



The use of cylindrical micro-wire electrodes for nano-impact experiments; facilitating the sub-picomolar detection of single nanoparticles



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ARTICLE INFO

Article history:

Received 13 February 2014

Received in revised form 18 March 2014

Accepted 20 March 2014

Available online 18 April 2014

Keywords:

Micro-electrode

Micro-cylinder electrode

Nanoparticle voltammetry

Detection limit

Silver nanoparticles

ABSTRACT

Electrochemical impact experiments can be used to detect and size single nanoparticles in suspension and at low concentrations. This is generally performed using a micro-disc working electrode; however, for the first time we report the use of cylindrical micro-wire electrodes for nanoparticle impact experiments. These electrodes provide much enhanced detection limits; specifically decreasing the concentration of nanoparticles measurable by over two orders of magnitude. In addition, the use of micro-wire electrodes reduces the shielding effect due to adsorption of particles to the insulating sheath that surrounds a micro-disc electrode. Micro-wire electrodes are fabricated and their electrochemical response analysed via cyclic voltammetry experiments using molecular species. This provides a theoretical framework which is used to calculate the reduced concentration of nanoparticles required for an impact experiment at a micro-cylinder electrode in comparison to the micro-disc. Experimentally, it is demonstrated that impact experiments on the micro-cylinder electrodes can indeed be used for accurate characterisation of ultra-low concentrations (≈ 0.1 pM) of silver nanoparticles.

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1. Introduction

The use of nanoparticles has rapidly expanded over recent years, leading to an increased need for their quantitative detection and characterisation in solution. This may be for environmental monitoring [1] or fundamental analysis. The properties of nanoparticles are both size and shape dependent [2], and these physical parameters can be tuned by changing the synthesis methodology [3–5]. Therefore, the need for reliable characterisation is imperative; specifically for fundamental studies, the need for detection of individual nanoparticles. Nanoparticles in a suspension often feature a diverse size distribution which may be due to the synthesis methodology and/or agglomeration effects [6–8]. Measurements based on the entire ensemble do not allow differentiation between discrete nanoparticle sizes, and hence do not provide crucial size information on the nanoparticle sample. However, single nanoparticle detection allows these variations to be analysed. There are several methods for identifying individual nanoparticles [9–12], though many of these involve the use of microscopy techniques which require the nanoparticles to be studied *ex situ*. *Ex situ*

methods are impractical for many nanoparticle research areas; for example investigations into aggregation effects, and the study of nanoparticles in environmental samples. In both these cases it is important to account for the effects of the solution media on the nanoparticles. Recently, significant work has gone towards the development of new *in situ* analytical methods for individual nanoparticle detection. Examples include both microscopy [13] and electrochemical methods. The latter of which encompasses both anodic particle coulometry [14] and resistive pulse sensing [15].

The focus of this paper will be nanoparticle impact experiments, specifically anodic particle coulometry. Here, single nanoparticles impact a microelectrode, which is held at a suitably oxidising or reducing potential, thus leading to the oxidation/reduction of impacting nanoparticles. This can be observed by an increase, ‘spike’, in the current-time response. Analysis of these individual current ‘spikes’ allows the characterisation of single nanoparticles in the solution, with the charge passed in the ‘spike’ related to the number of atoms in the nanoparticle. This method has been successfully demonstrated using silver [14], gold [16] and nickel [17,18] metal nanoparticles, as well as metal oxides [19] and organic nanoparticles [20], allowing their detection, sizing and determination of their agglomeration state [6]. Furthermore, impact experiments can be used for the study of mediated

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electrochemical reactions. Here, on contact with the working electrode surface, the nanoparticle itself can act as an electrode on which the electrochemical reaction can take place. If the electrochemical process under study occurs preferentially on the nanoparticle surface over that of the electrode, single nanoparticle collisions can be observed by the electrocatalytic amplification [21–29]. Throughout these impact experiments a microelectrode is almost involuntarily employed, providing benefits such as increased mass transport, low electrical noise and reduced capacitance [30,31]. Nevertheless, micro-disc electrodes do experience a shielding effect, which can cause perturbations in current due to absorption of particles to the surrounding insulating sheath, as discussed later.

Due to their comparatively large size, nanoparticles have fairly low diffusion coefficients. The diffusion coefficients can be estimated from the Stokes-Einstein equation [32] (assuming the nanoparticle radius is greater than 5 nm) [33], to give values of the order of magnitude $1.5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ for a 30 nm nanoparticle, where the radius is taken to be the hydrodynamic radius of the particle. A large number of total spikes are needed to allow statistically relevant analysis and thus this slow rate of diffusion experimentally results in relatively high concentrations of nanoparticles being required to ensure enough impacts with the electrode occur over the experimental time frame. For a micro-disc electrode of radius $5 \mu\text{m}$ a concentration of 15 pM of 30 nm diameter NPs would be required to detect a reasonable amount of impacts (20) [17] during a five second chronoamperogram. Therefore, there is a desire to reduce the concentration of nanoparticles required for detection. This decrease is critical for the detection of nanoparticles in the environment where typically very low concentrations would be present [34,35]. Moreover, from an analytical perspective, generally having large amounts of nanoparticles in a solution will lead to an increase in aggregation and agglomeration (aggregation is defined as the irreversible adhesion of particles, and agglomeration their reversible sticking to each other [6]). This can be minimised by careful choice of the solution medium [36], or by decreasing the nanoparticle concentration.

To date nanoparticle impact experiments have been performed using a micro-disc electrode, consisting of a thin (several microns in diameter) conducting wire surrounded by a much larger insulating glass sheath, onto which nanoparticles can adsorb throughout the experiment. However, it has recently been shown theoretically that this adsorption can significantly influence the magnitude of the observed current and decrease the number of impact 'spikes' seen [37]. One option for decreasing the concentration of nanoparticles required for impact experiments would be by the use of an array of microelectrodes. This would allow many electrode sites for nanoparticle impacts, thus allowing less nanoparticles to be present to achieve the same number of total recorded impact 'spikes'. However, this would likely encounter some of the shielding problems described above. A second option for enhanced nanoparticle detection would be the use of a cylindrical micro-wire electrode. Here, by virtue of the cylindrical electrode shape, there is a much enhanced surface area over which nanoparticle impacts can occur. In addition because the electrode will only be encapsulated at one end of the wire, any shielding effects are significantly reduced. The development and use of wire electrodes for nanoparticle impact experiments will be explored throughout this paper.

When using a wire electrode it is important to consider the wire material. In order for the micro-metre thin wire to retain its straight cylindrical shape in the solution and not bow over, it must be fairly rigid and thus have a high Young's Modulus, where Young's Modulus is given by the normal stress divided by the linear strain of the material [38]. This value is 78 GPa for gold and 168 GPa for platinum [39] and significantly higher (230 GPa [40]) for a carbon fibre

making it suitable for use as an electrode. Furthermore, carbon fibre is a less expensive and fairly electrochemically inert material and thus would be suitable for future indirect impact experiments, where the electrochemical process is required to occur preferentially on the nanoparticle over the electrode.

Herein, we report the fabrication and characterisation of carbon fibre wire electrodes and for the first time demonstrate their use for nanoparticle impact experiments. First, the fabricated micro-cylinder electrodes are analysed by considering their responses during cyclic voltammetry experiments and it shown that the results are in good agreement with those predicted theoretically [41]. Second, electrochemical impact experiments are then performed as proof-of-concept for the detection of low concentrations of nanoparticles in solution using silver nanoparticles (AgNPs). Specifically, chronoamperograms are run, and the resulting impact spikes analysed to give a size distribution of the nanoparticles. Third, this is then shown to be in good agreement with the SEM sizing of the nanoparticles; thus, demonstrating, that even at ultra-low concentrations ($\approx 0.1 \text{ pM}$) it is possible to accurately identify and size single nanoparticles using electrochemical impact experiments.

2. Experimental

2.1. Fabrication of electrodes

Cylindrical microelectrodes of approximately 1 mm in length were desired for impact experiments. First, $7.0 \mu\text{m}$ diameter carbon fibre (Goodfellow Cambridge Ltd.) was connected to a conducting metal wire using silver epoxy (RS Components Ltd.) conductive adhesive. The adhesive was set by heat treatment in an oven for 15 min at approximately 60°C . The wire was then threaded through a plastic pipette tip so that only the carbon fibre extended out of the end. The interstice between the carbon fibre/metal wire and the plastic tip was sealed using cyanoacrylate adhesive, thus preventing electrical leakage. Finally, the carbon fibre tip was cut down so that a length of approximately 1 mm protruded past the sealed pipette end.

2.2. Nanoparticle synthesis

Citrate-capped AgNPs were synthesised according to a method developed by Wan et al. [5] utilising a stepwise seeded growth method. Initially, AgNPs of nominally 4 nm diameter were synthesised as starter seeds by adding an aqueous solution of AgNO_3 (silver nitrate) and NaBH_4 (sodium borohydride) to a citrate solution at 70°C . This temperature was maintained for one hour before the solution was cooled to room temperature. The size of the NPs was confirmed to be 4 nm by transmission electron spectroscopy (TEM). These 'seed' particles were then added to a boiling citrate solution, and further amounts of AgNO_3 were added. This solution was then refluxed for 1 h, prior to cooling to room temperature. This process was repeated a total of three times. The exact size and shape of the NP was confirmed by SEM (Leo Gemini 1530, Zeiss). Here, the nanoparticles were drop cast onto a TEM grid in order to reduce the amount of AgNP agglomeration which is common on conventional SEM holders. Analysis of the SEM data showed spherical AgNPs with a radius with a mean and standard deviation of $13.6 \pm 3.7 \text{ nm}$ [36].

During the synthesis a total concentration of 3.1 mM Ag was used, providing a nanoparticle stock suspension with a concentration of 5 nM AgNPs (assuming a AgNP radius of 13.6 nm as derived from the SEM analysis). This stock suspension was diluted by a factor of one thousand and the diluted nanoparticle suspension added to the electrolyte to give a total AgNP concentration of 0.09 pM.

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