating fiber fabrication technique. *Biotechnol. Adv.*, 28(3):325–347, 2010.
- [164] H. Fong, W. Liu, C.-S. Wang, and R. A. Vaia. Generation of electrospun fibers of nylon 6 and nylon 6-montmorillonite nanocomposite. *Polymer*, 43(3):775–780, 2002.
- [165] Q. P. Pham, U. Sharma, and A. G. Mikos. Electrospun poly(epsilon-caprolactone) microfiber and multilayer nanofiber/microfiber scaffolds: characterization of scaffolds and measurement of cellular infiltration. *Biotechnol. Adv.*, 7(10):2796–2805, 2006.
- [166] X. Zhang, C. B. Baughmann, and D. L. Kaplan. In vitro evaluation of electrospun silk fibroin scaffolds for vascular cell growth. *Biotechnol. Adv.*, 29(14):2217–2227, 2008.
- [167] J. Jasper. The Surface Tension of Pure Liquid Compounds. *J. Phys. Chem. Ref. Data*, 1:841–1010, 1972.
- [168] H. Kahl, T. Wadehitz, and J. Winkelmann. Surface Tension of Pure Liquids and Binary Liquid Mixtures. *J. Chem. Eng. Data*, 48(3):580–586, 2003.
- [169] J. Zhang, L. Qian, J. Zhou, and G. Zhang. Molecular Weight Dependence of Surface Tension of Poly(ethylene oxide) Solution. *J. Phys. Chem. B*, 127(30):6743–6750, 2023.
- [170] X. Zong, K. Kim, D. Fang, S. Ran, B. S. Hsaio, and B. Chu. Structure and process relationship of electrospun bioabsorbable nanofiber membranes. *Polymer*, 43(16):4403–4412, 2002.
- [171] C. Zhang, X. Yuan, L. Wu, Y. Han, and J. Sheng. Study on morphology of electrospun poly(vinyl alcohol) mats. *Euro. Polym. J.*, 41(3):423–432, 2005.

- [172] H. Fong, I. Chun, and D. H. Reneker. Beaded nanofibers formed during electrospinning. *Polymer*, 40(16):4585–4592, 1999.
- [173] P. P. Mehta and V. S. Pawar. *Electrospun nanofiber scaffolds: Technology and applications*. In A. A. M. Inamuddin and A. Mohammad, editors, *Nanocomposite Materials in Drug Delivery*, chapter 22, pages 509–573. Woodhead Publishing, Cambridge, UK, 2018.
- [174] L. H. Sperling. *Introduction to Physical Polymer Science*. Wiley-Interscience, New York, 2005.
- [175] R. Kol, T. De Somer, D. R. D’hooge, F. Knappich, K. Ragaert, D. S. Achillas, and S. De Meester. State-Of-The-Art Quantification of Polymer Solution Viscosity for Plastic Waste Recycling. *Euro. Polym. J.*, 14(19):4071–4102, 2021.
- [176] A. Koshi, K. Yim, and S. Shivkumar. Effect of molecular weight on fibrous PVA produced by electrospinning. *Mater. Lett.*, 58(3):493–497, 2004.
- [177] C. Luo, Y. Zhang, X. Zeng, Y. Zeng, and Y. Wang. The role of poly(ethylene glycol) in the formation of silver nanoparticles. *J. Colloid Interface Sci.*, 288(2):444–448, 2005.
- [178] M. Seyhan, W. Kucharczyk, U. E. Yazar, K. Richard, D. Rende, N. Baysal, S. Bucak, and R. Oxisik. Interfacial surfactant competition and its impact on poly(ethylene oxide)/Au and poly(ethylene oxide)/Ag nanocomposite properties. *Nanotechnol. Sci. Appl.*, 10(3):69–77, 2017.
- [179] J. Luo, N. N. Kariuki, L. Wang, D. Mott, C.-J. Zhong, and T. He. Synthesis and Characterization of Monolayer-Capped PtVFeNanoparticles with Controllable Sizes and Composition. *Chem. Mater.*, 17:5282–5290, 2005.
- [180] J. K. Cooper, A. M. Franco, S. Gul, C. Corrado, and J. Z. Zhang. Characterization of Primary Amine Capped CdSe, ZnSe, and ZnS Quantum Dots by FT-IR: Determination of Surface Bonding Interaction and Identification of Selective Desorption. *Langmuir*, 27:8486–8493, 2011.
- [181] I. Pucic and T. Jurkin. FTIR assessment of poly(ethylene oxide) irradiated in solid state, melt and aqueous solution. *Radiat. Phys. Chem.*, 81:1426–1429, 2012.
- [182] M. A. Morsi, E. M. Abdelrazek, and A. M. Abdelghany. Evaluation of optical parameters and structural variations of UV irradiated (PEO/PVP)/Au polymer nanocomposites. *RJPBCS*, 2(2):1877–1890, 2016.
- [183] E. Senses, S. M. Ansar, C. L. Kitchens, Y. Mao, S. Narayanan, B. Natarajan, and A. Faraone. Small particle driven chain disentanglements in polymer nanocomposites. *Phys. Rev. Lett.*, 118:147801, 2017.
- [184] E. Senses, C. L. Kitchens, and A. Faraone. Viscosity reduction in polymer nanocomposites: insights from dynamic neutron and X-ray scattering. *J. Polym. Sci.*, 60:1130–1150, 2022.
- [185] P.-G. de Gennes. Reptation of a Polymer Chain in the Presence of Fixed Obstacles. *J. Chem. Phys.*, 55:572–579, 1971.
- [186] V. N. Pokrovskii. *The Mesoscopic Theory of Polymer Dynamics*. Springer, Amsterdam, 2010.
- [187] L. M. Amoo and R. Layi Fagbenle. *Overview of non-Newtonian boundary layer flows and heat transfer*. In R. O. Fagbenle, O. M. Amoo, S. Aliu, and A. Falana, editors, *Applications of Heat, Mass and Fluid Boundary Layers*, chapter 14, pages 413–435. Woodhead Publishing, Cambridge, UK, 2020.
- [188] U. Gurel and A. Giuntoli. Shear Thinning from Bond Orientation in Model Unentangled Bottlebrush Polymer Melts. *Macromolecules*, 56(15):5708–5717, 2023.
- [189] R. Datta, L. Yelash, F. Schmid, F. Kummer, M. Oberlack, M. Lukacova-Medvid’ova, and P. Virnau. Shear-Thinning in Oligomer Melts—Molecular Origins and Applications. *Polymers (Basel)*, 13(16):2806, 2021.

- [190] C. McFadden, K. Hughes, L. Raser, and T. Newcomb. Electrical Conductivity of New and Used Automatic Transmission Fluids. *SAE Int. J. Fuels. Lubr.*, 9(3):519–526, 2016.
- [191] P. Kiselev and J. Rosell-Llompart. Highly aligned electrospun nanofibers by elimination of the whipping motion. *J. Appl. Polym. Sci.*, 125(3):2433–2441, 2012.
- [192] M. Simko and D. Lukas. Mathematical modeling of a whipping instability of an electrically charged liquid jet. *Appl. Math. Model.*, 40(21):9565–9583, 2016.
- [193] B. K. Raghavan and D. W. Coffin. Control of Inter-fiber Fusing for Nanofiber Webs via Electrospinning. *J. Enf. Fibers. Fabr.*, 6(4):1–5, 2011.
- [194] S. Li, L. Ye, W. Zhao, S. Zhang, S. Mukherjee, H. Ade, and J. Hou. Energy-Level Modulation of Small-Molecule Electron Acceptors to Achieve over 12 *Adv. Mater.*, 28(42):9423–9429, 2016.
- [195] A. Mahmood and J.-L. Wang. A Review of Grazing Incidence Small- and Wide-AngleX-Ray Scattering Techniques for Exploring the FilmMorphology of Organic Solar Cells. *Solar RRL*, 4:2000337, 2020.
- [196] L. Ye, Y. Xiong, Q. Zhang, S. Li, C. Wang, Z. Jiang, J. Hou, W. You, and H. Ade. Surpassing 10% Efficiency Benchmark for Nonfullerene Organic Solar Cells by Scalable Coating in Air from Single Nonhalogenated Solvent. *Adv. Mater.*, 30(8):1705485, 2018.
- [197] H. Lee, D. Lee, D. H. Sin, S. W. Kim, M. S. Jeong, and K. Cho. Effect of donor–acceptor molecular orientation on charge photogeneration in organic solar cells. *NPG Asia Mater.*, 10:469–481, 2018.
- [198] S. Y. Son, T. Park, and W. You. Understanding of Face-On Crystallites Transitioning to Edge-On Crystallites in Thiophene-Based Conjugated Polymers. *Chem. Mater.*, 33(12):4541–4550, 2021.
- [199] X.-R. Zhang, L. J. Richter, D. M. DeLongchamp, R. J. Kline, M. R. Hammond, I. McCulloch, M. Heeney, R. S. Ashraf, J. N. Smith, T. D. Anthopoulos, B. Schroeder, Y. H. Geerts, D. A. Fischer, and M. F. Toney. Molecular Packing of High-Mobility Diketo Pyrrolo-Pyrrole Polymer Semiconductors with Branched Alkyl Side Chains. *J. Am. Chem. Soc.*, 133(38):15073–15084, 2011.
- [200] A. C. Mayer, M. F. Toney, S. R. Scully, J. Rivnay, C. J. Brabec, M. Scharber, M. Koppe, M. Heeney, I. McCullouch, and M. D. McGehee. Bimolecular Crystals of Fullerenes in Conjugated Polymersand the Implications of Molecular Mixing for Solar Cells. *Adv. Funct. Mater.*, 19:1173–1179, 2009.
- [201] P. E. Hopkinson, P. A. Staniec, A. J. Pearson, A. D. F. Dunbar, T. Wang, A. J. Ryan, R. A. L. Jones, D. G. Lidzey, and A. M. Donald. A Phase Diagram of the P3HT:PCBM Organic Photovoltaic System: Implications for Device Processing and Performance. *Macromolecules*, 44(8):2908–2917, 2011.
- [202] M. Imanishi, D. Kajiya, T. Koganezawa, and K. i. Saitow. Uniaxial orientation of P3HT film prepared by soft friction transfer method. *Solar RRL*, 7:5141, 2017.
- [203] E. Verploegen, C. E. Miller, K. Schmidt, Z. Bao, and M. F. Toney. Manipulating the Morphology of P3HT–PCBM Bulk Heterojunction Blends with Solvent Vapor Annealing. *Chem. Mater.*, 24(20):3923–3931, 2012.
- [204] D. Kajiya, S. Ozawa, T. Koganezawa, and K. i. Saitow. Enhancement of Out-of-plane Mobility in P3HT Film by Rubbing: Aggregation and Planarity Enhanced with Low Regioregularity. *J. Phys. Chem. C*, 119(15):7987–7995, 2015.
- [205] L. Biniek, S. Pouget, D. Djurado, E. Gonthier, K. Tremel, N. Kayunkid, E. Zaborova, N. Crespo-Monteiro, O. Boyren, N. Leclerc, S. Ludwigs, and M. Brinkmann. High-Temperature Rubbing: A Versatile Method to Align π -Conjugated Polymers with Alignment Substrate. *Macromolecules*, 119(15):7987–7995, 2015.

- [206] H. Yang, S. W. LeFevre, C. Y. Ryu, and Z. Bao. Solubility-driven thin film structures of regioregular poly(3-hexyl thiophene) using volatile solvents. *Appl. Phys. Lett.*, 47:3871–3879, 2014.
- [207] S. Qu, Q. Yao, L. Wang, Z. Chen, K. Qu, H. Wang, W. Shi, T. Zhang, C. Uher, and L. Chen. Highly anisotropic P3HT films with enhanced thermoelectric performance via organic small molecule epitaxy. *NPG Asia Mater.*, 8(8):e292, 2016.
- [208] D. H. Kim, J. T. Han, Y. D. Park, Y. Yang, J. H. Cho, M. Hwang, and K. Cho. Single-Crystal Polythiophene Microwires Grown by Self-Assembly). *Adv. Mater.*, 51(18):719–723, 2006.
- [209] G. Lu, L. Li, and X. Yang. Achieving Perpendicular Alignment of Rigid Polythiophene Backbones to the Substrate by Using Solvent-Vapor Treatment. *Adv. Mater.*, 19:3594–3598, 2007.
- [210] K. Rahimi, I. Botiz, N. Stingelin, N. Kayunkid, M. Sommer, F. P. V. Koch, H. Nyugen, C. Coulembier, P. Dubois, M. Brinkmann, and G. Reiter. Controllable Processes for Generating Large Single Crystals of Poly(3-hexylthiophene). *Angew. Chem. Int. Ed.*, 51:11131–11135, 2012.
- [211] V. Chaudhary, R. K. Pandey, R. Prakash, N. Kumar, and A. K. Signh. Highly aligned and crystalline poly(3-hexylthiophene) thin films by off-center spin coating for high performance organic field-effect transistors. *Synth. Met.*, 258:116221, 2019.
- [212] Y.-J. Kim, H.-T. Jung, C. W. Ahn, and H.-J. Jeon. Simultaneously Induced Self-Assembly of Poly(3-hexylthiophene) (P3HT) Nanowires and Thin-Film Fabrication via Solution-Floating Method on a Water Substrate. *Adv. Mater. Interfaces*, 4(19):1700342, 2017.
- [213] M. Brinkmann and J.-C. Wittmann. Orientation of Regioregular Poly(3-hexylthiophene) by Directional Solidification: A Simple Method to Reveal the Semicrystalline Structure of a Conjugated Polymer). *Adv. Mater.*, 18(7):860–863, 2006.
- [214] F. L. Faita, P. Tuzimoto, G. Farias, K. L. Andrade, D. L. S. Agostoni, A. E. Job, A. A. Vieira, H. Gallardo, J. Canejo, M. H. Godinho, and I. H. Bechtold. Strongly polarized light from highly aligned electrospun luminescent natural rubber fibers. *J. Lumin.*, 241:118498, 2022.
- [215] N. Tanigaki, C. Takechi, S. Nagamatsu, T. Mizokuro, and Y. Yoshida. Oriented Thin Films of Insoluble Polythiophene Prepared by the Friction Transfer Technique. *Polymers (Basel)*, 13(15):2393, 2021.
- [216] S. Pagliara, M. S. Vitiello, A. Camposeo, A. Polini, R. Congolani, G. Scamarcio, and D. Pisignano. Optical Anisotropy in Single Light-Emitting Polymer Nanofibers. *J. Phys. Chem. C*, 115:20399–20405, 2011.
- [217] V. Fasano, R. Laurita, M. Moffa, C. Gulandi, V. Colombo, M. Gherardi, E. Zussman, G. Vasilyev, L. Persano, A. Camposeo, M. L. Focarete, and D. Pisignano. Enhanced Electrospinning of Active Organic Fibers by Plasma Treatment on Conjugated Polymer Solutions. *ACS Appl. Mater. Inter.*, 12:26320–26329, 2020.
- [218] K. Yin, L. Zhang, L. Zhong, S. Smith, H. Fong, and Z. Zhu. Photoluminescence anisotropy of uni-axially aligned electrospun conjugated polymer nanofibers of MEH-PPV and P3HT. *J. Mater. Chem.*, 21:444–448, 2011.
- [219] K.-H. Lee, K.-W. Kim, A. Pesapane, H.-Y. Kim, and J. F. Rabolt. Polarized FT-IR Study of Macroscopically Oriented Electrospun Nylon-6 Nanofibers. *Macromolecules*, 41(4):1494–1498, 2008.
- [220] H. Yang, S. Jiang, H. Fang, X. Hu, G. Duan, and H. Hou. Molecular orientation in aligned electrospun polyimide nanofibers by polarized FT-IR spectroscopy. *Macromolecules*, 200:339–344, 2018.

- [221] M. Richard-Lacroix and C. Pellerin. Orientation and Structure of Single Electrospun Nanofibers of Poly(ethylene terephthalate) by Confocal Raman Spectroscopy. *Macromolecules*, 45(4):1946–1953, 2012.
- [222] D. Papkov, C. Pellerin, and Y. A. Dzenis. Polarized Raman Analysis of Polymer Chain Orientation in Ultrafine Individual Nanofibers with Variable Low Crystallinity. *Macromolecules*, 51(21):8746–8751, 2018.
- [223] A. W. Laramee, C. Lanthier, and C. Pellerin. Raman Investigation of the Processing Structure Relations in Individual Poly(ethylene terephthalate) Electrospun Fibers. *Appl. Spectrosc.*, 76(1):51–60, 2022.
- [224] M. Richard-Lacroix and C. Pellerin. Orientation and Partial Disentanglement in Individual Electrospun Fibers: Diameter Dependence and Correlation with Mechanical Properties. *Macromolecules*, 48(13):4511–4519, 2015.
- [225] A. W. Laramee, C. Lanthier, and C. Pellerin. Electrospinning of Highly Crystalline Polymers for Strongly Oriented Fibers. *ACS Appl. Polym. Mater.*, 2(11):5025–5032, 2020.
- [226] S. Qu, Q. Yao, L. Wang, Z. Chen, K. Xu, H. Zeng, W. Shi, T. Zhang, C. Uher, and L. Chen. Highly anisotropic P3HT films with enhanced thermoelectric performance via organic small molecule epitaxy. *NPG Asia Mater.*, 8:e292, 2016.
- [227] J.-Y. Chen, H.-C. Wu, Y.-C. Chiu, C.-J. Lin, S.-H. Tung, and W.-C. Chen. Electrospun Poly(3-hexylthiophene) Nanofibers with Highly Extended and Oriented Chains Through Secondary Electric Field for High-Performance Field-Effect Transistors. *Adv. Electron. Mater.*, 1(1):1400028, 2015.
- [228] J.-Y. Chen, C.-Y. Su, C.-H. Hsu, Y.-H. Zhang, Q.-C. Zhang, C.-L. Chang, C.-C. Hua, and W.-C. Chen. Solvent Effects on Morphology and Electrical Properties of Poly(3-hexylthiophene) Electrospun Nanofibers. *Polymers*, 11:1501, 2019.
- [229] M. Kim, S. B. Jo, J. H. Park, and K. Cho. Flexible lateral organic solar cells with core-shell structured organic nanofibers. *Nano Energy*, 18:97–108, 2015.
- [230] T. Rodlmeier, T. Marszalek, M. Held, S. Beck, C. Muller, R. Eckstein, A. J. Morfa, R. Lovrincic, A. Pucci, U. Lemmer, J. Zaumsei, W. Pisula, and G. Hernandez-Sosa. Controlled Molecular Orientation of Inkjet Printed Semiconducting Polymer Fibers by Crystallization Templating. *Nano Energy*, 29(23):10150–10158, 2017.
- [231] F. Bastianini, G. E. Perez, A. R. Hobson, S. E. Rogers, A. J. Parnell, M. Grell, A. F. Gutierrez, and A. D. F. Dunbar. Insitu monitoring Poly(3-hexylthiophene) nanowire formation and shape evolution in solution via small angle neutron scattering. *Sol. Energy Mater. Sol. Cells*, 202:110128, 2019.
- [232] J. D. Roehling, I. Arslan, and A. J. Moule. Controlling microstructure in poly(3-hexylthiophene) nanofibers. *J. Mater. Chem.*, 22:2498–2506, 2012.
- [233] J. A. Lim, F. Liu, S. Lerdous, M. Muthukumar, and A. L. Briseno. Polymer semiconductor crystals. *Mater. Today*, 13(5):14–24, 2010.
- [234] Y.-W. Cheng, H.-A. Lu, Y.-C. Wang, A. Thierry, B. Lotz, and C. Wang. Syndiotactic Polystyrene Nanofibers Obtained from High-Temperature Solution Electrospinning Process. *Macromolecules*, 43(5):2371–2376, 2010.
- [235] Y. Lee, A. Mongare, A. Plant, and D. Ryu. Strain-Microstructure-Optoelectronic Inter-Relationship toward Engineering Mechano-Optoelectronic Conjugated Polymer Thin Films. *Polymers*, 13:935, 2021.
- [236] L. H. Jimison, M. F. Toney, I. McCulloch, M. Heeney, and A. Salleo. Charge-Transport Anisotropy Due to Grain Boundaries in Directionally Crystallized Thin Films of Regioregular Poly(3-hexylthiophene). *Adv. Mater.*, 21:1568–1572, 2009.

- [237] L. M. Bellan and H. G. Craighead. Molecular orientation in individual electrospun nanofibers measured via polarized Raman spectroscopy. *Polymer*, 49:3125–3159, 2008.
- [238] Z. Wang, B. Sun, X. Lu, C. Wang, and Z. Su. Molecular Orientation in Individual Electrospun Nanofibers Studied by Polarized AFM–IR. *Macromolecules*, 52(24):9639–9645, 2019.
- [239] K. Hinrichs, B. Blevins, A. Furchner, N. Sekhar Yadavalli, and S. Minko. Infrared polarimetry: Anisotropy of polymer nanofibers. *Micro. Nano. Eng.*, 14:100116, 2022.
- [240] F. Selli, U. H. Erdogan, R. Hufenus, and e. Perret. Mesophase in melt-spun poly(ϵ -caprolactone) filaments: Structure–mechanical property relationship. *Polymer*, 206:122870, 2020.
- [241] D. Papkov, N. Delpouve, L. Delbrilh, S. Araujo, T. Stockdale, S. Mamedov, L. Maleckis, Y. Zou, M. N. Andalib, E. Dargent, V. P. Draid, M. V. Holt, C. Pellerin, and Y. A. Dzenis. Quantifying Polymer Chain Orientation in Strong and Tough Nanofibers with Low Crystallinity: Toward Next Generation Nanostructured Superfibers. *ACS Nano*, 13(5):4893–4927, 2019.
- [242] C. Riekkel, M. Burghammer, and M. Rosenthal. Nanoscale X-Ray Diffraction of Fibers. *Front. Mater. Sci.*, 6:315, 2019.
- [243] R. Dersch, T. Liu, A. K. Schaper, A. Greiner, and J. H. Wendorff. Electrospun nanofibers: Internal structure and intrinsic orientation. *J. Polym. Sci. Part A: Polym. Chem.*, 41:545–553, 2002.
- [244] D. Papkov, C. Pellerin, and Y. A. Dzenis. Highly Oriented Crystalline PE Nanofibrils Produced by Electric-Field-Induced Stretching of Electrospun Wet Fibers. *Macromol. Mater. Eng.*, 295:1082–1089, 2010.
- [245] A. J. Sneyd, T. Fukui, D. Palecek, S. Prodhan, I. Wagner, Y. Zhang, J. Sang, S. M. Collins, T. J. A. Salter, Z. Andaji-Garmaroudi, Y. Zhang, L. R. MacFarlane, J. Diego Garcia-Hernandez, L. Wang, G. R. Whitell, J. M. Hodgkiss, K. Chen, D. Beljonne, I. Manner, R. H. Friend, and A. Rao. Efficient energy transport in an organic semiconductor mediated by transient exciton delocalization. *Sci. Adv.*, 7(32):eabh4232, 2021.
- [246] X. Xiao, Z. Wang, Z. Hu, and T. He. Single Crystals of Polythiophene with Different Molecular Conformations Obtained by Tetrahydrofuran Vapor Annealing and Controlling Solvent Evaporation. *J. Phys. Chem. B*, 114(7):7452–7460, 2010.
- [247] 4D-STEM of Beam-Sensitive Materials. K. C. Bustillo and S. E. Zeltmann and M. Chen and J. Donohue and J. Ciston and C. Orphus and A. M. Minor. *Acc. Chem. Res.*, 54(11):2543–2551, 2021.
- [248] D. B. Williams and C. Barry Carter. *Transmission Electron Microscopy: A Textbook for Materials Science*. Springer, New York, USA, 2009.
- [249] M. Wu, C. Harreiss, C. Orphus, M. Johnson, R. H. Fink, and E. Spiecker. Seeing structural evolution of organic molecular nano-crystallites using 4D scanning confocal electron diffraction (4D-SCED). *Nat. Comm.*, 13:2911, 2022.
- [250] X. Mu, A. Mazilkin, C. Sprau, A. Colsmann, and C. Kubel. Mapping structure and morphology of amorphous organic thin films by 4D-STEM pair distribution function analysis. *Microscopy*, 68(8):301–309, 2019.
- [251] N. J. Hestand and F. C. Spano. Expanded Theory of H- and J-Molecular Aggregates: The Effects of Vibronic Coupling and Intermolecular Charge Transfer. *Chem. Rev.*, 118(15):7069–7163, 2018.
- [252] F. C. Spano and C. Silva. H- and J-aggregate behavior in polymeric semiconductors. *Ann. Rev. Phys. Chem.*, 65:477–500, 2014.

- [253] M. Mas-Montoya and R. A. J. Janssen. The Effect of H- and J-Aggregation on the Photophysical and Photovoltaic Properties of Small Thiophene–Pyridine–DPP Molecules for Bulk-Heterojunction Solar Cells. *Adv. Funct. Mater.*, 27(16):1605779, 2017.
- [254] E. T. Niles, J. S. Roehling, H. Yamagata, A. J. Wise, F. S. Spano, A. J. Moule, and J. K. Grey. J-Aggregate Behavior in Poly-3-hexylthiophene Nanofibers. *J. Phys. Chem. Lett.*, 3(2):259–263, 2012.
- [255] H. Yamagata and F. C. Spano. Interplay between intrachain and interchain interactions in semiconducting polymer assemblies: The HJ-aggregate model. *J. Chem. Phys.*, 136:184901, 2012.
- [256] S. Cook, A. Furube, and R. Katoh. Matter of minutes degradation of poly(3-hexylthiophene) under illumination in air. *J. Mater. Chem.*, 22:4282, 2012.
- [257] K. Rahimi, I. Botiz, J. O. Agumba, S. Motamen, N. Stingelin, and G. Reiter. Light absorption of poly(3-hexylthiophene) single crystals. *RSC Adv.*, 4:11121, 2014.
- [258] F. C. Spano. The Spectral Signatures of Frenkel Polarons in H- and J-Aggregates. *J. Mater. Chem.*, 43(3):429–439, 2010.
- [259] G. Jo, J. Jung, and M. Chang. Controlled Self-Assembly of Conjugated Polymers via a Solvent Vapor Pre-Treatment for Use in Organic Field-Effect Transistors. *Polymers*, 11:332, 2019.
- [260] J. Rivnay, S. C. B. Mannsfeld, C. E. Miller, A. Saleo, and M. F. Toney. Quantitative determination of organic semiconductor microstructure from the molecular to device scale. *Chem. Rev.*, 112(10):5488–5519, 2012.
- [261] A. Salleo. Charge transport in polymeric transistors. *Mater. Today*, 10(3):38–45, 2007.
- [262] L. Deng and G. Chen. Recent progress in tuning polymer oriented microstructures for enhanced thermoelectric performance. *Nano Energy*, 80:105448, 2021.
- [263] G. Jo, J. Jung, and M. Chang. Polymeric solar cells based on P3HT:PCBM: Role of the casting solvent. *Sol. Energy. Mat. Sol. C.*, 95:3408–3418, 2011.
- [264] H.-C. Chang, C.-L. Liu, and W.-C. Chen. Flexible Nonvolatile Transistor Memory Devices Based on One-Dimensional Electrospun P3HT:Au Hybrid Nanofibers. *Adv. Funct. Mater.*, 23:4960–4968, 2013.
- [265] K. Monobe and Y. Yamashita. Giant Crystals of Poly(ethylene oxide). *Memoirs of the School of Engineering, Okayama University*, 2(1):84–87, 1967.
- [266] L. Zhu, S. Z. D. Chang, B. H. Calhoun, Q. Ge, R. P. Quirk, E. L. Thomas, B. S. Ksiao, F. Yeh, and B. Lotz. Crystallization Temperature-Dependent Crystal Orientations within Nanoscale Confined Lamellae of a Self-Assembled Crystalline-Amorphous Diblock Copolymer. *J. Am. Chem. Soc.*, 122:5957–5967, 2000.
- [267] J.-Y. Chen, C.-Y. Su, C. H. Hsu, Y.-H. Zhang, Q.-C. Zhang, C.-L. Chang, C.-C. Hua, and W.-C. Chen. Solvent Effects on Morphology and Electrical Properties of Poly(3-hexylthiophene) Electrospun Nanofibers. *Polymers*, 11(9):1501, 2019.
- [268] K. E. Roskov, K. A. Kozek, W.-C. Wu, R. K. Chhetri, A. L. Oldenvurg, R. J. Spontak, and J. B. Tracey. Long-Range Alignment of Gold Nanorods in Electrospun Polymer Nano/Microfibers. *Langmuir*, 27(23):13965–13969, 2011.
- [269] R. Nain, M. Jassal, and A. K. Agrawal. Polymeric nanofiber composites with aligned ZnO nanorods. *Compos. Sci. Technol.*, 86:9–17, 2013.
- [270] X. Pu, J.-W. Zha, C.-L. Zhao, S.-B. Gong, J.-F. Guo, and R. K. Y. Li. Flexible PVDF/nylon-11 electrospun fibrous membranes with aligned ZnO nanowires as potential triboelectric nanogenerators. *Chem. Eng. J.*, 398:125526, 2020.

- [271] H. Koerner, Y. Luo, X. Li, C. Cohen, R. C. Hedden, and C. K. Ober. Structural Studies of Extension-Induced Mesophase Formation in Poly(diethylsiloxane) Elastomers: In Situ Synchrotron WAXS and SAXS. *Macromolecules*, 36:1975–1981, 2003.
- [272] B. Li, P. I. Xidas, K. S. Triantafyllidis, and E. Manias. Effect of crystal orientation and nanofiller alignment on dielectric breakdown of polyethylene/montmorillonite nanocomposites. *Appl. Phys. Lett.*, 111:082906, 2017.
- [273] X. Wang, H. Zao, L.-S. Turng, and Q. Li. Crystalline Morphology of Electrospun Poly(ϵ -caprolactone) (PCL) Nanofibers. *Ind. Eng. Chem. Res.*, 52:4939–4949, 2013.
- [274] B. W. Caplins, J. D. Holm, R. M. White, and R. R. Keller. Orientation mapping of graphene using 4D STEM-in-SEM. *Ultramicroscopy*, 219:113137, 2020.
- [275] P. D. Nellist. Electron-optical sectioning for three-dimensional imaging of crystal defect structures. *Mater. Sci. Semicond. Process.*, 65:18–23, 2017.
- [276] G. Behan, E. C. Cosgriff, A. I. Kirkland, and P. D. Nellist. Three-dimensional imaging by optical sectioning in the aberration-corrected scanning transmission electron microscope. *Phil. Trans. R. Soc. A*, 367:3825–3944, 2009.
- [277] J.-Y. Chen, C.-C. Kuo, C.-S. Lai, W.-C. Chen, and H.-L. Chen. Manipulation on the Morphology and Electrical Properties of Aligned Electrospun Nanofibers of Poly(3-hexylthiophene) for Field-Effect Transistor Applications. *Macromolecules*, 44(8):2883–2892, 2011.
- [278] X. Geng, Y. Liu, X. Zou, E. M. J. Johansson, and J. Sa. Can photoluminescence quenching be a predictor for perovskite solar cell efficiencies? *Phys. Chem. Chem. Phys.*, 25:22607, 2023.
- [279] V. Campanari, F. Martelli, A. Agresti, S. Pescetelli, N. Y. Nia, F. Di Giacomo, D. Catone, P. O’Keeffe, S. Turchini, B. Yang, J. Suo, A. Hagfeldt, and A. Di Carlo. Reevaluation of Photoluminescence Intensity as an Indicator of Efficiency in Perovskite Solar Cells. *Solar RRL*, 6(8):2200049, 2022.
- [280] T. Du, W. Wu, M. Daboczi, J. Kim, S. Xu, C.-T. Lin, H. Kang, K. Lee, M. J. Heeney, J.-S. Kim, J. R. Durrant, and M. A. McLachlan. p-Doping of organic hole transport layers in p-i-n perovskite solar cells: correlating open-circuit voltage and photoluminescence quenching. *J. Mater. Chem. A*, 7:18971–18979, 2019.
- [281] L. Feng, M. Niu, Z. Wen, and X. Hao. Recent Advances of Plasmonic Organic Solar Cells: Photophysical Investigations. *ACS Appl. Polym. Mater.*, 10(2):123, 2018.
- [282] M. Sygletou, P. Tzourmpakis, C. Petridis, D. Konios, C. Fotakis, E. Kymakis, and E. Stratakis. Laser induced nucleation of plasmonic nanoparticles on two-dimensional nanosheets for organic photovoltaics. *Small*, 4:1020–1027, 2016.
- [283] H. Shen, P. Beinstman, and B. Maes. Plasmonic absorption enhancement in organic solar cells with thin active layers. *J. Appl. Phys.*, 106:073109, 2009.
- [284] H. Liu, W.-P. Goh, M.-Y. Leung, Y. Li, and T. B. Norsten. Effect of nanoparticle stabilizing ligands and ligand-capped gold nanoparticles in polymer solar cells. *ACS Appl. Mater. Interfaces*, 96:302–306, 2012.
- [285] K. Smolarek, B. Ebenhoch, N. Czechowski, A. Pryaczek, M. Twardowska, I. D. W. Samuel, and S. Mackowski. Silver nanowires enhance absorption of poly(3-hexylthiophene). *Appl. Phys. Lett.*, 103:203302, 2013.
- [286] D. Chi, S. Lu, R. Xu, K. Liu, D. Cao, L. Wen, Y. Mi, Z. Wang, Y. Lei, S. Qu, and Z. Wang. Fully understanding the positive roles of plasmonic nanoparticles in ameliorating the efficiency of organic solar cells. *Nanoscale*, 7:15251–15257, 2015.

- [287] Y. Yang, J. Qing, J. Ou, X. Lin, Z. Yuan, D. Yu, X. Zhou, and X. Chen. Rational design of metallic nanowire-based plasmonic architectures for efficient inverted polymer solar cells. *Nanoscale*, 122:231–238, 2015.
- [288] P. Du, P. Jing, Y. Cao, Z. Liu, and Z. Sun. Plasmonic Ag@Oxide Nanoprisms for Enhanced Performance of Organic Solar Cells. *Small*, 11(20):2454–2462, 2015.
- [289] M. Salvador, B. A. MacLeod, A. Hess, A. P. Kulkarni, K. Menechika, J. I. L. Chen, and D. S. Ginger. Electron Accumulation on Metal Nanoparticles in Plasmon-Enhanced Organic Solar Cells. *ACS Nano*, 6(11):10024–10032, 2012.
- [290] U. Zhokhavets, G. Gobsch, H. Nope, and N. Serbar Sariciftci. Anisotropic optical properties of thin poly(3-octylthiophene)-films as a function of preparation conditions. *Synth. Met.*, 143:113–117, 2003.
- [291] J. Schneider and S. Hudson. The Finite-Difference Time-Domain Method Applied to Anisotropic Material. *Synth. Met.*, 41(7):994–999, 1993.
- [292] G. R. Werner and J. R. Cary. A stable FDTD algorithm for non-diagonal, anisotropic dielectrics. *J. Comput. Phys.*, 226(1):1085–1101, 2007.
- [293] R. Geetu, C. Sudha Kartha, and K. P. Vijayakumar. Improving the performance of ITO/ZnO/P3HT:PCBM/Ag solar cells by tuning the surface roughness of sprayed ZnO. *J. Sol. Energy*, 120:65–71, 2015.
- [294] Y.-M. Shen, C.-S. Chen, P.-C. Yang, S.-Y. Ma, and C.-F. Lin. Improvement of surface morphology of thin films and performance by applying electric field on P3HT:PCBM based solar cells. *J. Sol. Energy*, 99:263–267, 2012.
- [295] A. L. Ayzner, C. J. Tassone, S. H. Tolbert, and B. J. Schwartz. Reappraising the Need for Bulk Heterojunctions in PolymerFullerene Photovoltaics: The Role of Carrier Transport in All-Solution-Processed P3HT/PCBM Bilayer Solar Cells. *J. Phys. Chem. C*, 113(46):20050–20060, 2009.
- [296] N. Seidler, G. M. Lazzerini, G. li Destra, G. Marletta, and D. Cacialli. Enhanced exciton migration in electrospun poly[2-methoxy-5- (2'-ethylhexyloxy)-1,4- phenylenevinylene]/poly(vinyl pyrrolidone) nanofibers. *J. Mater. Chem. C*, 1:7748, 2013.
- [297] R. Zhou, W. Chern, X. Jiang, S. Wang, and Q. Gong. Enhanced exciton migration in electrospun poly[2-methoxy-5- (2'-ethylhexyloxy)-1,4- phenylenevinylene]/poly(vinyl pyrrolidone) nanofibers. *Appl. Phys. Lett.*, 96:133309, 2010.
- [298] H. Okhito and S. Ito. Transient absorption spectroscopy of polymer-based thin-film solar cells. *Polymer*, 52:4397–4417, 2011.
- [299] O. P. Dimitriev. Effect of Confinement on Photophysical Properties of P3HT Chains in PMMA Matrix. *Nanoscale Res. Lett.*, 12:4397–4417, 2017.
- [300] E. Lioudakis and I. Alexandrou. Ultrafast Dynamics of Localized and Delocalized Polaron Transitions in P3HT/PCBM Blend Materials: The Effects of PCBM Concentration. *Nanoscale Res. Lett.*, 4:1475–1480, 2009.
- [301] Y. Ogata, D. Kawaguchi, and K. Tanaka. An Effect of Molecular Motion on Carrier Formation in a Poly(3-hexylthiophene) Film. *Sci. Rep.*, 5:8436, 2015.
- [302] H. Okhita, S. Cook, Y. Astuti, W. Duffy, S. Tierney, W. Zhang, M. Heeney, I. McCullohc, J. Nelson, D. D. C. Bradley, and J. R. Durrant. Charge Carrier Formation in Polythiophene/Fullerene Blend Films Studied by Transient Absorption Spectroscopy. *J. Am. Chem. Soc.*, 130:3030–3042, 2008.
- [303] A. Solanki, B. Wu, T. Salim, Y. M. Lam, and T. C. Sum. Correlation between blend morphology and recombination dynamics in additive-added P3HT:PCBM solar cells. *Phys. Chem. Chem. Phys.*, 17:26111–26120, 2015.

- [304] J. Guo, H. Okhito, H. Benten, and S. Ito. Charge Generation and Recombination Dynamics in Poly(3-hexylthiophene)/Fullerene Blend Films with Different Regioregularities and Morphologies. *J. Am. Chem. Soc.*, 132(17):6154–6164, 2010.
- [305] O. G. Reid, J. A. Nekuda Malik, G. Latini, S. Dayal, N. Kopidakis, C. Silva, N. Stingelin, and G. Rumbles. The influence of solid-state microstructure on the origin and yield of long-lived photogenerated charge in neat semiconducting polymers. *J. Polym. Sci. Part B: Polym. Phys.*, 1:27–37, 2011.
- [306] F. Paquin, G. Latini, M. Sakowicz, P.-L. Karsenti, L. Wang, D. Beljonne, N. Stingelin, and C. Silva. Charge Separation in Semicrystalline Polymeric Semiconductors by Photoexcitation: Is the Mechanism Intrinsic or Extrinsic? *Phys. Rev. Lett.*, 106:197401, 2011.
- [307] C. Deibel, D. Mack, J. Gorenflot, A. Schöll, S. Krause, F. Reinert, D. Rauh, and V. Dyakonov. Energetics of excited states in the conjugated polymer poly(3-hexylthiophene). *Phys. Rev. B*, 81:085202, 2010.
- [308] X. Hu, L. Chen, and Y. Chen. Universal and Versatile MoO₃-Based Hole Transport Layers for Efficient and Stable Polymer Solar Cells. *J. Phys. Chem. C*, 118(19):9930–9938, 2014.
- [309] D. W. Zhao, P. Liu, X. W. Sun, S. T. Tan, L. Ke, and A. K. K. Kyaw. An inverted organic solar cell with an ultrathin Ca electron-transporting layer and MoO₃ hole-transporting layer. *Phys. Rev. Lett.*, 95:153304, 2009.
- [310] D. H. Wang, D. Y. Kim, K. W. Choi, J. H. Seo, S. H. Im, J. H. Park, O. O. Park, and A. J. Heeger. Enhancement of donor - Acceptor polymer bulk heterojunction solar cell power conversion efficiencies by addition of Au nanoparticles. *Angew. Chem., Int. Ed. Engl.*, 50:5519–5523, 2011.
- [311] L. Lu, Z. Luo, T. Xu, and L. Yu. Cooperative Plasmonic Effect of Ag and Au Nanoparticles on Enhancing Performance of Polymer Solar Cells. *Nano Lett.*, 13(1):59–64, 2013.
- [312] V. Vohra, U. Giovanella, R. Tubino, H. Murata, and C. Botta. Electroluminescence from Conjugated Polymer Electrospun Nanofibers in Solution Processable Organic Light-Emitting Diodes. *ACS Nano*, 5(7):5572–5578, 2011.
- [313] C. J. Lin, J. C. Hsu, J. H. Tsai, C. C. Kuo, W. Y. Lee, and W. C. Chen. High-Performance FETs Prepared From Electrospun Aligned P4TDPP Nanofibers. *Macromol. Chem. Phys.*, 212(22):2452–2458, 2011.
- [314] A. Manuelli, L. Persano, and D. Pisignano. Flexible organic field-effect transistors based on electrospun conjugated polymer nanofibers with high bending stability. *Org. Electr.*, 15(5):1056–1061, 2014.
- [315] C.-C. Chou, H.-C. Wu, C.-J. Lin, E. Ghelichkhani, and W.-C. Chen. Morphology and Field-Effect Transistor Characteristics of Electrospun Nanofibers Prepared From Crystalline Poly(3-hexylthiophene) and Polyacrylate Blends. *Macromol. Chem. Phys.*, 214:751–760, 2013.
- [316] J.-Y. Chen, H.-C. Hsieh and Y.-C. Chiu, W.-Y. Lee, C.-C. Hung, C.-C. Chueh, and W.-C. Chen. Electrospinning-induced elastomeric properties of conjugated polymers for extremely stretchable nanofibers and rubbery optoelectronics. *J. Mater. Chem. C*, 8(1):873–882, 2020.
- [317] Q. Guo, H. Meguro, S. Okamoto, and M. Kimura. Flexible Tactile Sensor Using the Reversible Deformation of Poly(3-hexylthiophene) Nanofiber Assemblies. *Langmuir*, 28(51):17593–17596, 2012.
- [318] M. Y. Lee, J. Hong, E. K. Lee, H. Yu, H. Kim, J. U. Lee, W. Lee, and J. H. Oh. Highly Flexible Organic Nanofiber Phototransistors Fabricated on a Textile Composite for Wearable Photosensors. *Adv. Funct. Mater.*, 26(9):1445–1453, 2016.

- [319] Y. Lee, J. Y. Oh, W. Xu, O. Kim, T. R. Kim, J. Kang, Y. Kim, D. Son, J. B.-H. Tok, and M. J. Park. Stretchable organic optoelectronic sensorimotor synapse. *Sci. Adv.*, 4(11):eeat7387, 2018.
- [320] M.-F. Lin, K.-W. Chang, C.-H. Lee, X.-X. Wu, and Y.-C. Huang. Electrospun P3HT/PVDF-HFP semiconductive nanofibers for triboelectric nanogenerators. *Sci. Rep.*, 12:14842, 2022.
- [321] J.-Y. Chen, H.-C. Wu, Y.-C. Chiu, C.-J. Lin, S.-H. Tung, and W.-C. Chen. Electrospun Poly(3-hexylthiophene) Nanofibers with Highly Extended and Oriented Chains Through Secondary Electric Field for High-Performance Field-Effect Transistors. *Adv. Electr. Mater.*, 1(1):1400028, 2015.
- [322] C. Lu, J. Wang, H.-C. Chang, Y.-C. Chiu, H.-Y. Chen, H.-C. Wu, T. Higashihara, and W.-C. Chen. Ambipolar field-effect transistors using conjugated polymers with structures of bilayer, binary blends, and paralleled nanofibers. *Adv. Electr. Mater.*, 2:7489–7493, 2014.
- [323] A. Laforgue and L. Robitaille. Fabrication of poly-3-hexylthiophene/polyethylene oxide nanofibers using electrospinning. *Synth. Met.*, 158:577–584, 2007.
- [324] A. Bianco, C. Bertarelli, S. Frisk, J. F. Rabolt, M. C. Gallazzi, and G. Zerbi. Electrospun polyalkylthiophene/polyethyleneoxide fibers: Optical characterization. *Synth. Met.*, 157:276–281, 2007.
- [325] E. V. Canesi, A. Luzio, B. Saglio, A. Bianco, M. Caironi, and C. Bertarelli. n-Type Semiconducting Polymer Fibres. *ACS Macro Lett.*, 158:577–584, 2007.
- [326] H. A. Liu, D. Zepeda, J. P. Farraris, and K. J. Balkus Jr. Electrospinning of poly (alkoxyphenylenevinylene) and methanofullerene nanofiber blends. *ACS Appl. Mater. Inter.*, 1(9):1958–1965, 2009.
- [327] D. H. Wang, K. H. Park, J. H. Seo, J. Seifter, J. H. Jeon, J. K. Kim, J. H. Park, O. O. Park, and A. J. Heeger. Enhanced Power Conversion Efficiency in PCDTBT/PC₇₀BM Bulk Heterojunction Photovoltaic Devices with Embedded Silver Nanoparticle Clusters. *Adv. Energy Mater.*, 1:766–770, 2011.
- [328] X. Li, W. C. H. Choy, L. Huo, F. Xie, W. E. I. Sha, B. Ding, X. Guo, Y. Li, J. Hou, J. You, and Y. Wang. Dual Plasmonic Nanostructures for High Performance Inverted Organic Solar Cells. *Adv. Mater.*, 24(22):3046–3052, 2012.
- [329] V. Jankovic, Y. Yang, J. You, L. Dou, Y. Liu, P. Cheung, J. P. Chang, and Y. Yang. Active Layer-Incorporated, Spectrally Tuned Au/SiO₂ Core/Shell Nanorod-Based Light Trapping for Organic Photovoltaics. *ACS Nano*, 7(5):3815–3822, 2013.
- [330] G. Kakavelakis, E. Stratakis, and E. Kymakis. Synergetic plasmonic effect of Al and Au nanoparticles for efficiency enhancement of air processed organic photovoltaic devices. *Chem. Commun.*, 50:5285–5287, 2014.
- [331] W.-H. Tseng, C.-Y. Chiu, S.-W. Chou, H.-C. Chen, M.-L. Tsai, Y.-C. Kuo, D.-H. Lien, Y.-C. Tsao, K.-Y. Huang, C.-T. Yeh, J.-H. He, C.-I. Wu, and P.-T. Chou. Shape-Dependent Light Harvesting of 3D Gold Nanocrystals on Bulk Heterojunction Solar Cells: Plasmonic or Optical Scattering Effect? *J. Phys. Chem. C.*, 119(14):7554–7564, 2015.
- [332] E. Kymakis, G. D. Spyropoulos, R. Fernandes, G. Kakavelakis, A. G. Kanaras, and E. Stratakis. Plasmonic Bulk Heterojunction Solar Cells: The Role of Nanoparticle Ligand Coating. *ACS Photonics*, 2(6):714–723, 2015.
- [333] M. A. M. Teridi, M. Sookhakian, W. J. Basirun, R. Zakaria, F. K. Schneider, W. Jose de Silva, J. Kim, S. J. Lee, H. P. Kim, A. R. bin Mohd Yusoff, and J. Jang. Plasmon enhanced organic devices utilizing highly ordered nanoimprinted gold nanodisks and nitrogen doped graphene. *Nanoscale*, 7:7091–7100, 2015.

- [334] Y. He, C. Liu, J. Li, X. Zhang, Z. Li, L. Shen, W. Guo, and S. Ruan. Improved Power Conversion Efficiency of Inverted Organic Solar Cells by Incorporating Au Nanorods into Active Layer. *ACS Appl. Mater. Interfaces*, 7(29):15848–15854, 2015.
- [335] P. Du, P. Jing, Y. Cao, Z. Liu, and Z. Sun. Plasmonic Ag@Oxide Nanoprisms for Enhanced Performance of Organic Solar Cells. *Small*, 11(20):2454–2462, 2015.
- [336] C. C. D. Wang, W. C. H. Choy, C. Duan, D. D. S. Fung, W. E. I. Sha, F.-X. Xie, F. Huang, and Y. Cao. Optical and electrical effects of gold nanoparticles in the active layer of polymer solar cells. *J. Mater. Chem.*, 22:1206–1211, 2012.
- [337] F.-C. Chen, J.-L. Wu, C.-L. Lee, Y. Hong, C.-H. Kuo, and M. H. Huang. Plasmonic-enhanced polymer photovoltaic devices incorporating solution-processable metal nanoparticles. *Appl. Phys. Lett.*, 95:013305, 2009.
- [338] J.-L. Wu, F.-C. Chen, Y.-S. Hsiao, F.-C. Chien, P. Chen, C.-H. Kuo, M. H. Huang, and C.-S. Hsu. Surface plasmonic effects of metallic nanoparticles on the performance of polymer bulk heterojunction solar cells. *ACS Nano*, 5(2):959–967, 2011.
- [339] D. D. S. Fung, L. Qiao, W. C. H. Choy, C. Wang, W. E. I. Sha, F. Xie, and S. He. Optical and electrical properties of efficiency enhanced polymer solar cells with Au nanoparticles in a PEDOT-PSS layer. *J. Mater. Chem.*, 21(41):16349–16356, 2011.
- [340] J. Yang, J. You, C.-C. Chen, W.-C. Hsu, H. r. Tan, X. W. Zhang, Z. Hong, and Y. Yang. Plasmonic Polymer Tandem Solar Cell. *J. Mater. Chem.*, 5(8):6210–6217, 2011.
- [341] L. Qiao, D. Wang, L. Zuo, Y. Ye, J. Qian, H. Chen, and S. He. Localized surface plasmon resonance enhanced organic solar cell with gold nanospheres. *Appl. Chem.*, 88(3):848–852, 2011.
- [342] X. Yang, C.-C. Chueh, C.-Z. Li, H.-L. Yip, P. Yin, H. Chen, W.-C. Chen, and A. K.-Y. Jen. High-Efficiency Polymer Solar Cells Achieved by Doping Plasmonic Metallic Nanoparticles into Dual Charge Selecting Interfacial Layers to Enhance Light Trapping. *Adv. Energy Mater.*, 3(5):666–673, 2013.
- [343] K. Yao, M. Salvador, C.-C. Chueh, Y.-X. Xu, D. W. deQuilettes, T. Hu, Y. Chen, D. S. Ginger, and A. K.-Y. Jen. General Route to Enhance Polymer Solar Cell Performance using Plasmonic Nanoprisms. *Adv. Energy Mater.*, 4(9):1400206, 2014.
- [344] M.-K. Chuang, S.-W. Lin, F.-C. Chen, C.-W. Chu, and C.-S. Hsu. Gold nanoparticle-decorated graphene oxides for plasmonic-enhanced polymer photovoltaic devices. *Nanoscale*, 6:1573–1579, 2014.
- [345] T. Z. Oo, N. Mathews, G. Xing, B. Wu, B. Xing, L. G. Wong, T. C. Sum, and S. G. Mhasalker. Ultrafine Gold Nanowire Networks as Plasmonic Antennae in Organic Photovoltaics. *J. Phys. Chem. C*, 116(10):6453–6458, 2012.
- [346] N. Kalfagiannis, P. G. Karagiannidis, C. Pitsalidis, N. T. Panagiotopoulos, C. Gravalidis, S. Kassavetis, P. Patsalas, and S. Logothetidis. Plasmonic silver nanoparticles for improved organic solar cells. *Sol. Energy Mater. Sol. Cells*, 104:165–174, 2012.
- [347] H. Choi, J.-P. Lee, S.-J. Ko, J.-W. Jung, H. Park, S. Yoo, O. Park, J.-R. Jeong, S. Park, and J. Y. Kim. Multipositional Silica-Coated Silver Nanoparticles for High-Performance Polymer Solar Cells. *Nano. Lett.*, 13(5):2204–2208, 2013.
- [348] M.-C. Chuang and F.-C. Chen. Synergistic Plasmonic Effects of Metal Nanoparticle-Decorated PEGylated Graphene Oxides in Polymer Solar Cells. *ACS Appl. Mater. Interfaces*, 7:7397–7405, 2015.