

## Single Particle Electrochemistry for Detecting Nanoparticles in Water Environments

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In the past few decades scientific interest is focused on the potential impact of nanoparticles (NPs) in human health and the environment. Naturally occurring NPs are present throughout the Earth's crust including oceans, lakes, rivers, groundwater and hydrothermal vents. NPs are also formed in the lithosphere, which is comprised of rocks, soils, magma or lava and the biosphere, which covers micro-organisms and higher organisms, including humans (Hochella *et al.*, 2015). During a single eruption event more than 30 million tonnes of ash, may be released to a height of tens of kilometres and reach the stratosphere, where volcanic ash NPs may spread worldwide and affect multiple areas for years (Ermolin *et al.*, 2018).

Further, the environment contains the so called incidental nanoparticles, *i.e.*, those that are unintentionally produced from human activities (*e.g.*, through friction and combustion processes). These particles are the by-products of human activities and generally have varying sizes and shapes. Many of the processes that generate incidental NPs are frequent activities, such as diesel engines or large-scale mining. Also, wear and corrosion processes release particles and molecular precursors to air and water, which can produce incidental NPs (Westerhoff *et al.*, 2018).

Engineered NPs, on the other hand, are a relatively new type of NPs and recent concerns have been placed that they may induce adverse environmental and human health effects. They are specifically designed and synthesised in order to be used as ingredients in commercial goods. A few examples of products containing NPs are ship paints, food, sunscreens, and cosmetics.

In aquatic systems, NPs may undergo various geochemical and biological processes and may negatively impact aquatic ecosystems (Zhao *et al.*, 2013). It is, therefore, essential to understand and investigate the fate and behaviour of NPs in the marine environment and examine their biological effects on organisms. The fate and the behaviour of NPs in sea water depends on physicochemical characteristics, such as salinity, composition, organic matter, *etc.* Microscopic and spectroscopic techniques are often used to characterise NPs. The particle size and shape, aggregation/agglomeration state, surface chemistry, chemical composition, and dissolution state are examples of key NP physicochemical characteristics.

Several state-of-the-art analytical techniques, namely, transmission electron microscopy (TEM), atomic force microscopy (AFM), and dynamic light scattering (DLS), are widely applied to characterise NPs. The advanced microscopic methods (*e.g.*, TEM, AFM, *etc.*) can generally provide accurate dimensions of NPs that are free from artefacts, but these techniques suffer from low analysis speed and high operating costs. Light scattering is strongly influenced by particle radius, aggregates contaminants (*e.g.*, dust) that might mask the signal of NPs (Solokov *et al.*, 2017). Therefore, there is a necessity for producing analytical handles for detecting and characterising engineering and natural NPs, while exploring the applicability of advanced environmental nanometrology techniques in marine water systems.

Here, we present a new detection strategy, based on the Faradaic charge transfer when NPs impact an electrode (Tschulik *et al.*, 2013). The direct detection of particle collisions at electrodes is a recent field and presents several competitive advantages over the state-of-the-art methods. It is characterised by high sensitivity, high frequency of measurements, high selectivity, ability to measure non-opaque samples, and has the potential to be developed into a portable device for conducting direct, spatially resolved measurements.

In this technique, a microelectrode is kept under suitable electrochemical control and is introduced into a suspension containing nanoparticles. When a nanoparticle arrives at the electrode due to Brownian motion, electron tunnelling between the particle and the electrode occurs. Upon contact and depending on the applied potential, an electrochemical reaction is triggered: the nanoparticle can be electrochemically reduced or oxidised, or can mediate (catalyse) a charge transfer process giving a transient current that appears as a 'spike' or a 'step' in the chronoamperometric scan (Fig. 1).

The number of atoms in the nanoparticle can be derived from the detected electrical charge using Faraday's 1<sup>st</sup> Law (the amount of charge passed through an electrode during an impact is determined by its size). The charge (Q) resulting from the oxidation or reduction of a particle impacting the electrode can be subsequently calculated from the area under the current intensity signal:

$$Q = \int I dt = ezN$$

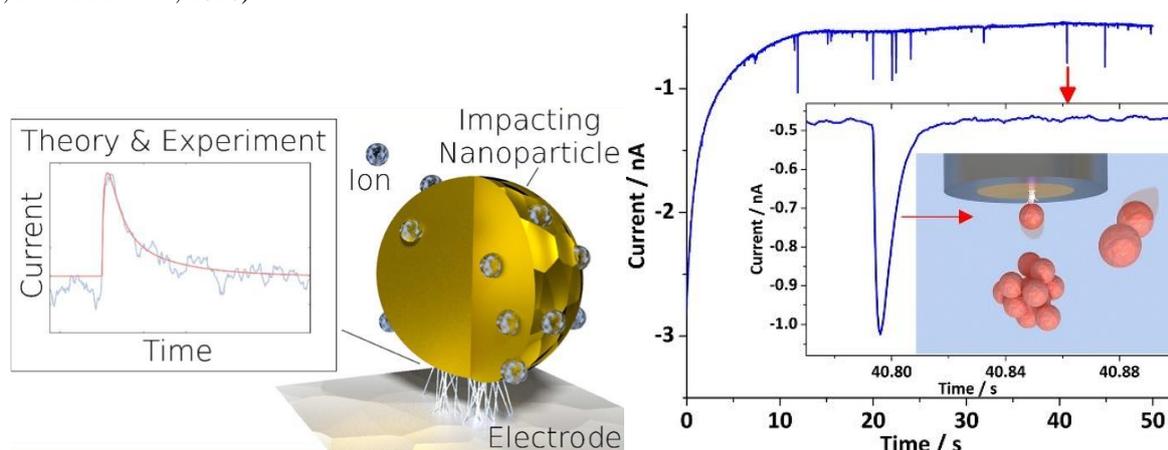
where  $I$  is the current,  $t$  the spike duration,  $e$  the electronic charge,  $z$  the average number of exchanged electrons per reduced or oxidised formula unit of the NP and  $N$  the number of reduced NP units.

Under the assumption of spherical geometry, the effective radius of the particle can be ascertained:

$$r = \sqrt[3]{\frac{3MQ}{4\pi e N_A z \rho}}$$

where  $r$  is the radius of the nanoparticle,  $M$  is the molar mass,  $F$  is the Faraday constant,  $z$  is the number of electrons

transferred per atom in the particle, and  $\rho$  is the density of the nanoparticle. Time-resolved measurements of the electrochemical signal provide information about the rate of agglomeration and/or dissolution of NPs (Tschulik *et al.*, 2013; Katelhon *et al.*, 2016).



**Figure 1. Schematic of an electron tunnelling between particle and electrode during a ‘nano-impact’ (left); A chronoamperogram recorded at a gold microelectrode with dispersed NPs at an applied potential of -0.4V (right) (Katelhon *et al.*, 2016).**

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