

Electrochemical Detection of Nanoparticles by “Nano-Impacts”

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Abstract

There is an urgent demand from both environmental and human health areas to detect and characterise nanoparticles both from the perspective of their physical properties as well as the fundamental understanding of the electrochemical interface at the nano-scale and associated reactions and kinetics. Recently, “Nano-impact” based electrochemical methods have shown great promise for efficient detection and quantification of individual nanoparticles properties such as size, concentration, and aggregation/agglomeration state in liquid phase, and the study of the kinetics of individual nanoparticles or chemical reactions at the nano-scale involving nanoparticles as a mediator. This review covers the recent developments in this emerging and important field, and summarises the latest developments (from the year of 2012 to date) addressing the following aspects of “Nano-impacts: direct detection of nanoparticles *via* electrochemical reduction and oxidation; detection of surface-modified nanoparticles; and reactions through mediated nanoparticles.

1. Introduction

In the last two decades, nanomaterials have attracted an enormous diversity of applications for both commercial manufacturing and fundamental research. Metal and inorganic nanoparticle containing products have been available in the market for some years and range from clothing to mobile phones and refrigerators, as well as finding applications in the health industry. For example, silver nanoparticles have been widely used as an antibacterial product in toothpaste and medical instruments. Concerns have been raised regarding possible outcomes for environmental systems [1], particularly resulting from their inevitable release into the environment [2].

In the food industry, nanoparticles such as diverse as titanium dioxide, silicon oxide and metallic silver find their application as food additives and in packaging [3]. Currently, a wide range of organic nanoparticles including lipid nanospheres, and micelles are also available as food-production materials, and in food processing and food products [4]. Therefore, additional concerns have been raised regarding the possible nanotoxicity of those nanoparticles for humans. However, information on the use of nanomaterials in consumer products at the moment is somewhat sketchy and often hypothetical as there are no legal requirements for reporting to consumers and/or regulatory authorities. This in turn is partly due to the lack of satisfactory techniques able to routinely and affordably characterise nanoparticles in complex matrices. For example, the variety of environmental matrices where nanoparticles are present, their extremely low concentration, and the heterogeneous

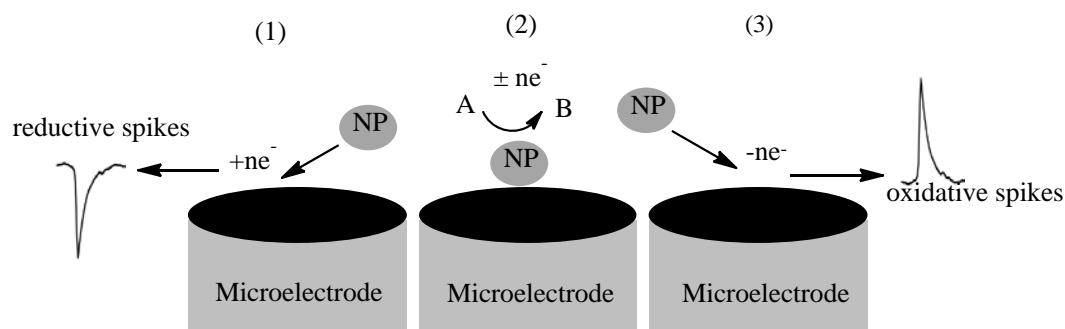
character of nanoparticles render the reliable detection or quantification of nanoparticles a significant challenge, though obviously there is an urgent demand from both environmental and human health areas to characterise, detect and quantify nanoparticles. This requires an efficient technique for measurement of physical properties of nanoparticles such as size, concentration, and aggregation/agglomeration state. Recently electrochemistry has proven to be an efficient and cost-effective approach to detect, to size, to quantify nanoparticles in liquid phase[5], even in highly complex matrices such as sea waters intrinsically containing high concentrations of salts[6]. Recently, disposable electrodes for real-time detecting and quantifying silver nanoparticles in authentic sea water have been developed[7].

Besides this analytical demand from environments and commercial products, nanoparticles are also fundamentally very interesting due to their altered properties compared to the macroscale, such as high surface to volume ratios, changed transport properties and modified physical properties. They therefore have found applications as alternative catalysis and energy systems such as in nanomaterial based energy storage[8] and capacitors[9] and transistors[10]. Organic nanoparticles, because of their large range of molecular structures, and the capability to tailor their binding affinity toward various materials, in particular have attracted significant attention in biomedicine and bioimaging over the past few years. Recent examples include delivering hydrophobic drugs to target cells [11], and acting as carriers for the controlled release of drugs under specific stimuli [12]. Despite the enormous interest in nanoparticles, a wide range of fundamental issues regarding the “size-effect” need to be addressed. For example, considering the reduction of particle diameter down to nanometer, the increased surface to volume ratios causes dramatic changes in physical properties (notably optical) and altered electronic structures arise some confinement effects at the nano-scale.

Beyond the physical properties of nanoparticle themselves, chemical reactions associated with nanoparticles as well as the mass-transport to and from the particle surface may also be influential in altering the observed reactivity at the nano-scale. In particular, fundamental understanding of the electrochemical interface at the nano-scale and associated reactions and kinetics, is expected to have a significant impact on emerging applications[13]. Recently, “Nano-impact” based electrochemical methods have shown great promise for the study of the thermodynamics and kinetics of nanoparticles or chemical reactions at the nano-scale involving nanoparticles as a mediator.

In this “Nano-impact” method (Schematic 1), a microelectrode is inserted into a suspension of nanoparticles which are subject to Brownian motion. Accordingly from time to time there are random collisions of the nanoparticles with the electrode surface. If the electrode is held at a suitable potential then the nanoparticle can be reduced (1) or oxidised (3) or else mediate electron transfer processes (2) can take place, enabling characterisation and detection of individual nanoparticles during

nanoparticle–electrode collisions. By measuring the Faradaic charge transfer resulting from direct reduction or oxidation of nanoparticles or alternatively the catalytic current amplification mediated electron transfer by individual nanoparticles when nanoparticles strike the electrode, this method provides quantitative information on the impacting nanoparticles such as their size, concentration, aggregation, and catalytic reactivity.



Scheme 1: illustration of “Nano-impact” method.

2. Existing Technologies

Hitherto, microscopy (electron microscopy) and spectroscopy techniques (light-scattering based methods) have played central roles in nanoparticle detection; however, the widespread use of microscopy such as TEM or SEM is limited since they are expensive to acquire and run with the additional need of extensive sample preparation that potentially introduces bias in measuring the particle size relative to the original samples. For example, the particle size, particularly of organic particles may be compromised after drying when imaging is conducted. Most importantly they also cannot detect nanoparticles *in situ* in liquid phase and this limits their application in real-time detection of nanoparticles present in environmental matrices.

Dynamic Light Scattering (DLS) provides a powerful *in situ* sizing technique for nanoparticles in liquid solution; however, DLS measures the overall signal from the whole bulk of nanoparticles which makes it very sensitive to the presence of large particles. This is particularly compromising when monitoring the aggregation and agglomeration state of particles. The presence of possible dust particles or small amounts of large aggregates makes it hard to size both aggregated nanoparticles and nanoparticles of high polydispersity. Alternatively, Nanoparticle Tracking Analysis (Nanosight, UK, and www.nanosight.com) can measure the signal from single particles but it has a fundamental

limitation on the lowest particle size that can be detected due to lower scattering from smaller particles. In addition, the image analysis requires a significant input from the operator, and as such may cause bias. Other optimised optical [14] and ultracentrifugation methods [15] have recently been developed for sizing of nanoparticles, but they generally require expensive instrumentation and long processing times.

3. Electrochemical Detection of Nanoparticles

Electrochemistry as an alternative method to microscopy and spectroscopy provides an efficient and cost-effective approach for the characterisation and detection of nanoparticles (NPs) [16]. In particular, a recent innovative method for electrochemical detection (“nano-impacts” or “single nanoparticle collisions”) is based on the *in-situ* detection of solution phase NPs by virtue of their random collision due to their Brownian motion and has been successfully applied to measure both physical and chemical properties of metal nanoparticles, metal oxides and organic nanoparticles, such as determining their size [5], concentration [17], the presence of molecular tags [18], their aggregation and agglomeration state [19], and electron transfer associated with the nanoparticles [20],[21],[22]. This review will cover the most recent developments in this emerging and important field. We will summarise the latest developments (from the year of 2012 to date) following an early review [16]. We address the following aspects: direct detection of nanoparticles *via* reduction and oxidation; detection of surface-modified nanoparticles; and reactions through mediated nanoparticles.

3.1 Reduction and Oxidation of Nanoparticles

3.1.1 Measurement of Nanoparticle Concentrations, Aggregation, and Extension to Real World Media

The Compton group have pioneered the new area of nanoparticle coulometry based on the direct electrochemistry (such as oxidation and reduction) of individual nanoparticles impacting at a solid ultramicroelectrode [16], [23]. The advantages of nanoparticle coulometry are that a variety of information on the impacting nanoparticles can be derived. For instance, the oxidative charge associated with an individual spike can be used to measure the size of an individual metal nanoparticle such as silver, gold, nickel nanoparticles as reported previously [5], [18, 24].

In a typical experiment to size nanoparticles (taking Nickel nanoparticles for example), a carbon fibre microelectrode was placed in a degassed solution of 10 mM HClO₄ and 100 mM NaClO₄, and a known concentration of pre-dispersed NiNPs added. The electrode potential was held at +1.7 V (relative to Ag/AgCl) for chronoamperometry and oxidative current spikes were observed, whilst no

oxidative spikes were observed at 1.0 V, confirming that the current spikes correspond to Faradaic oxidation of NiNPs ($\text{Ni(NP)} - 2\text{e}^- \rightarrow \text{Ni}^{2+}(\text{aq})$). A relationship between diameter and charge of single NiNPs is established based assuming that NiNPs are spherical (diameter, D_{np}), and the charge Q passed as a result of complete reduction of single NiNPs is given by:

$$D_{\text{np}} = 2 \sqrt[3]{\frac{3 A_r Q}{4nF\pi\rho}}$$

where ρ is the NP density, and A_r is the relative atomic mass. The size distribution of NiNPs can be derived by analysing the individual impact spikes.

Recent developments in direct reduction and oxidation of nanoparticles have seen the nano-impact method being further applied to determine nanoparticle concentration, aggregation state and detection of nanoparticles in authentic real world environment. Using Nickel nanoparticles as a model, nanoparticle concentrations were determined by analysing the frequency of the impact events [17]. In this study, the cumulative number of impacts was measured as a function of time and interpreted using the *Shoup-Szabo* expression[17], to fit the experimental data so that theoretical model, the concentration of nickel nanoparticles can be determined. The experimental and theoretical fitting for three samples with different nanoparticles concentrations was shown in Figure 1. The theoretical lines were obtained by the integrated form of the *Shoup-Szabo* flux equation with the nanoparticle diffusion coefficient estimated by the *Stokes-Einstein* equation and the size of nanoparticle determined by the anodic charge associated with impact spikes. The best fit concentration were 30 pM, 60 pM and 80 pM that was in excellent agreement with the known values, demonstrating the feasibility (proof-of-concept) to determine the nanoparticle concentration using nano-impact methods.

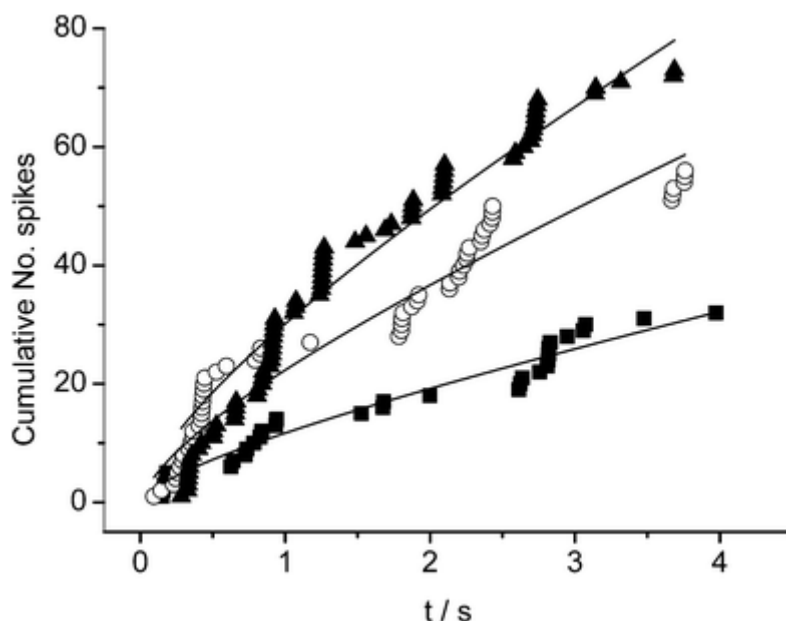


Fig. 1 Integrated Shoup–Szabo fit for the accumulative number of spikes against time at varying NiNPs concentrations of (■) 28, (○) 54, and (▼) 77 pM respectively. The dotted lines show the experimental data and theoretical fit. Reproduced from Ref [17] by permission of The Royal Society of Chemistry.

This above proposed methodology is highly beneficial in understanding the sensitivity of nanoparticles to their surrounding medium, opening a new door to address many interesting questions such as quantitative characterisation of nanoparticle aggregation and finding the “ideal” electrolyte to allow accurate information (such as kinetic information) from single nanoparticle rather than nanoparticle aggregates.

The aggregation state of nanoparticles is found to be dependent not only on the electrolytes where the nanoparticle are present (such as composition, ionic strength and pH), but on the size and capping agent of the nanoparticle. For instance, the agglomeration of silver nanoparticles in a solution containing 90 mM potassium chloride and 10 mM mono-sodium citrate has been studied *via* impact based anodic particle coulometry (APC) [19]. The agglomerates of silver nanoparticles (such as monomers, dimers, trimers, tetramers, pentamers and hexamers) was analysed by relating the number of nanoparticle monomers to the number of atoms in this nanoparticle which was determined by the charge from the quantitative oxidation of the particles while impacting a micro electrode, as shown in Figure 2.

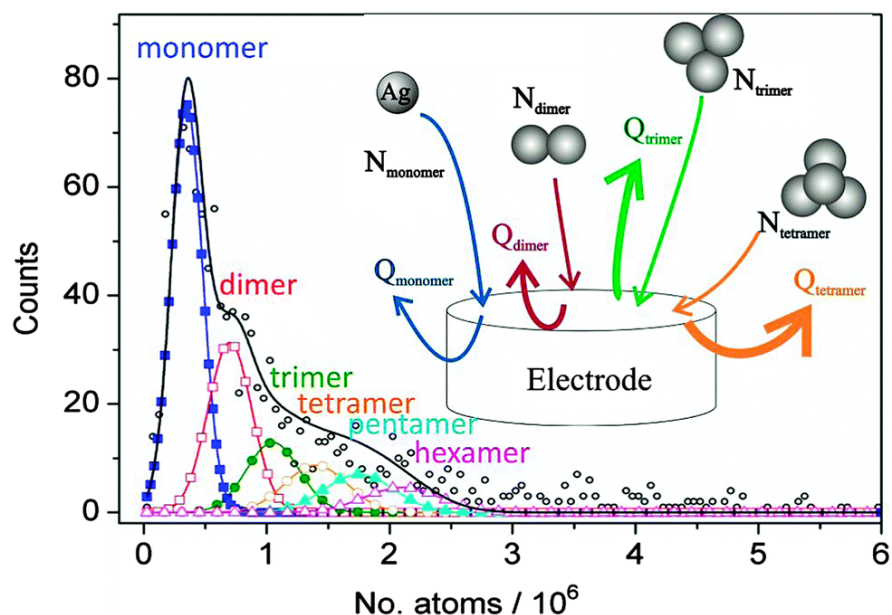


Fig. 2 Agglomeration state of silver nanoparticles (radius = 11 nm) in an aqueous solution of 0.09 M KCl and 0.01 M $\text{NaC}_6\text{H}_7\text{O}_7$, as determined by anodic particle coulometry (APC). The principle of using APC to size agglomerates impacting a micro electrode is schematically summarised in the inset. The charge per impact spike (and the number of atoms per particle) relate as 1 : 2 : 3 : 4 : 5 : 6 for impacting monomers, dimers, trimers, tetramers, pentamers and hexamers, respectively; Reproduced from Ref [23] by permission of the PCCP Owner Societies.

Recently, good stability of gold nanoparticles was shown in an acidic media so that ‘zero-aggregation’ collisions were realised [25]. This allows anodic dissolution currents from individual nanoparticles to be obtained in a ‘one particle at a time’ manner, based on which accurate particle sizing with a resolution of 1–2 nm can be achieved. A homogeneous solution of nanoparticles during a particle impact electrochemical experiment is critically important for accurate particle sizing, and acquiring information from single nanoparticles. In a study to understand the effect of electrolyte on nanoparticle aggregation, four different samples of silver nanoparticle with different size distribution were analysed by anodic particle coulometry during nanoparticle impact experiments in the 0.1 M citrate solution [26]. The sizing of those batches of silver nanoparticles using the APC method show excellent agreement with SEM analysis, where a TEM grid modified sample holder was used to minimise nanoparticle agglomeration upon sample drying. This result clearly indicates that aggregation of the citrate-capped silver nanoparticles is minimised in the presence of such electrolyte, in contrast to a silver aggregation study in real authentic seawater [6], which showed a few number of silver nanoparticles quickly aggregates.

As discussed above, microscopic methods reliably measure the size of dry nanoparticles, However, those methods cannot *in-situ* characterise nanoparticles which are mostly present in liquid phases such as biological media or natural aquatic systems. Recent studies have demonstrated that silver

nanoparticles can be identified, characterised, and sized in seawater using the impact approach [27],[6]. The impact experiments have found that 2, 3, 4 and 5 silver nanoparticles aggregate in the seawater during 40 min upon the addition of nanoparticles by determining the number of atoms of aggregates [27]. Subsequently, the same authors successfully applied the methodology to detect silver nanoparticles from a commercial product, a colloidal silver disinfectant spray [6]. The size distributions of the commercial nanoparticles achieved *via* APC and nanoparticle tracking analysis method showed the excellent agreement in both a standard electrolyte solution and seawater where the commercial nanoparticles were dispersed. The studies show great promise for impact method to detect nanoparticles in commercial products where effective detection and characterisation techniques are urgently required.

3.1.2 Metal Oxide and Organic Nanoparticles

Besides direct oxidation of metal nanoparticle (anodic particle coulometry), particle coulometry methodology has recently extended to the reduction and oxidation of other types of nanoparticles.

Fe₃O₄ nanoparticles were studied at both oxidising and reductive potentials [28]. The charges passed for the reduction and oxidation were seen to be in the ratio of 2:1 reflecting the stoichiometry of Fe(III)₂Fe(II)O₄. The nanoparticle sizing from both approaches were coincided and were in good agreement with independent SEM analysis. The results confirm complete oxidation and reduction of the nanoparticle during impact experiments, and both the reduction and oxidation providing quantitative nature of the electrolysis of the nanoparticles.

The size of organic nanoparticles plays a crucial role in biomedicine. For example, the bioavailability of water insoluble drugs can be significantly increased by reducing the drug particle size [29]; drug delivery through nanoparticles to tumour blood vessels was found to be size-dependent in a recent study [30]. Unlike metal nanoparticles, the detection and characterisation of organic nanoparticles (often present in complex matrices) is particularly challenging using existing technologies as the particle size is more likely to be compromised during elaborate sample preparation before imaging [31]. Most recently, direct electrochemical sizing of organic NPs through direct reduction of individual organic nanoparticles during random collision events at electrodes have shown to be feasible and quantitative [32]. In this study, indigo nanoparticles synthesised using re-precipitation methods was selected as a model system. Under potentiostatted conditions (between -0.7 V and -0.9 V), reductive spikes from individual indigo NPs were observed, showing that direct reduction of individual organic nanoparticles during random collision events can be observed and quantified, as shown in Figure 3. The onset of these Faradaic spikes was found to be dependent on the reduction potential. No spikes were observed when reducing the reduction potential (for example, to -0.3 V),

showing those spikes result from the Faradaic reduction of indigo NPs. The frequency of spikes increased with the increased amount of added indigo NPs, further confirming that the spikes correspond to Faradaic reduction of indigo NPs. Batches of synthesised indigo nanoparticles of two different sizes showed excellent agreement of the resulting sizing distribution obtained from the electrochemical sizing and from DLS analysis.

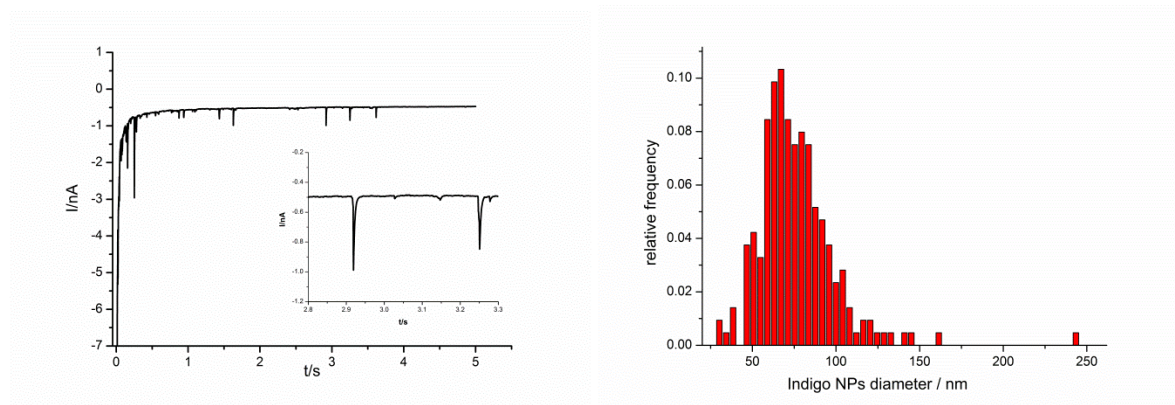


Fig 3. a) Chronoamperometric profiles showing reductive Faradaic spikes of indigo NPs in PBS buffer (pH7) at -0.70 V versus saturated calomel electrode. The inset shows the detailed impact spikes. b) Distribution of the NP diameter derived from a charge per current spike. Reprinted with permission from Ref. [32].

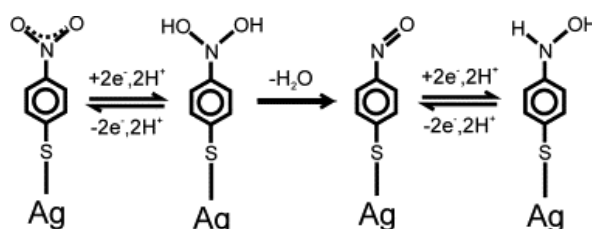
3.1.3 Kinetics and Mechanism of Electron Transfer to and from Nanoparticles

Quantitative information from nanoparticles in collision with electrodes using APC was extended to investigate the electron transfer kinetics to and from nanoparticles. For example, using copper nanoparticles as a model, the two electrons and one electron oxidation of the nanoparticles were observed in 1.0 M HNO_3 and in 1.0 M HNO_3 - 0.1 M KCl , respectively [33]. Both lead to complete oxidation of the particle allowing their sizing and also from detailed impact-charge vs. potential data give the charge transfer kinetics for nanoparticle oxidation. The Butler-Volmer transfer coefficients were determined by fitting the experimental data to theoretical models for reversible and irreversible charge transfer kinetics. In the case of copper, both 1 and 2 electron oxidations are best described by irreversible charge transfer kinetics. The best fit parameters were found to be $k_0 = 4.0 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$, and $\beta = 0.60$ for Cu/Cu (I) , and $k_0 = 1.0 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$, and $(n' + \beta) = 1.35$ for Cu/Cu (II) both in good agreement with the literature values of 0.66 and 1.25 respectively. The kinetics of electron transfer of electro oxidation of silver and nickel nanoparticles was also studied [34], with silver NPs displaying an electrochemically reversible one-electron oxidation, whilst the nickel NPs exhibiting slow irreversible 2-electron kinetics with $(n' + \beta) = 1.50$ and $k_0 = 5 \times 10^{-4} \text{ mol cm}^{-2} \text{ s}^{-1}$. Very recently this type of analysis has been extended to indigo nanoparticles[35].

3.2 Tagged Nanoparticles

Tagged nanoparticles have become increasingly attractive for analytical investigation particularly in biosensing applications. In the traditional electrochemical detection of those tagged nanoparticles, the tagged NPs have been immobilised onto the electrode before the electrochemical measurement [36],[37]. In a recent study, the method of particle coulometry has allowed detecting AgNPs tagged with 1, 4-nitrothiophenol (NTP) without immobilisation [18]. NTP is pre-adsorbed onto the silver NPs which were dispersed in the electrochemical cell. Sharp reductive current transients are observed as the tagged NPs collide with the electrode corresponding to reduction of the attached NTP molecules. The average charge passed per transient was found to vary according to the pre-adsorption time which controlled the NTP coverage of the NPs.

In a subsequent study, using the NTP-Ag NP model system, tagged Ag NPs were used to quantitatively measure the size distribution of the core of Ag NPs *via* the non-destructive reduction of tag molecules when tagged Ag NPs collide with the electrode [38], as illustrated in Scheme 2.



Scheme 2: The four-electron, four-proton reduction of NTP on silver nanoparticles

The approximate determination of size of the core of Ag NPs was based on the following equation:

$$R = \sqrt{\frac{S Q}{4 \pi f e n}}$$

S is the two-dimensional area occupied by a tag molecule, and f the fractional filling efficiency assuming optimal close-packing of tag molecules, Q is the charge passed per spike, n is the number of electrons transferred for reduction of a tag molecule, e is the electronic charge

The results showed excellent agreement with the size results from the destructive, exhaustive oxidation APC experiment, and suggests the above assumption of complete, four-electron reduction of the entire NTP monolayer may be justified.

This tag-redox coulometry (TRC) strategy achieves the same sizing and detection role as conventional APC on naked NPs. Further, this strategy is non-destructive and, in principle, can be applied to size

any type of nanoparticles (even non-conducting or non-redox nanoparticles) and is expected therefore to significantly widen the scope of particle-impact coulometry.

Most recently, the tag-redox coulometry was extended to determine surface adsorbed species associated with oxidative damage by reactive oxygen species (ROS) and demonstrate the use of this strategy as a predictive screening tool of the antioxidant activity of CeO₂ NPs[39]. In this work, redox induced changes of the NP surface (reduced and unreduced forms of CeO₂), as illustrated in Figure 4 after exposure to ROS was monitored by the electrochemical collision signals of the NPs with a Pt microelectrode (PtME).

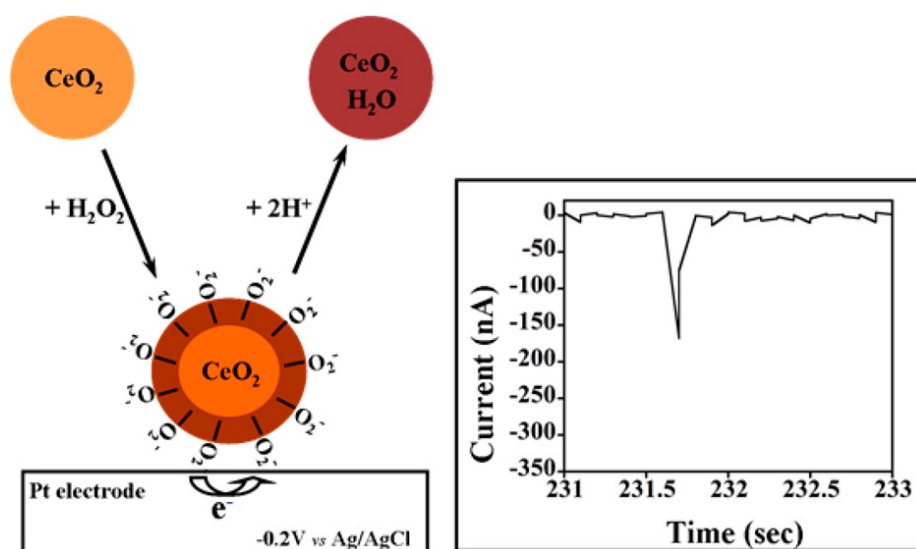


Fig 4: Schematic illustration of single CeO₂ NP collision events and the reduction current “spike” for the Ce-O₂^{•-}/O₂²⁻ NPs in contact with the Pt microelectrode ($\varphi = 125 \mu\text{m}$). Reprinted with permission from [39]. Copyright [2013] American Chemical Society.

After exposure of CeO₂ NPs to H₂O₂ which was selected as a model ROS, resulting in surface bound peroxo (O₂²⁻) and superoxo (O₂^{•-}) species, the reduction of reactive O₂^{•-}/O₂²⁻ species on the surface of nanoparticles was monitored in the collision process. The frequency of collision spikes was used as an indicator to assess the ability of these particles to bind and inactivate ROS, and to evaluate a series of commercially available CeO₂ NPs, showing a clear difference in spike frequency for the different types of particles, which was in good agreement with the antioxidant activity assessed using other conventional tests.

3.3 Electron Transfer Mediated Via Nanoparticles

Another use of the impact-method is to detect electrocatalytic processes when nanoparticles collide with an inert electrode that otherwise could not electrocatalyse the reaction. The early work in observing the particle electrocatalytic amplification was pioneered by Heyrovský [40],[41],[42],[43], and more recently by Bard's group [20],[21],[44],[45],[46] including the reduction of protons at PtNPs[44], the oxidation of hydrazine at AuNPs [22] and PtNPs [46], and the oxidation of water at IrO_xNPs [20]. The work of the Bard group has been reviewed recently[45].

A model was developed to explain the observed frequencies for two distinctive transient shapes “staircase” and “spike” type transients for electrocatalytic amplification: the “staircase” response as a result of an irreversible adsorption of the NPs with the electrode surface; “spike” responses arise when the contact time between NP and electrode is shorter. Recent studies also show that the charged NP can also be attracted on the electrode by the electric field in solution (i.e., migration) thereby causing an enhancement in the collision frequency [47].

The catalytic amplification current resulting from nanoparticle collisions also enables probing electron transfer kinetics on the surface of individual nanoparticles. Using gold and silver nanoparticles, Compton's group investigated the electron transfer kinetics of catalytic reaction at single nanoparticles. The NPs maintain contact with an electrode surface for only a short time following the collision and show a transient response to enable the current-voltage analysis of proton reduction at single silver or gold nanoparticles. The quantitative measurement of the kinetics of electron transfer at the nanoscale at individual free nanoparticles has shown to be feasible [48], as shown in Figure 5. The electron transfer kinetics results show the acceleration of proton reduction kinetics at silver nanoparticle, but not on the gold nanoparticles studied. The strategy opens a new door to quantitatively analyse protonation at individual nanoparticle which is highly beneficial for understanding the nanomaterial based energy devices [49]. In further evaluating the hydrogen evolution reaction on bare Ni and NiO microelectrodes, a kinetic acceleration has been discovered favouring NiO over Ni [50] while no catalytic size effect was found at Ni/NiO nanoparticles at the sizes studied.

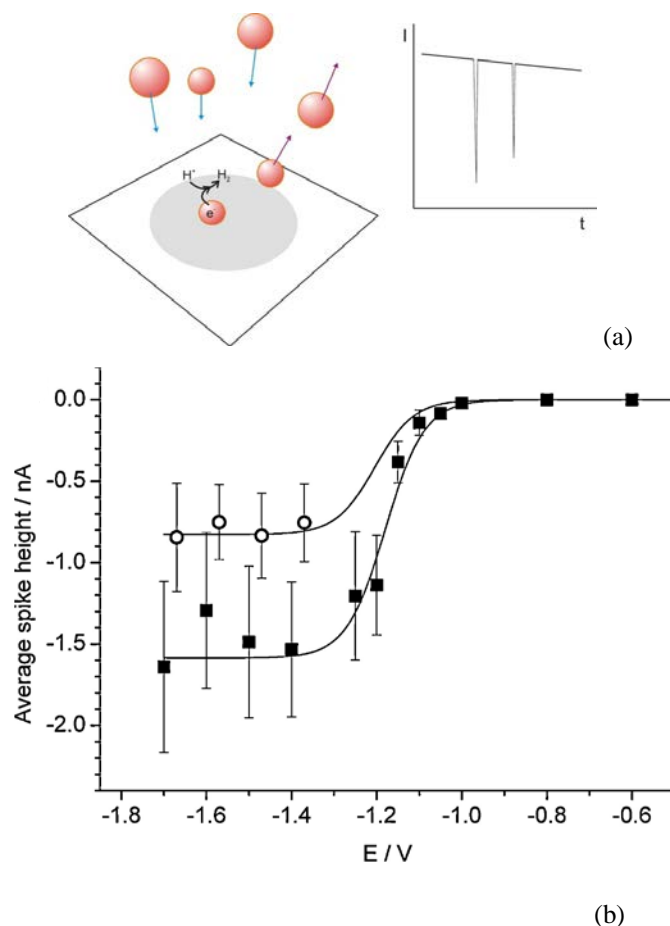


Fig 5: (a) Schematic diagram illustrating hydrogen evolution at single nanoparticles when nanoparticles collide with the substrate electrode. (b) Electron transfer kinetics at single gold nanoparticles was analysed by plotting spike height vs. potential plots for AuNPs with mean radii of 7 nm (\circ) and 15 nm (\blacksquare). Reproduced from Ref [48] with permission from Elsevier.

In earlier studies, the NP type and the indicator redox reaction were found to influence the shape and magnitude of the response for individual NP collisions[45]. The type of electrode employed in the particle collision experiment has also been claimed to show distinct electrocatalytic responses when the particle comes in contact [51],[52],[53]. By employing a Hg-modified Pt ultramicroelectrode (Hg/Pt UME) [51], size distributions and catalytic activity from single Pt NPs has been detected through an increase in current caused by electrocatalytic oxidation of N_2H_4 at the surface of the NP. The current response is a “spike” for Hg/Pt UME rather than a stepwise “staircase” response as for a Au UME, as shown in Figure 6. It was speculated here that Pt NPs are deactivated after they stick to the Hg/Pt UME so there was no NP accumulation though there is the possibility that Pt NPs bounce back into the solution.

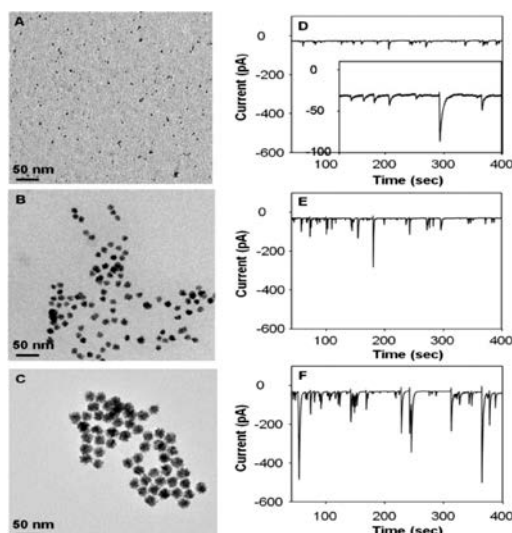


Fig 6: TEM images of Pt NP colloidal solutions containing various sizes of Pt NPs and (D–F) corresponding chronoamperometric plots for single Pt NP collisions at a Hg/Pt UME (radius 12.5 μm). Reprinted with permission from [51]. Copyright [2013] American Chemical Society.

Current amplification through nanoparticle electron transfer mediation has been employed to detect DNA[54], and applied to the photolithographically fabricated electrodes in microfluidic systems[55]. An electrocatalytic response was seen from the electrochemical oxidation of hydrazine in the presence of a target oligonucleotide (31 bases) that hybridized with both capture and detection probes to bring single Pt NPs in contact with the electrode surface, as shown in Figure 7. However, the limitation of this method is that detection of only low concentration of target (10 pM) is possible due to high background currents at higher target DNA concentrations which made it impossible distinguish the electro-catalytic current from the background.

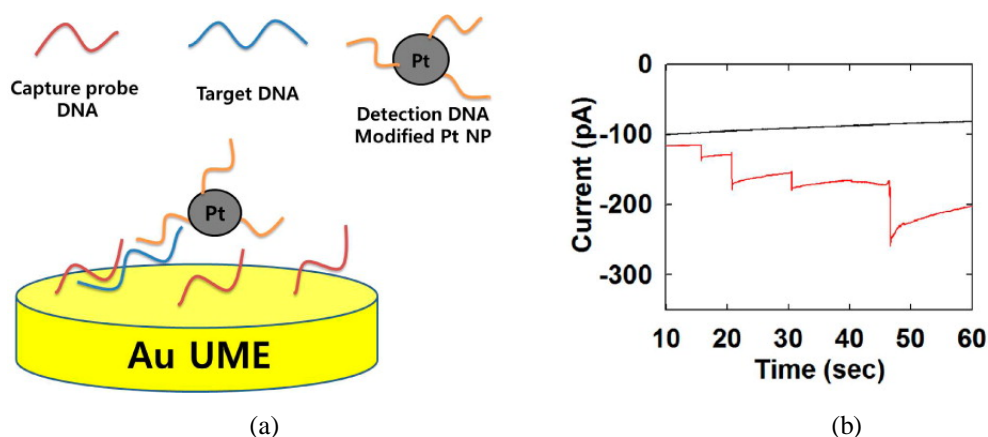


Fig 7: (a) Illustration of Sandwich-Type DNA Sensor on the Au UME (b) The single NP staircase increase of current represents the result of individual DNA-tethered Pt NPs colliding with and attaching to the UME and

existing within an electron tunneling distance with the UME surface. Reprinted with permission from [54]. Copyright [2013] American Chemical Society.

Catalytic amplification currents assist detecting NP collisions at a micrometer-scale electrode. However, deactivation of the NP for the electrocatalytic reaction (e.g., by adsorption of impurities or aggregation of NPs) can cause a decay in the current, making it difficult to model the NP current after the collision [56],[57]. In addition, during chronoamperogram recording, a typical microelectrode often shows a considerable background signal compared with the electrochemical signal from the NP reaction [58]. Recent studies have seen several new approaches towards improving the signal-noise ratio of the catalytic current. A pipet based approach to study the landing of individual AuNPs nanoparticles on TEM grid was proposed [59]. Because of the small electrode area defined by the pipet dimensions, the background current is low, allowing for the detection of minute current signals with good time resolution. Recently, the electrochemical detection of gold NP-decorated single wall carbon nanotubes attachment on a Pt nanoelectrode was demonstrated by the increase in the active electrode area, where current–time transients for ferrocenemethanol (FcMeOH) oxidation is observed[60].

Besides employing chronoamperograms to record single nanoparticle collisions, Bard's group have developed a potentiometric measurement to measure the open circuit potential of a Au ultramicroelectrode (UME) changes to monitor single nanoparticle (NP) collisions when the Pt NPs collide with the UME in a hydrazine solution[61]. The OCP changes were found to be related to the redox processes, the concentration of particles, particle size, and electrode size. The principle of electrode OCP change upon a particle collision event was investigated based on mixed potential theory using a “mimic experiment” where two different ultramicroelectrodes were brought into contact[62]. The OCP changes were found to be very sensitive to the relative ratio of the rate constant of the individual half reactions at the different materials, confirming the observations in the particle collision experiment.

Theoretical models were developed for both impacting or absorption of nanoparticles on the electrode [63],[64], showing significant differences in the impact transients, principally in terms of contact time and the likelihood that impacting NPs either rebounds or adheres to the surface. In developing new physical models to characterise the nanoparticles, the reduction of hydrogen peroxide was monitored during collisions of the nanoparticles with an inert carbon electrode giving the complete, two-electron reduction of hydrogen peroxide [65]. The current passed during each impact is shown to be quantitatively approximated to that of the diffusion-limited current at an isolated NP-sphere of radius, thereby enabling the sizing of the nanoparticles. Based on previous findings from Quinn [66], Bard's group have recently developed methods to characterise insulating particles by particle adsorption on

the electrode during collision. The individual adsorption events of silica and polystyrene spheres were detected by monitoring the blocking of redox mediator diffusion to Pt ultramicroelectrode substrates by the adsorbing spheres [67]. Each time a sphere struck the surface, a step-like decrease in the current was observed due to the their blocking of FcMeOH diffusion. The current change resulting from the blocking was correlated optical tracking of collisions revealing the motion of beads on the electrode surface following collisions, including aggregation behaviour [68], as shown in Figure 8.

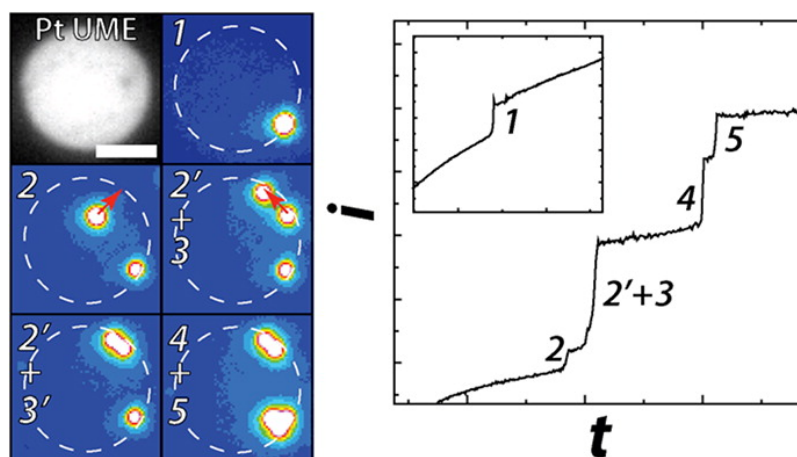


Fig 8: A series of micrographs showing bead collisions at a Pt UME (the white scale bar indicates 5 μm), and the corresponding electrochemical current steps due to the blocking of FcMeOH diffusion at the electrode during bead collisions. Reprinted with permission from [68]. Copyright [2013] American Chemical Society.

Method	NP and electrode	NP Properties studied	Redox Indicator Reaction	Ref	Year
Direct oxidation	Nickel NPs, carbon fibre microelectrode	Concentration	N/A	17	2012
Direct oxidation	Silver NPs, carbon fibre microelectrode	Aggregation Sate	N/A	19	2013
Direct oxidation	Gold NPs, carbon microelectrode	Size	N/A	24	2012
Direct oxidation	Silver NPs, carbon microelectrode	the effect of electrolyte on nanoparticles aggregation	N/A	26	2013
Direct oxidation	Gold NPs, carbon fibre microelectrode	the effect of electrolyte on nanoparticles aggregation	N/A	25	2013
Direct oxidation	Commercial Silver NPs, carbon microelectrode	Size and aggregation in seawaters	N/A	6,27	2013
Oxidation and reduction	Fe ₃ O ₄ nanoparticles, carbon fibre microelectrode	Size	N/A	28	2013
Direct reduction	Indigo organic nanoparticles, carbon microelectrode	Size	N/A	32	2013
Direct oxidation	Copper nanoparticles, carbon fibre microelectrode	Charge transfer kinetics	N/A	33	2012
Direct oxidation	silver and nickel NPs, carbon fibre microelectrode	Charge transfer kinetics	N/A	34	2012
Direct reduction	NTP on silver NPs, carbon microelectrode	Tag detection without immobilisation	N/A	18	2012
Direct reduction	NTP on silver NPs, carbon microelectrode	NPs sizing by tag reduction	N/A	38	2012
Direct oxidation	ROS on CeO ₂ NPs, Pt microelectrode	Antioxidant activity of CeO ₂ NPs by tag reduction	N/A	39	2013
Electrocatalytic	Pt NPs, Au UME	DNA detection	oxidation of hydrazine	54	2013
Electrocatalytic	Pt NPs, planar electrode	DNA detection	oxidation of hydrazine	55	2013
Electrocatalytic	Pt NPs, Pt and Au UMEs	NPs collision frequency	oxidation of hydrazine	47	2013
Electrocatalytic	Pt NPs, planar Au UME	Deactivation of the redox reaction by NPs	hydrazine oxidation	57	2013
Electrocatalytic	AuNPs, TEM grid	Landing and Catalytic Characterization of NPs	hydrazine oxidation	59	2012
Electrocatalytic	single wall carbon nanotubes, Pt nanoelectrode	Area Amplification by NPs collision	FcMeOH oxidation	60	2013
Electrocatalytic	Pt NPs, Au UME	NPs detection	hydrazine oxidation	61, 62	2013
Electrocatalytic	Au and Pt NPs, BDD ultramicroelectrodes	NPs detection	hydrazine oxidation	53	2013
Electrocatalytic	Pt NPs, Hg-modified Pt ultramicroelectrode	Sizing	hydrazine oxidation	51	2013
Electrocatalytic	Pt NPs, Hg/Pt and Bi/Pt UMEs	Deactivation of the redox reaction by NPs	hydrazine oxidation and proton reduction	52	2013
Electrocatalytic	Silica and polystyrene spheres, Pt UME	Detection of insulating particles	FcMeOH oxidation	67	2013
Electrocatalytic	Carboxyl-modified fluorescent PS beads, Pt UME	Detection of insulating particles with optical microscopy	FcMeOH oxidation	68	2013
Electrocatalytic	Silver NPs, carbon microelectrode	Detection, sizing, and simulation	reduction of hydrogen peroxide	65	2012
Electrocatalytic	Silver and gold NPs, carbon microelectrode	Electron transfer kinetics at single nanoparticles	proton reduction	48	2012
Electrocatalytic	Ni NPs, carbon fibre microdisk	Electron transfer kinetics at single nanoparticles	proton reduction	50	2013

Table 1 Summary of the latest studies (since 2012) in detection of nanoparticles using single nanoparticle collisions

4. Future Work

The use of direct oxidation/reduction, tagged nanoparticles and indirect mediated electrocatalytic shows great promise for general NP detection and characterisation strategies which are urgently required for monitoring of NPs within both health and environmental contexts. The direct oxidation/reduction of nanoparticles enables the sizing, aggregation and, kinetic studies of single nanoparticles of a wide range of types such as metal, metal oxides, organic nanoparticles. It is confidently expected that this NP detection strategy will be further extended to other types of nanoparticle which are urgently in demand to be identified and characterised. Integrated devices such as fluidics and planar electrodes fabrication would make more elegant designs which are attractive to commercial applications particularly for environmental monitoring and diagnostics in healthcare[69].

There are inherent advantages to measurements at single particle with the ability to thoroughly characterise heterogeneities in structure or reactivity that would be hidden in ensemble measurements. This requires the development of methods with higher spatial and temporal resolution, to enable heterogeneities in the catalytic activity of single nanoparticle to be measured. Recent studies on imaging the electrocatalytic activity of single nanoparticles have shown some promise [70]. Most recently, new studies have involved the optical methods to obtain the additional information from individual nanoparticles, including correlated optical tracking of collisions between insulating microbeads and an ultramicroelectrode surface to electrochemical measurements by blocking of the electrode surface[68]; applying dark-field scattering and electrochemistry to analyse the electrochemical formation of individual Ag nanoparticles at the surface of an indium tin oxide electrode[71]; detect individual semiconducting nanoparticles (NPs) using the photoelectrochemical current measured at an ultramicroelectrode[72]. It would be expected that complementing other analytical techniques, the nano-impact method will provide high spatial and temporal information from single nanoparticles.

Improvement in measurement sensitivity of the impact-method (both the direct oxidation/reduction of nanoparticles or amplification through the electrocatalytic effect) would be likely by optimising the interplay of experimental factors such as particle-electrode contact time, size and types of NP and the electrode, and selecting the desired Faradaic process, with the potential aimed at the single-particle electrochemical sensing for diverse applications[73].

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