

Electrochemical observation of single collision events: fullerene nanoparticles

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Abstract: Individual fullerene nanoparticles are detected and sized in a non-aqueous solution *via* cathodic particle coulometry where the direct, quantitative reduction of single nanoparticles is achieved upon collision with a potentiostated gold electrode. This is the first time that the nanoparticle impact technique has been shown to work in a non-aqueous electrolyte and utilised to *coulometrically* size carbonaceous nanoparticles. Contrast is drawn between single nanoparticle electrochemistry and that seen using nanoparticle ensembles *via* modified electrodes.

Keywords: fullerene nanoparticles, nano-C₆₀, single nanoparticle sizing, cathodic particle coulometry, nanoparticle-electrode collision, nano-impacts

Electrochemical techniques have been invaluable in the investigation of fullerene molecules with the most studied being buckminsterfullerene, C₆₀.¹ C₆₀ has been found to undergo both oxidation and reduction.² Up to six successive one electron reductions of C₆₀ in solution have been reported under certain conditions.³ While the electrochemistry of C₆₀ molecules, C₆₀ molecular films and other colloidal carbon-based materials⁴ have been studied in detail the electrochemical properties of C₆₀ nanoparticles (NPs), or nano-C₆₀, remains unexplored.^{5, 6} The nanoparticulate form of C₆₀ has gained increasing attention due to the spontaneous aggregation of C₆₀ molecules in environmental waters to form nano-C₆₀.⁷ Significant environmental exposure to C₆₀ and thus nano-C₆₀ formation is likely given the mass production of C₆₀ for manifold applications ranging from cosmetics⁸ to photovoltaics⁹ while C₆₀ has also been found to occur naturally in the environment.^{10, 11} Reports that nano-C₆₀ is bactericidal¹² and toxic to human cell lines¹³ has resulted in a need to monitor these carbonaceous nanoparticles.

A method to detect individual NPs has been developed where an electrocatalytic reaction occurs exclusively on NPs in contact with an inert electrode surface thereby resulting in an amplification of the current response upon NP-electrode collision.¹⁴⁻¹⁹ The detection of single walled carbon nanotubes (SWCNTs) has been achieved using this non-coulometric NP-impact technique *via* investigation of increasing electrode area and therefore amplified currents for ferrocenemethanol oxidation upon SWCNT collision.²⁰ One drawback of this electrocatalytic amplification method for NP detection is that the types of NP and electrode materials that can be studied are limited as the electrode needs to be inert while the NP needs to catalyse the redox reaction of interest.

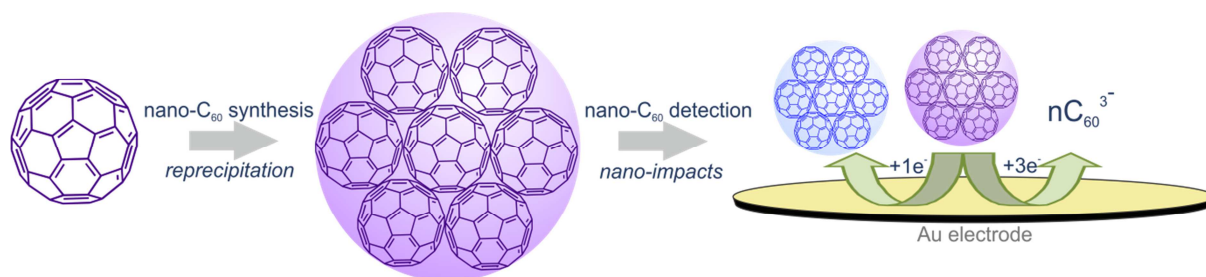


Figure 1. Schematic for the synthesis and electrochemical detection of impacting nano-C₆₀ particles at a gold microelectrode where nano-C₆₀ is reduced upon collision *via* the transfer of one (represented by the colour change from purple to blue) or three electrons resulting in dissolution of the generated C₆₀³⁻ anions.

Particle coulometry is an alternate technique to detect individual NPs that is not limited by NP and electrode materials. Anodic particle coulometry detects NPs in aqueous solution *via* their direct oxidation during stochastic collision events at a potentiostated electrode and was originally developed to study single metal NPs.²¹ The technique has been further adapted and applied to size impacting organic²² and metal oxide²³ NPs and termed cathodic particle coulometry as these NPs are reduced upon contact with an electrode. Particle coulometry techniques can provide the user with information regarding NP size,²¹ concentration,²⁴ stability²⁵ and electron transfer kinetics.²⁶ Importantly in the present work the particle coulometry method not only provides an analytical methodology but it also allows direct investigation of the morphology dependency of the redox properties of the C₆₀.

Herein cathodic particle coulometry is used to electrochemically size individual nano-C₆₀ particles impacting upon a gold electrode and it is shown for the first time that this *coulometric* NP sizing technique can be employed not only for the detection of carbonaceous NPs but also in non-aqueous conditions. The morphological influence of transitioning from a molecular microcrystal-ensemble to a nanoparticle-ensemble to isolated NPs on the electrochemical response of C₆₀ is also investigated and contrasts drawn between single nanoparticle and nanoparticle ensemble studies.

RESULTS AND DISCUSSION

nano- C_{60} particles were synthesised *via* the reprecipitation method²⁷ and DLS used to gain a size distribution for the NP radius which had a maximum of 16 nm (Fig. 1), a size that was confirmed with SEM (19 ± 4 nm).

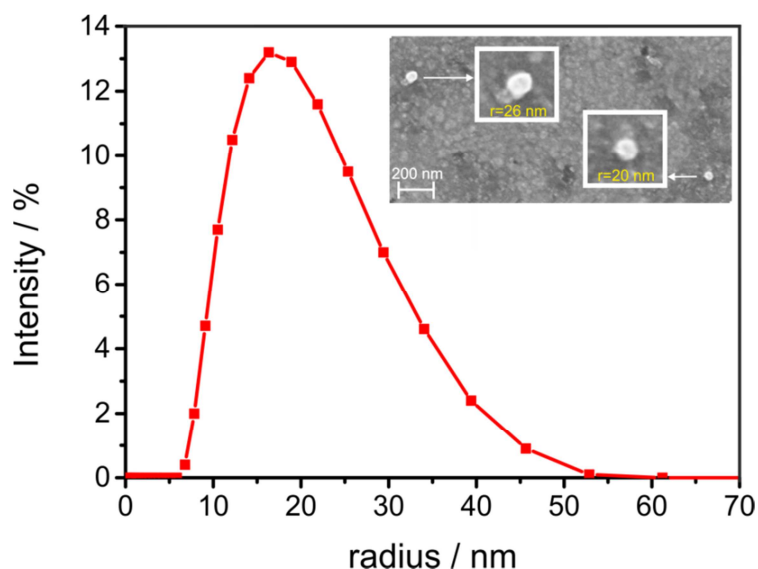


Figure 2. Size distribution for the synthesised stock suspension of nano- C_{60} particles (0.1 mM nano- C_{60} particles in 10% NMP:90% MeCN) measured *via* DLS and SEM image (shown inset) of the same nano- C_{60} stock suspension

The electrochemistry of *molecular* C_{60} was investigated prior to the electrochemical characterisation of the synthesised nano- C_{60} particles. This approach was chosen as the electrochemical response of molecular C_{60} films has been previously explored in the literature.²⁸⁻³⁰ Therefore the voltammetry of these well-studied molecular C_{60} films provides a useful comparison for the electrochemistry of the synthesised *nanoparticulate* nano- C_{60} . Fig. 3a shows the voltammetric response of a molecular C_{60} film in 0.1 M $NBu_4PF_6/MeCN$ where a gold electrode has been modified with 0.15 mM C_{60} in CH_2Cl_2 (20 μ L) as in the work of Tan *et al.*²⁸ Molecular C_{60} microcrystals form on the electrode surface upon evaporation of the solvent.²⁸ Ferrocene (2 mM) was added as an internal redox marker for voltammetric

experiments and all potentials are referenced to the ferrocene/ferrocenium redox couple (Fc/Fc^+). Cathodic waves were observed for the first three electron reductions of the molecular C_{60} microcrystals at -1.21 V, -1.43 V and -1.90 V vs. Fc/Fc^+ . The large potential separation between the cathodic and corresponding anodic peaks observed for the molecular C_{60} microcrystal ensemble has been explained by structural reorganisation on the electrode surface to accommodate cation insertion.^{29, 30} As reported by Jehoulet *et al.*, scanning the potential over the third reduction resulted in the first and second re-oxidation waves being significantly altered.³⁰ This observed change suggests that C_{60}^{3-} is soluble and hence dissolution of the C_{60} microcrystals occurs after the third electron transfer.^{30, 31} Dissolution of the third reduction product of the molecular C_{60} microcrystals was confirmed by holding the potential past the third reduction wave for 20 s and then scanning backwards revealing the loss of all re-oxidation peaks (S.I. Fig. S1a).

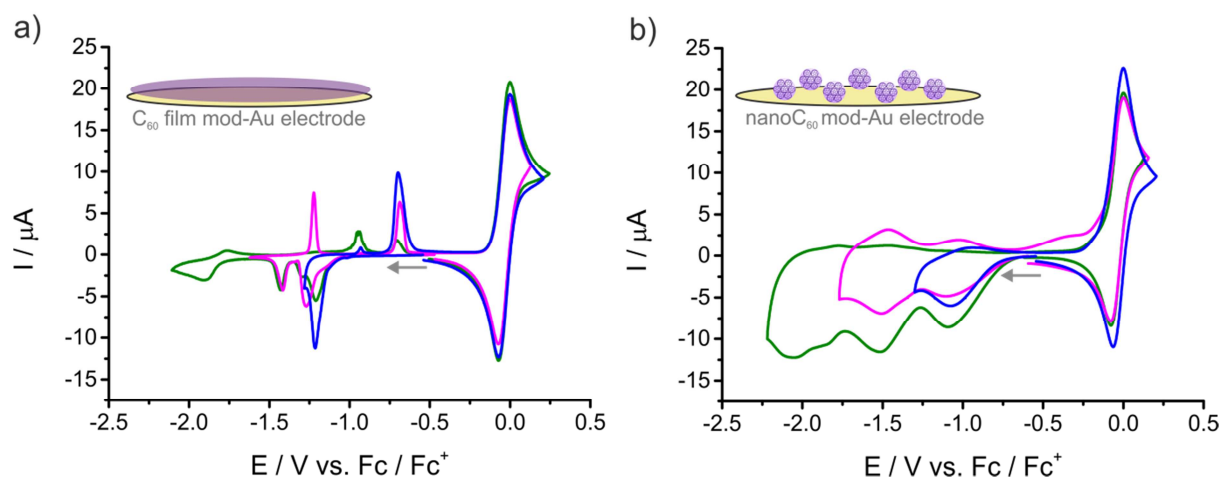


Figure 3. Voltammetric profiles for a Au macroelectrode ($r = 0.8$ mm) modified with a) 20 μL solution of 0.15 mM C_{60} in CH_2Cl_2 and b) 20 μL suspension of 0.1 mM nano- C_{60} particles in 10% NMP:90% MeCN to observe the one (blue line), two (pink line) and three (green line) electron reductions of the C_{60} ensembles. All measurements were performed in MeCN (2 mM $\text{Fe}(\text{C}_5\text{H}_5)_2$, 0.1 M NBu_4PF_6) at a scan rate of 100 mV s^{-1} . The redox couple observed at $\sim 0\text{V}$ is Fc/Fc^+ . Arrows represent scan direction.

Having observed the same voltammetric response for a C₆₀ microcrystal film as reported in the literature,²⁸ electrochemical characterisation was performed on an ensemble of the nano-C₆₀ particles sized in Fig. 2. A gold electrode was modified by dropcasting 20 µL of the nano-C₆₀ stock suspension (nano-C₆₀ as-synthesised in the absence of electrolyte) and cyclic voltammetry was performed in 2mM Fc/0.1 M NBu₄PF₆/MeCN (Fig. 3b). Three reduction waves were observed at -1.09 V, -1.51 V and -2.06 V vs. Fc/Fc⁺. The redox response was found to be markedly different from that of the molecular C₆₀ microcrystal film. In contrast to the large separation between cathodic and anodic peaks for the C₆₀ microcrystal ensemble, the nano-C₆₀ modified electrode exhibited a much smaller peak to peak splitting reflecting voltammetry reported for molecular C₆₀³ and C₆₀ Langmuir-Blodgett Films.³⁰ This difference in electrochemical response demonstrates that a change in the morphology of C₆₀ on the electrode surface markedly affects electron transfer. The only similarity between the responses at the microcrystal and nano-C₆₀ ensembles is that the third electron reduction of nano-C₆₀ is also irreversible as evidenced by the absence of oxidative features in the reverse scan. The dissolution of nano-C₆₀ on the third electron reduction was confirmed *via* the same potential holding method used for the micro ensemble study above (S.I, Fig. S1b). A scan rate study of the three electron reduction of nano-C₆₀ (S.I., Fig. S2) demonstrated that it is the dissolution of the generated C₆₀³⁻ anions as opposed to the electron transfer that is the irreversible step in this third electron reduction as the proportion of material being re-oxidised back onto the electrode surface following the transfer of three electrons increases with increasing scan rate.

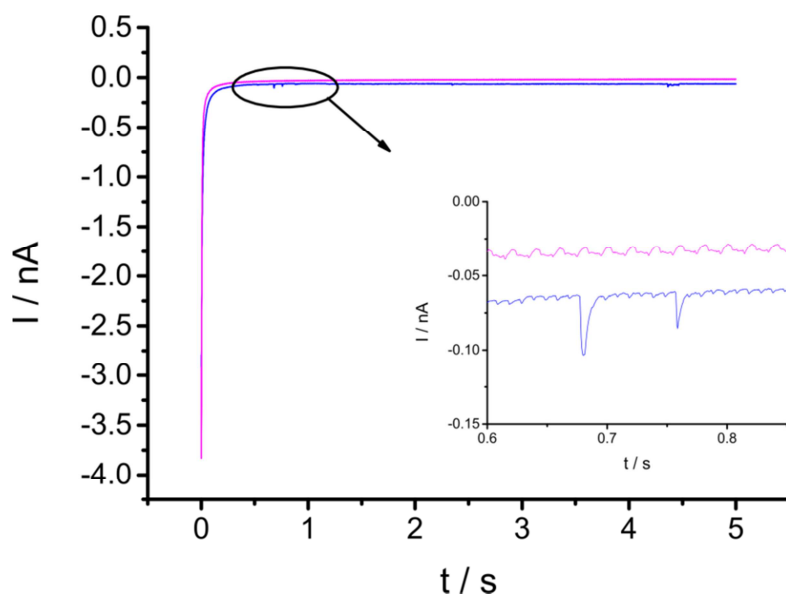


Figure 4. 5 s chronoamperogram for a gold microelectrode ($r = 5 \mu\text{m}$) immersed in a 0.1 M $\text{NBu}_4\text{PF}_6/\text{MeCN}$ solution containing 116 pM nano- C_{60} particles measured at $E = -1.27 \text{ V}$ vs. Fc/Fc^+ (blue line) and $E = -0.655 \text{ V}$ vs Fc/Fc^+ (pink line)

Having investigated the change in C_{60} electrochemistry when transitioning from a molecular C_{60} microcrystal ensemble to a nanoparticulate nano- C_{60} ensemble, cathodic particle coulometry was subsequently employed to study the electrochemistry of nano- C_{60} nanoparticles at the single nanoparticle scale. Cathodic particle coulometry detects and sizes *individual* particles in solution. An aliquot of nano- C_{60} was added to a thoroughly degassed solution of 0.1 M NBu_4PF_6 in MeCN resulting in a nano- C_{60} concentration of 116 pM before a gold microelectrode ($r = 5 \mu\text{m}$) suspended in solution was potentiostated to -1.27 V vs. Fc/Fc^+ . This chosen potential corresponds to the one electron reduction of nano- C_{60} as inferred from Fig. 3b. Fig. 4 shows the reductive spikes that were observed in the 5 s chronoamperometric scans measured post addition of nano- C_{60} particles (Fig. 4, blue line). Note that no impact spikes were observed in solutions pre addition of nano- C_{60} . Each of the reductive spikes observed results from the charge transfer upon a collision between nano- C_{60} , moving *via* Brownian motion in solution, and the gold microelectrode. Increasing the

electrode potential to one at which the reduction of nano-C₆₀ does not occur (-0.655 V vs. Fc/Fc⁺) caused the observed spikes to disappear (Fig. 4, pink line).

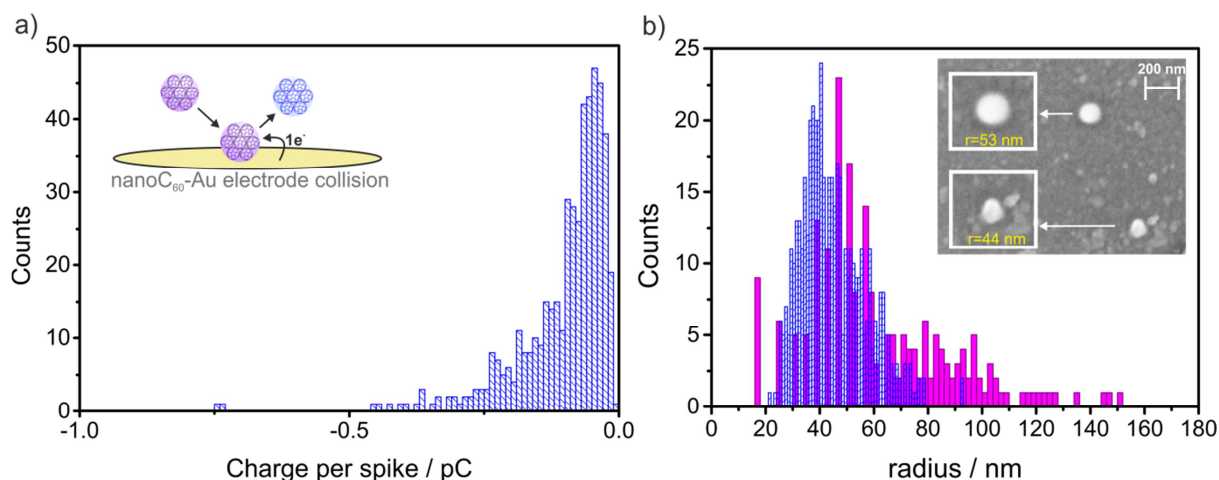


Figure 5. a) Charge distribution with a bin size of 0.01 pC for the one electron reduction of nano-C₆₀ (116 pM) impacting a gold microelectrode ($r = 5 \mu\text{m}$) in MeCN (0.1 M NBu₄PF₆) b) Size distribution with a bin size of 1 nm for the one electron reduction of nano-C₆₀ (116 pM) impacting a Au electrode ($r = 5 \mu\text{m}$) in MeCN (0.1 M NBu₄PF₆) (blue) overlaid with the size distribution determined by SEM imaging of nano-C₆₀ particles dispersed in 0.1 M NBu₄PF₆/MeCN (pink, bin size=2 nm) and SEM image shown inset.

A total of 481 impact spikes were recorded for the one electron reduction of impacting nano-C₆₀ ($E = -1.27 \text{ V vs. Fc/Fc}^+$) and the area under each current-time spike was integrated to give the charge for the reduction of each impacting NP. The charge distribution for the impact events recorded where one electron is exchanged is shown in fig. 5a and the mean charge of the spikes observed was $-0.102 \pm 0.004 \text{ pC}^1$. If the whole NP is reduced upon impact

¹ The error of the NP size distribution is given by the standard deviation (SD) while the error of the mean charge is the standard error of the mean given by $\frac{SD}{\sqrt{n}}$ where n is the sample number, in this case the number of spikes.

and a spherical particle shape is assumed the Faradaic charge measured for the observed NP-electrode collisions can be reinterpreted to determine the radius of each impacting NP *via* (1):

$$r = \sqrt[3]{\frac{3MQ}{4\pi Fz\rho}} \quad (1)$$

where M is the molecular mass of C_{60} in kg mol^{-1} , Q is the charge measured in coulombs (C), F is Faraday's constant in C mol^{-1} , z is the number of electrons transferred and ρ is the density of C_{60} measured in kg m^{-3} .

The NP size distribution determined using (1) is shown in fig. 5b (blue) and the mean radius was 45 ± 12 nm, significantly larger than the size of nano- C_{60} in the synthesised stock NP suspension measured using DLS and SEM (≈ 20 nm radius). It is well known that nano- C_{60} particles are prone to aggregation upon the addition of salt^{7, 32} therefore we suggest that the larger NP size determined from the cathodic particle coulometry experiment is due to the aggregation of nano- C_{60} NPs when dispersed in a 0.1 M $\text{NBu}_4\text{PF}_6/\text{MeCN}$ solution. A size distribution of nano- C_{60} in the presence of the electrolyte could not be measured via DLS as the aggregating particles resulted in a very high polydispersity within the sample. SEM analysis of nano- C_{60} particles in 0.1 M $\text{NBu}_4\text{PF}_6/\text{MeCN}$ was performed to determine if the NPs aggregate in the presence of the electrolyte used for the cathodic particle coulometry experiments. The measurements were carried out by dropcasting a sample of the nano- C_{60} particles suspended in electrolyte on a SEM sample holder that had been modified with a transmission electron microscopy grid in order to minimise NP aggregation during sample preparation. SEM analysis showed that NP size increased upon nano- C_{60} dispersion in 0.1 M $\text{NBu}_4\text{PF}_6/\text{MeCN}$ and relatively good agreement was found between the nano- C_{60} size distributions measured via SEM and cathodic particle coulometry in the presence of electrolyte (Fig. 5b). There is an increased occurrence of larger particles (radius ≈ 80 -150 nm) in the SEM determined NP size distribution which could be due to the aggregation of

nano-C₆₀ during preparation of the SEM sample despite steps having been taken to minimise this effect. Another possible explanation for the discrepancy between the cathodic particle coulometry and SEM determined size distributions is that slower diffusion co-efficients of larger NPs will result in a reduced collision probability during impact experiments and therefore larger NPs are less likely to be measured via particle coulometry; this phenomenon has been investigated using silver NPs by Lees et al.³³.

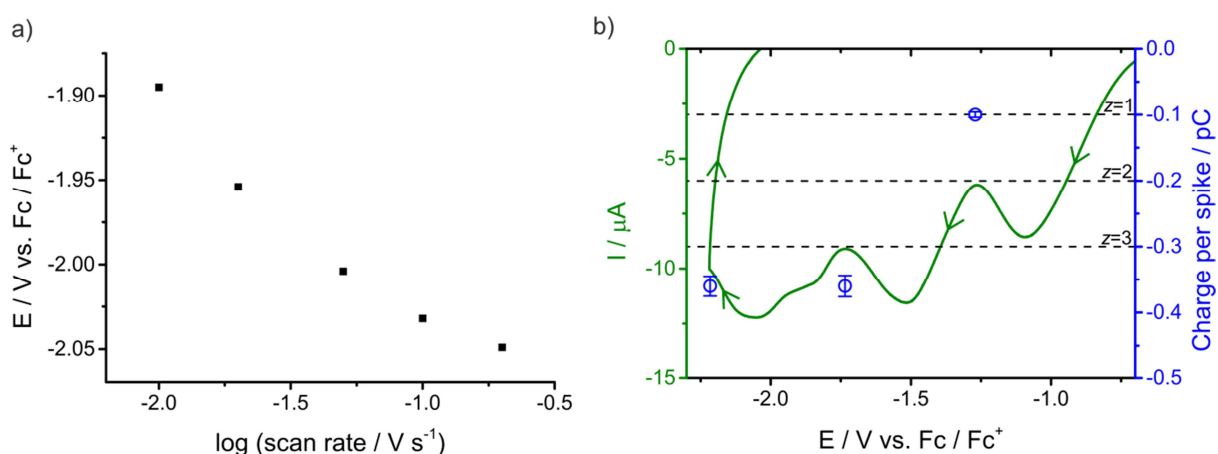


Figure 6. a) Plot of potential for the third electron reduction peak of nano-C₆₀ against $\log(\text{scan rate})$ for a 20 μL nano-C₆₀ modified Au macroelectrode ($r = 0.8 \text{ mm}$) in a solution of 2 mM $\text{Fe}(\text{C}_5\text{H}_5)_2$, 0.1 M NBu_4PF_6 in MeCN b) Voltammogram of a Au macroelectrode ($r = 0.8 \text{ mm}$) modified with 20 μL 0.1 mM nano-C₆₀ particles scanned in MeCN (2 mM $\text{Fe}(\text{C}_5\text{H}_5)_2$, 0.1 M NBu_4PF_6) at a scan rate of 100 mV s^{-1} (green line) overlaid with a plot of potential against the mean charge transfer per impacting nano-C₆₀ particle where the error bars are determined by the standard error of the mean (blue symbols)

The accurate sizing of nano-C₆₀ from impact events observed when the electrode is held at the potential for a one electron reduction, as determined from the voltammetric response of the nano-C₆₀ ensemble (Fig. 3b), demonstrates that there is no change in the potential at which this first electron transfer occurs when changing from a NP ensemble to individual NPs. In contrast changes are observed for the third electron reduction of nano-C₆₀ when the

electrochemical response of the NP ensemble is compared to single collision events. It is known that peak potentials can shift by up to hundreds of millivolts when the voltammetry of a NP ensemble with strongly overlapping NP diffusion layers is compared to a case where the NPs are isolated and therefore diffusionally independent.³⁴ The voltammetric response shown in fig. 3b for the NP ensemble, where the NP diffusion layers will be overlapping, demonstrates that the second electron reduction of nano-C₆₀ is a reversible process whilst the third cathodic wave observed is irreversible and results in the formation of the soluble C₆₀³⁻ product that will diffuse away from the electrode.^{30, 31} For single collision events, a shift in potential occurs only for the irreversible third electron transfer as the ease of nano-C₆₀ dissolution at the isolated NP scale lowers the potential required for the third electron reduction and results from the strong divergent diffusion of products away from individual NPs as compared to the semi-infinite, planar diffusion seen for high coverage layers on electrode surfaces. Fig. 6a demonstrates that as the scan rate for nano-C₆₀ ensemble studies is decreased, the third electron reduction of nano-C₆₀ becomes more favourable and is observed at increasingly positive potentials (voltammograms are shown in the S.I., Fig. S2).

Cathodic particle coulometry experiments performed at potentials corresponding *nominally* to the second ($E = -1.74$ V vs. Fc/Fc⁺) and third ($E = -2.22$ V vs. Fc/Fc⁺) electron transfers as inferred from the ensemble studies (Fig. 3b) show a shift in potential at the *single* NP scale. For impact events measured at the former potential the mean charge was -0.360 ± 0.016 pC, this charge transfer is identical to the mean charge for current-time spikes observed for nano-C₆₀ particles undergoing a three electron reduction upon collision (-0.360 ± 0.015 pC). This similarity in charge suggests that a three electron reduction is observed for impacting NPs held at the potentials where the NP ensemble shows a two and three electron reduction of nano-C₆₀ should be occurring. This change in redox behaviour is due to the study of *isolated* NPs *via* particle coulometry as opposed to a NP ensemble.

Fig. 6b shows that if the charge transfer for a one electron reduction of a single impacting nano-C₆₀ particle is fixed at -0.10 pC, the value observed for the cathodic particle coulometry experiment performed at E=-1.27 V vs. Fc/Fc⁺, we can make the assumption that a three electron transfer occurs for cathodic particle coulometry experiments at both -1.74 V and -2.22 V vs. Fc/Fc⁺ as the mean charge measured at these potentials (-0.36 pC) is approximately three times the value of that for a one electron reduction at the single NP scale. This is further supported by reinterpretation of the charge transfer data measured at E=-1.74 V vs. Fc/Fc⁺ in terms of radius *via* (1) with the assumption $z=3$ giving a mean radius of 44±17 nm (S.I, Fig. S4b), in good agreement with mean radius values determined for the other two potentials studied (r=45±12 nm at E=-1.27 V vs. Fc/Fc⁺, r=44±17 nm at E=-2.22 V vs. Fc/Fc⁺). Hence for single NP studies, the third electron reduction of nano-C₆₀ occurs at an earlier potential than that observed for the NP ensemble demonstrating that the electrochemical response of nano-C₆₀ can differ when an NP ensemble is examined as opposed to an isolated NP.

CONCLUSIONS

In summary, we have reported the electrochemical detection and sizing of individual nano-C₆₀ nanoparticles demonstrating for the first time that NP-electrode impact studies can be performed in non-aqueous systems and cathodic particle coulometry can be applied to size carbonaceous nanoparticles. It is shown that a potential shift of the third electron transfer process occurs at the single NP scale when compared to the peak potential at which this process is observed in the voltammetry of a nano-C₆₀ ensemble. Thus the electrochemical response is altered when changing from an ensemble of nano-C₆₀ NPs present on an electrode surface to an isolated NP scenario. Another factor that was found to strongly influence C₆₀ electron transfer is the morphology of C₆₀ on the electrode surface with significant changes in the voltammetric response observed between micro- and nano-C₆₀ ensembles.

METHODS

nano-C₆₀ particles were synthesised using the reprecipitation method²⁷. The method used here is based on the work by Zhang *et al.*³⁵ however the nanoparticles were reprecipitated in acetonitrile rather than water as in the nano-C₆₀ synthesis reported by Alargova *et al.*³⁶ First, 17.2 mg C₆₀ (99.5% pure, SES Research, Texas, U.S.) was dissolved in 20 mL *N*-Methyl-2-pyrrolidone (NMP, Sigma Aldrich) by stirring in the dark for 24 hours. The C₆₀ containing NMP solution was then added dropwise to 200 mL of stirring MeCN (Sigma Aldrich) at a speed of 0.9 mL min⁻¹ before continuing to stir for 30 min in the dark. The NP solution was passed through a 0.2 µm filter (Whatman International Ltd., Kent, U.K.) resulting in a transparent orange solution of 0.1 mM² nano-C₆₀ NPs (radius ≈16 nm according to DLS) in 10% NMP: 90% MeCN. DLS measurements were performed using a Malvern Zetasizer Nano ZS and a LEO Gemini 1530 (Zeiss, Oberkochen, Germany) was employed for SEM imaging. A SEM holder that had been modified with a transmission electron microscopy grid was used for SEM experiments in order to minimise nano-C₆₀ aggregation during sample preparation.

All electrochemical studies were carried out using a µAutolab II (Metrohm-Autolab BV, Utrecht, Netherlands) at 25 ± 0.2 °C in an oxygen-free 0.1 M NBu₄PF₆/MeCN solution using a three electrode set-up with a carbon rod counter electrode, a silver wire pseudo-reference electrode and either a macro (r=0.8 mm) or micro (r=5 µm) gold working electrode (CH Instruments). Working electrodes were polished with alumina power (1 µm, 0.3 µm and 0.05 µm) prior to each experiment. Ferrocene (2 mM) was added to the electrolyte solution to act as an internal redox marker for voltammetric measurements. To prepare a solution of 0.15 mM C₆₀ in CH₂Cl₂, the solution was stirred in the dark for 24 hours. Modification of the gold

² This concentration does not take into account the loss of material during filtration

macroelectrode was performed by drop casting 4 x 5 μ L layers of C₆₀ solution/nano-C₆₀ suspension before drying at 35 \pm 0.2 °C. Due to the low surface tension of the solvents used solution run off onto the insulator surrounding the electrode surface could not be prevented and therefore quantification of the amount of nano-C₆₀ immobilised on the electrode was not possible. Cathodic particle coulometry experiments were performed within a double faraday cage to reduce noise. All glassware was cleaned with aquaregia (75% HCl: 25% HNO₃) and oven-dried to remove any traces of water. The nitrogen flow used to degas solutions was purged with acetonitrile that had been dried with molecular sieves to ensure no water was introduced to the system.

Image J (Version 1.38) was used to analyse the NP size determined *via* SEM whilst SignalCounter developed by Dr Dario Omanović at the Ruđer Bošković Institute in Zagreb, Croatia was employed for the analysis of spikes observed in cathodic particle coulometry experiments.

ASSOCIATED CONTENT

Supporting Information Available: voltammetric profiles measure post 20s chronamperograms for the first three electron reductions of microcrystalline C₆₀ and nano-C₆₀, scan rate study of a nano-C₆₀ modified Au macroelectrode, impact spikes observed for cathodic particle coulometry experiments at E=-1.74 V and -2.22 V vs. Fc/Fc⁺, charge and size distributions determined from these observed impact spikes. This material is available free of charge *via* the Internet at <http://pubs.ac.org>.

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Electrochemical observation of single collision events: fullerene nanoparticles

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SUPPORTING INFORMATION

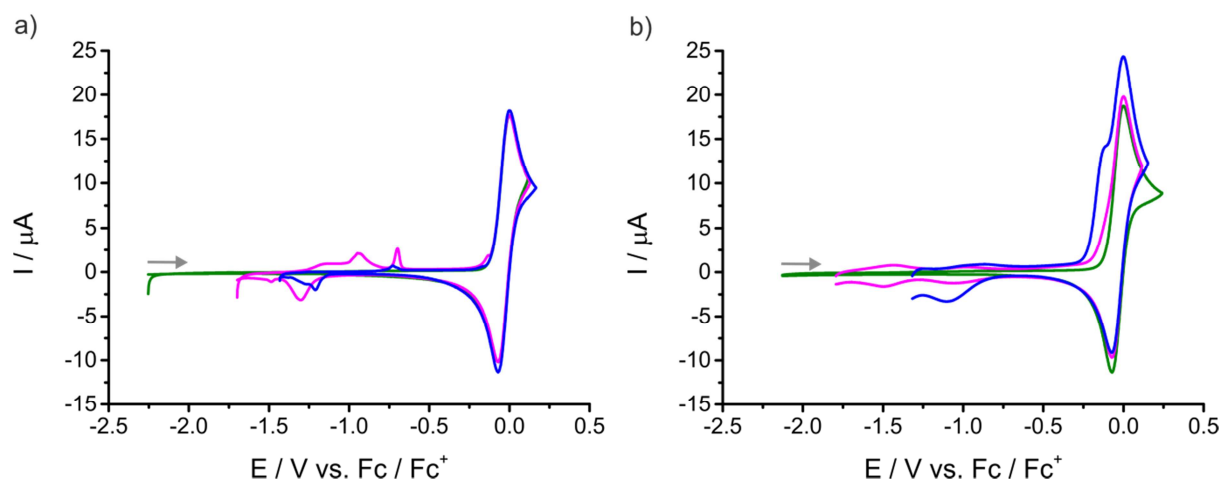


Figure S1. Voltammetric profiles in 2 mM Fc/0.1 M NBu₄PF₆/MeCN for a Au macroelectrode ($r = 0.8$ mm) modified with (a) 20 μ L 0.15 mM C₆₀ in CH₂Cl₂ measured post 20 s chronoamperomograms where the potential applied was -1.43 V (blue), -1.70 V (pink) and -2.25 V (green) (b) modified with 20 μ L 0.1 mM nano-C₆₀ particles in 10% NMP:90% MeCN measured post 20 s chronoamperomograms where the potential applied was -1.32 V (blue), -1.80 V (pink) and -2.14 V (green). All measurements were performed at a scan rate of 100 mV s⁻¹. The arrow infers the direction of scanning.

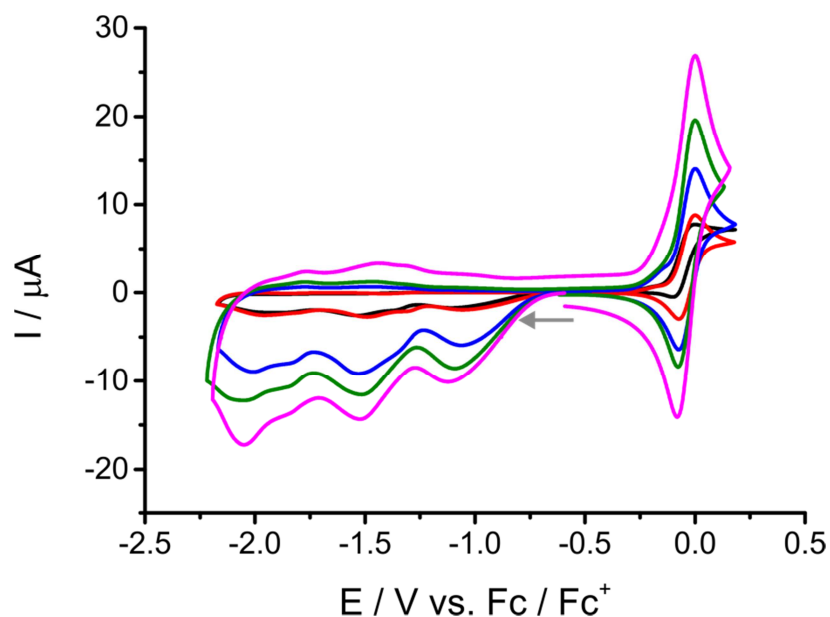


Figure S2. Voltammetric profiles for a Au macroelectrode ($r = 0.8$ mm) modified with (a) 20 μL 0.1 mM nano- C_{60} particles measured in 2mM $\text{Fc}/0.1$ M $\text{NBu}_4\text{PF}_6/\text{MeCN}$ at a scan rate of 10 (black), 20 (red), 50 (blue), 100 (green) and 200 (pink) mV s^{-1} . The arrow infers the scanning direction.

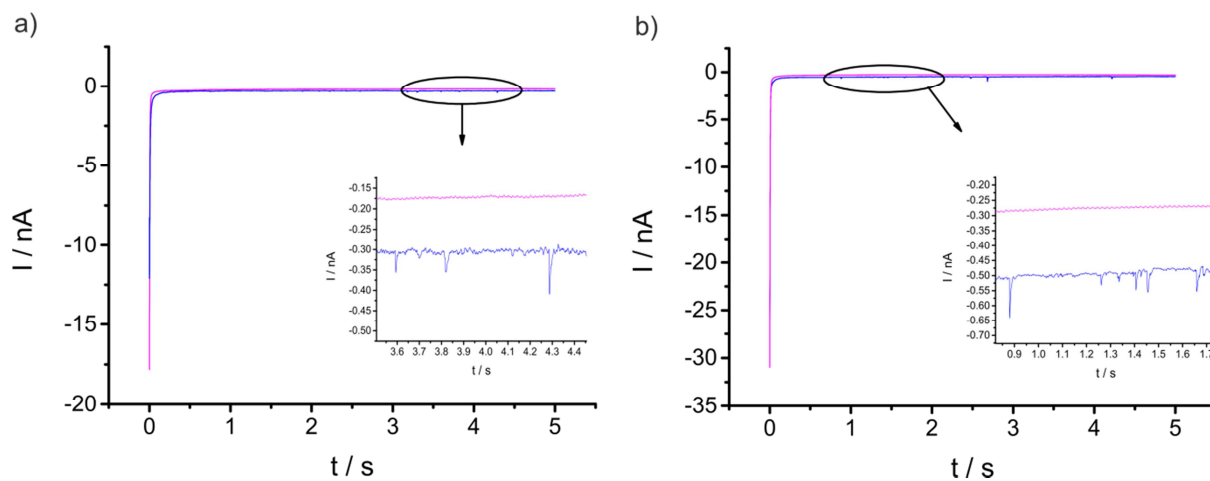


Figure S3. 5 s chronoamperograms measured at (a) $E = -1.74$ V vs. Fc/Fc^+ and (b) $E = -2.22$ V vs. Fc/Fc^+ for a gold microelectrode ($r = 5$ μm) immersed in 0.1 M $\text{NBu}_4\text{PF}_6/\text{MeCN}$ solution with (blue line) and without (pink line) 116 pM nano- C_{60} nanoparticles.

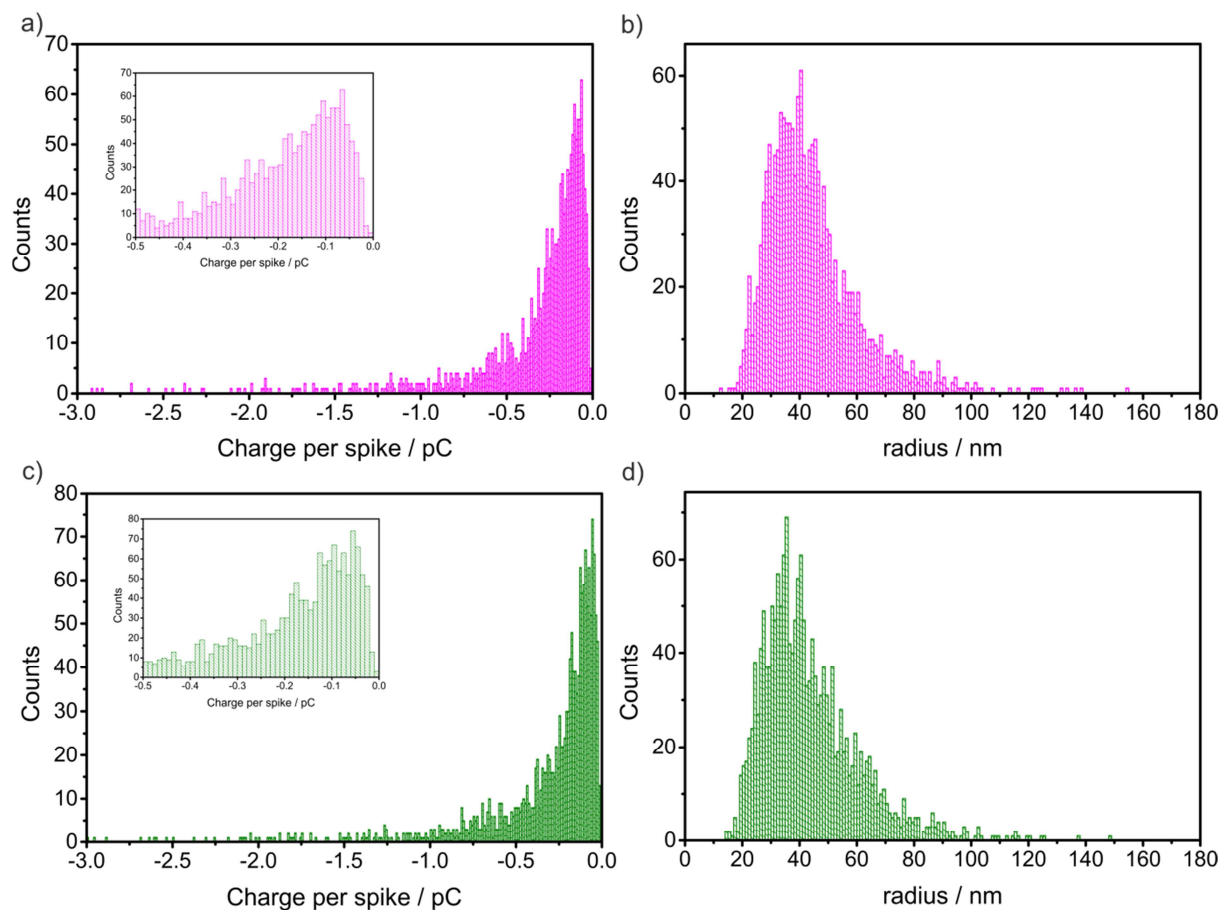


Figure S4. Charge distribution (a) and size distribution assuming $z=3$ (b) of 1581 spikes recorded for the reduction of nano-C₆₀ (116 pM) impacting a gold microelectrode ($r = 5 \mu\text{m}$) in MeCN (0.1 M NBu₄PF₆) at a potential of -1.74 V vs. Fc/Fc⁺. Charge distribution (c) and size distribution assuming $z=3$ (d) of 1714 spikes recorded for the reduction of nC₆₀ (116 pM) impacting a gold microelectrode ($r = 5 \mu\text{m}$) in MeCN (0.1 M NBu₄PF₆) at a potential of -2.22 V vs. Fc/Fc⁺. For clarity spikes with a charge above -3.0 pC have not been included in the charge distribution plots.

