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Review Article

Electrochemical detection and characterization of nanoparticles: A potential tool for environmental purposes ☆

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Electrochemical detection and characterization of nanoparticles: a potential tool for environmental purposes

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This paper is dedicated to the memory of Professor Agustín Costa-García.

Abstract

The incorporation of engineered nanoparticles in commercial products and industrial processes has broadly increased in recent years, which raises concerns about their environmental impact. In this review, we present electrochemistry as a promising analytical tool towards the detection and characterization of nanoparticles for environmental purposes. Recent research has not only demonstrated the applicability of electrochemical methods for the quantification of nanoparticles in environmental samples but also for the study of properties and transformations of nanoparticles. All of these aspects are very relevant to understand their toxicity in the environment. In this context, we discuss several electrochemical methods to quantify and study the size and shape, surface properties, inter-particle interactions, chemical reactivity and speciation of nanoparticles.

Keywords: Nanoparticles, Environmental analysis, Nanoparticle properties; Nanoparticle transformations; Electrochemical detection

1. Nanomaterials in the environment – a potential risk and an analytical issue

The unique properties of nanoparticles (NPs) have proven valuable for many commercial products and industrial applications.[1,2] This has led to a significant increment in the number of end-user products containing NPs[2] which is likely to further increase in the near future. However, their extensive use raises important environmental concerns particularly related to their end-of-life phase.[3] Indeed, several studies have shown that NPs could have adverse physiological effects on cells and living organisms,[4] and, therefore, be potentially harmful to environmental ecosystems and ultimately human health.[5] While it is not clear that the concentrations of NPs currently found in the environment can actually pose a high risk,[6] there still is a substantial lack of knowledge in this area.[3] This knowledge gap combined with the expected increase of the presence of NP in natural systems in the coming years should lead to an increased effort to undertake efficient control measures. Beyond the typical dose effect (i.e. concentration dependence), a major challenge in toxicity studies of NPs is related to other intrinsic properties such as their size, shape and surface chemistry.[1] The fate of NPs in the environment, involving physical transformations, such as aggregation or agglomeration, or chemical reactivity, such as dissolution or oxidation, could also have significant implications related to their toxicity.[4]

Consequently, providing powerful analytical tools to unambiguously detect and characterize NPs is of utmost importance to improve the knowledge about their environmental risks.[5] Application of these tools to understand the fate of NPs in the environment could also be extremely useful to provide a complete picture of their toxicity and reactivity. A vast range of analytical techniques has been reported for the quantification and characterization of NPs.[7,8] However, all these techniques present some limitation that impede their use as universal tools for the monitoring of NPs in environmental samples. It is clear that a combination of techniques will be needed to elucidate all the relevant properties of NPs in the environment.

In this review, we present recent advances of electrochemical methods towards the study and detection of NPs in samples of environmental interest. While this is a narrow scientific area, electrochemistry has a strong potential to be further extended and applied in the coming years for environmental analysis of nanoparticles due to its inherent high sensitivity and the ability to survey NPs properties beyond

quantification. Since the recent literature about this specific area is limited, we have extended the scope of this review to include recent electrochemical studies of physical and chemical properties and transformations of NPs, which might play a significant role in the NPs toxicity and their associated environmental risks. The main aspects addressed in this review are summarized in **Figure 1**.

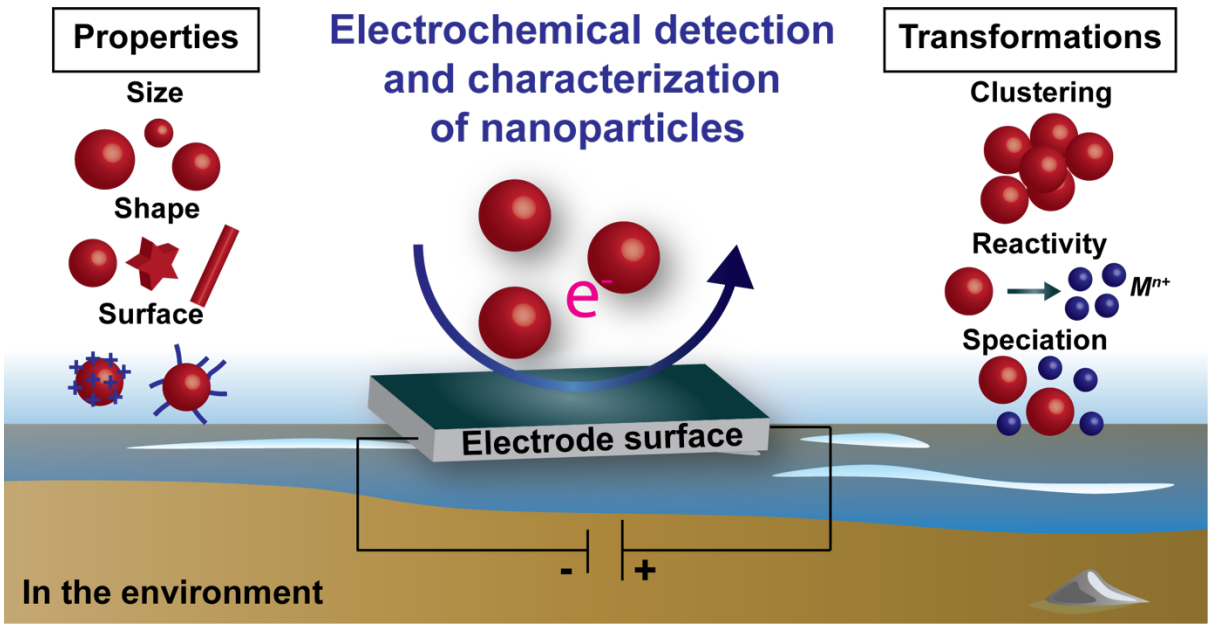

Figure 1. Schematic summary of the main topics discussed in this review involving the electrochemical detection and characterization of nanoparticles as a potential tool for environmental purposes.

2. Electrochemistry for detection and study of nanoparticles of environmental concern

Electrochemical techniques provide an efficient, fast and cost-effective alternative to conventional techniques for the detection of NPs.[9] Electrochemical instrumentation can be composed of small-sized, portable and low-cost devices, allowing decentralized analysis, which is especially suitable for *in situ* environmental analysis. Several electrochemical strategies have been proposed for the detection of NPs such as direct processes from redox-active NPs or after their pre-digestion to release electroactive species into the solution. The advent of the electrochemical nanoimpact method widened the scope to study NPs at the single-entity level.[10,11] This method is based on the direct impact of individual particles on the electrode surface, leading to current spikes in function of time, whose features

such as frequency, charge or shape can be related to the NPs' properties.[12,13] This method provides information about the properties of individual NPs in heterogeneous samples that would otherwise be masked by particle interactions in macroscopic measurements. Although electrochemical methods have been excellent to solve a vast number of environmental analytical issues,[14] they have only been scarcely employed for the detection of NPs in environmental samples. However, they have a great versatility to obtain broad information about NPs such as concentration, physicochemical properties (size, morphology or surface chemistry) and transformations (dissolution, aggregation/agglomeration, etc.), which are very relevant for environmental studies as previously stated (*vide supra*).

2.1. Electrochemical detection and quantification of nanoparticles in environmental samples

Metal nanoparticles. Several electrochemical strategies have been reported to detect and quantify metallic nanoparticles. Among these particles, silver NPs (AgNPs) are the most relevant for environmental studies due to their wide commercial use. For instance, anodic stripping voltammetry (ASV) was employed to detect AgNPs in commercial products with screen-printed electrodes (SPEs).[15] Regarding more environmentally relevant samples, a "sticky" electrode was reported to detect AgNPs in spiked natural seawater samples.[16] This device consisted of an SPE modified with cysteine that was able to immobilize AgNPs after dipping it into the sample for a short time, showing the potential of this method for *in situ* analysis. This method was also reported with other kinds of electrodes but with higher variability to immobilize AgNPs in seawater.[17] The nanoimpact method was also applied for the identification, detection and sizing of AgNPs found in commercial products at the single-entity level in environmental media (also seawater).[18] It was recently extended to other environmentally relevant media such as bottled and tap water.[19*] The detection was performed directly without any electrolyte addition, and interesting information about the aging behaviour of the AgNPs in these samples, such as their quick agglomeration in potable water, was obtained (**Figure 2**). Addition of citrate avoided the NPs agglomeration, leading to the successful detection of individual NPs in these media.

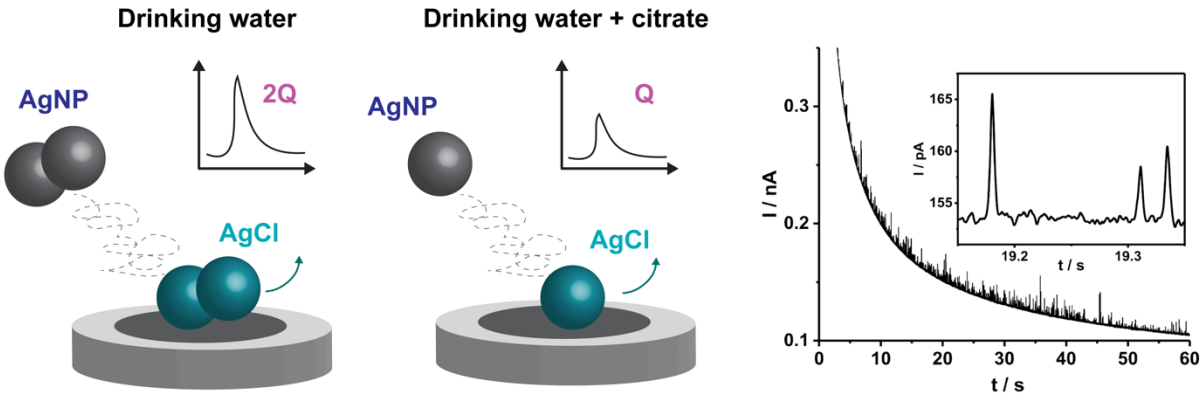

Figure 2. Schematic representation of the agglomeration of AgNPs in drinking water with improved dispersion after addition of citrate. The right part of the figure shows the current spikes resulting from collisions of AgNPs. Adapted with permission from [19]. Copyright (2019) American Chemical Society.

Metal chalcogenides. Metal chalcogenides are another group of NPs that need to be analysed in environmental samples since they are increasingly used in commercial products and many of them contain heavy metals that may reach the environment and become an important issue in the future.[20] Electrochemical detection of these NPs has been widely performed by direct ASV[21] or after acidic digestion to initially release the metal ions into the solution.[22] The latter is a better choice in terms of analytical sensitivity. This is a popular method for the determination of NPs such as HgSe (**Figure 3**), which are believed to be the ultimate metabolic product of the Hg detoxification pathway in biological systems. These NPs were detected by an oxidative digestion to release Hg^{2+} followed by ASV with gold-modified SPEs.[23*] As a proof-of-concept towards environmental applications, the HgSe NPs were successfully quantified in real seawater samples. Electrochemical methods allowing the detection of these NPs at very low concentrations would be very useful in order to monitor the possible environmental risks. Some novel methodologies to detect CdSe/ZnS NPs with excellent results in terms of sensitivity (orders of magnitude higher than the conventional digestion method) were reported. These methodologies were based on the interaction between the NPs surface and metal ions, allowing the quantification of NPs in solution without any previous acidic digestion but with extremely low limits

of detection. This was possible by discovering novel surface processes of these NPs such as selective electrodeposition of Ag[24] or their role in the stabilization of electrogenerated Cu(I) species.[25,26]

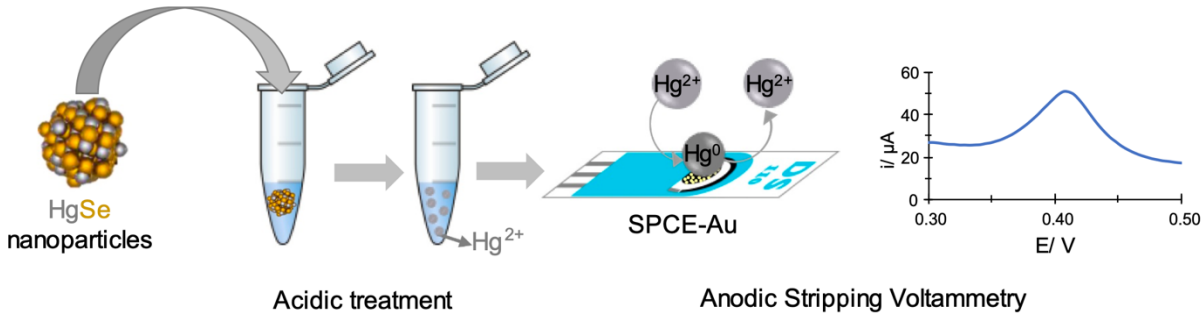

Figure 3. Schematic representation of the anodic stripping voltammetric determination of HgSe NPs through the release of Hg^{2+}. Reprinted with permission from [23]. Copyright (2019) Elsevier B.V.

Other nanoparticle materials: NPs composed of other materials with environmental relevance such as oxides can also be detected by electrochemical methods as reported for CuO NPs in different media by nanoimpacts[27*] or for CeO_x NPs exploiting their electrocatalytic activity.[28] Gold-coated membranes acting as both the electrode surface and a filter for preconcentration were successfully applied to the simultaneous detection of ZnO and Ag nanowires.[29] Integrating a pre-treatment process into the electrochemical platform could become very adequate for the analysis of environmental samples, which are usually complex matrices with very low NPs concentrations. An example of such a device was successfully applied to the detection of nanowires in spiked tap water.[29] Electrochemical detection of non-metallic NPs such as carbon-based NPs or particulate matter that may also be found in the environment have also been reported. For instance, graphene oxide NPs were detected by exploiting their electrocatalytic properties,[30,31] while the detection of nanoscale aerosol particulate matter was possible by electrochemical impedance spectroscopy using interdigitated electrodes.[32*]

2.2. Electrochemical study of nanoparticle properties with environmental interest

Size and shape. The toxicity of NPs is strongly influenced by properties such as size and shape[33] and the determination of these parameters is essential to understand possible environmental hazards.

Electrochemical sizing of CdSe NPs was reported by indirectly relating the amount of Cd in the NPs with the diameter after acidic digestion and ASV.[22] The main limitation of this approach is that the sample must have a low polydispersity since it can only provide average results. In contrast, the nanoimpact method can overcome this limitation by detecting and sizing individual NPs in a heterogeneous sample. NPs with environmental relevance such as AgNPs were successfully sized with microelectrodes[34] or even portable SPEs.[35] As discussed in the previous section, the nanoimpact method has also been successfully applied to environmental samples,[18,19*] demonstrating its possibilities not only in NPs detection and quantification but also in the determination of the NPs size distribution in seawater. The nanoimpact method also provides volumetric information of individual NPs together with size distribution, enabling the determination of their geometrical shape. This was demonstrated for quasi-spherical icosahedral-shaped AgNPs[36] or to determine the aspect ratio of anisotropic Au nanorods.[37] Additional NPs features such as the surface area-to-volume ratio are also possible to determine by measuring the conventional ASV peak potential of Au NPs by controlling the method of the NPs' assembly on the electrode.[38]

Surface properties. Surface properties of NPs could also play a role in their toxicity and reactivity leading to further environmental issues, but they could also be used for selective detection of NPs. For instance, positively charged carbon NPs induced a strong electrocatalytic effect on ascorbic acid oxidation that was not observed for negatively charged NPs.[39] In addition, a possible way to distinguish natural from engineered NPs in environmental samples could be the detection of specific coatings only available in engineered NPs such as gallic acid-capped Au NPs[40*], which were detected in natural waters by redox-active coating. Interaction and pre-concentration of heavy metals with NPs surfaces acting as sorbents could potentially increase the environmental risks. Nanoimpact stochastic electrochemistry was also successfully reported to study the reactivity, speciation and loading of As on individual CeO_2 NPs,[41] even allowing the quantification of As^{3+} concentrations in spiked river waters since the frequency of the NPs collisions was proportional to this parameter.

2.3. Electrochemical study of nanoparticle transformations with environmental interest

A further step to understand the fate of NPs in the environment is the study of their possible physical and chemical transformations. These interactions and transformations are largely unknown, but electrochemical methods could be useful to understand some of these processes.

Inter-particle interactions. Inter-particle interactions such as cluster formation, agglomeration and aggregation processes can affect NPs reactivity and distribution in the environment.[42] The main findings from electrochemical studies of NPs clustering revealed that aggregation of NPs may lead to incomplete stripping,[43,44] is strongly affected by interactions of the NPs double layer [45], depends on NPs size[46] and the presence of metal ions can induce cluster formation and agglomeration.[47] The nanoimpact method was also able to differentiate between aggregation (irreversible) and agglomeration (reversible) [48], which is very challenging with conventional techniques such as electron microscopy.

Electro-dissolution / surface oxidation. In general, dissolution or surface oxidation of NPs occurring in the environment are inherent redox processes, which could be effectively studied by electrochemical techniques. Several studies have shown that the electro-dissolution of NPs strongly depends on electrolyte media.[49,50] The formation of an oxide layer on the NPs surface has been observed as an initial stage of electro-dissolution,[51] and its heterogeneity may affect the subsequent dissolution (**Figure 4**).[52]

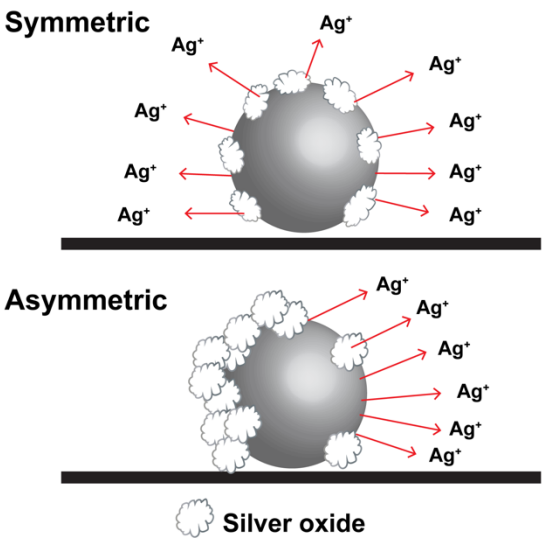

Figure 4. Scheme showing how the properties of the oxide layer formed on AgNPs influences the electro-dissolution process. Adapted with permission from [52]. Copyright (2018) American Chemical Society.

Speciation. Complementary to the last topic on NPs dissolution, speciation studies that focus on discrimination of NPs and ions are important in environmental studies since in some cases the ions could be more hazardous to living organisms than the original NPs themselves. Electrochemical studies of speciation have been reported such as the selective detection of AgNPs in presence of Ag^+ by tuning the chemical or electrostatic interaction of these species with modified electrode surfaces[53] or the selective detection of Ag^+ in presence of AgNPs in commercial products.[54**]

Conclusions and outlook

The widespread use of nanotechnology may provide great advances and benefits to society, but it also entails unknown environmental risks that must be addressed to preserve a sustainable world. There is a lack of quantitative knowledge and appropriate analytical methods for detection and characterization of NPs in the environment. Electrochemistry can play an important role in the future as a quick and cost-effective tool since it can provide information about concentrations but also about physical and chemical properties and transformations of NPs. However, electrochemistry, or any other analytical technique, has scarcely been employed for monitoring NPs in environmental samples. Many challenges remain to be solved in order to overcome the inherent difficulties of detecting NPs in complex natural media. For instance, there is not enough data on environmental concentrations, and are usually found in very low amounts in these samples. The absence of standard analytical methods and certified reference materials are also problematic to validate newly developed methods. Differentiation of natural versus engineered NPs and the opaque and dynamic market of commercial products give rise to new difficulties for NPs detection and characterization in the environment. In conclusion, there are still many issues to be solved to equip the world with analytical tools able to monitor NPs in the environment. This will be a major

challenge for the Analytical Chemistry community in the coming years and will likely involve an effective collaboration between different techniques and scientific fields.

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**54: This work shows the successful quantification of released Ag^+ ions in presence of Ag NPs. This kind of chemical speciation is very relevant for environmental studies since the toxicity of ions and NPs can be different. In addition, just a few analytical techniques are able to discriminate both species without previous separation.