Impact Electrochemistry: Measuring Individual Nanoparticles

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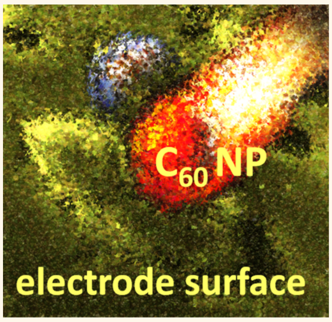
ABSTRACT While the electrochemistry of redox-active ions or molecules has been studied for decades, the electrochemistry of individual nanoparticles remains largely unexplored. In this issue of *ACS Nano*, Stuart *et al.* report the direct electrochemical detection of impacting carbon C_{60} nanoparticles in a non-aqueous solution. This study opens up the possibility of detecting and counting various redox-active inorganic, organic, and carbon-based nanoparticles, one by one, in colloids and suspensions by a simple and highly sensitive technique. The method developed by Stuart *et al.* enables the determination of the type, size, and concentration of the nanoparticles. One can foresee a wide scope of potential applications, ranging from the environmental monitoring of nanoparticles to the detection of self-propelled autonomous nano- and micromachines.



When an ion or molecule impacts an electrode surface that has an electrode potential large enough to initiate an oxidation/reduction process of the ion or molecule, one may think that electrons are sent flying everywhere, but, in fact, electrons are transferred from/to the corresponding ionic/molecular orbitals. Such an exciting event is often more prosaically called electrochemistry. By looking at the electrode potential at which the event occurred, one can infer the type of ion or molecule involved because the oxidation/reduction process happens at an exactly defined potential. By further measuring the number of electrons exchanged, the amount of impacted ions/molecules can be deduced. This has indeed been the basic concept of electroanalytical methods for decades.[1] We can measure the electric current and charge exchanged during such events with such high precision that the most fundamental chemical constant, the Avogadro constant, can be determined very precisely by the measurement of the electric charge that passes through during the electrochemical dissolution of a bulk amount of silver.

Nanoparticles (NPs) and quantum dots (QDs) are broadly defined as materials exhibiting properties in between those of discrete molecules and bulk materials. In this issue of *ACS Nano*, Stuart *et al.* describe a method for the exact size determination of individual carbon C_{60} NPs in a colloidal solution.[2] In their work, a constant potential was applied to a gold electrode surface while its current was recorded as a function of time. In the presence of carbon C_{60} NPs and by applying an adequate electrode potential capable of driving a one-electron reduction process of C_{60} NPs, strange spikes (or noises) on the recorded current−time ($I-t$) plot were observed (Figure 1A). These spikes were neither equipment-based noises nor artifacts but were well-defined events of C_{60} NPs impacting on the gold electrode surface. The area of a spike (in $I-t$ coordinates) is equal to the amount of electric charge exchanged between the electrode surface and a C_{60} nanocluster from which one can thus exactly deduce the number of molecules (C_{60}) in the nanocluster (Figure 1B,C). This study[2] is an important extension of previous work on impact electrochemistry of metallic NPs. One can, in principle, measure

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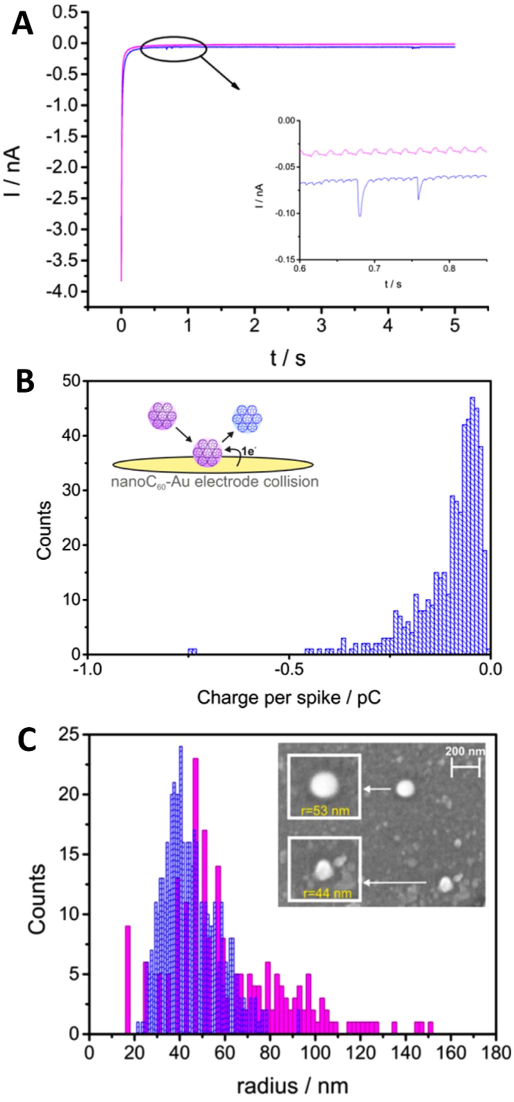

Figure 1. Electrochemistry of the individual C_{60} nanoparticles (NPs). (A) Chronoamperogram for a gold electrode immersed in buffered acetonitrile solution containing C_{60} NPs. The pink line is recorded at a potential at which electrochemical reduction cannot take place (there is no electron transfer to the C_{60} NPs); the blue line is recorded below the reduction potential of C_{60} where electron transfer to C_{60} NP does take place and spikes are seen in the magnified inset. (B) Charge distribution with a bin size of 0.01 pC for the one-electron reduction of C_{60} NPs impacting a gold microelectrode in buffered acetonitrile. (C) From the charge transferred, one can infer the size distribution, scanning electron microscope image of C_{60} NPs shown in inset. Adapted from ref 2. Copyright 2014 American Chemical Society.

the size, composition, and concentration of NPs as well as their proportions of mixtures in a solution with the highest precision. This is of immense importance for environmental monitoring, for example, because the widespread use of NPs and QDs in commercial products means that they are often eventually released into the environment.

Although one may initially view the electrochemistry of individual NPs as classical electrochemistry of ions or molecules, there are nevertheless important differences. Upon electrochemical reduction/oxidation, electrons are not simply transferred to the corresponding molecular or ionic orbitals but are instead transferred to/from the electronic levels of the NPs.[3] Thus, the electrochemical potential of the oxidation/reduction may depend on the NP size and crystal lattice structure. It was observed that smaller particles undergo reduction at lower potentials.[3] In some ways, this is similar to the distinct fluorescence properties for NPs made up of the same material but of different sizes.

Back to the Future. Historically, there were attempts to analyze particle suspensions electrochemically;[4] electrochemistry of stable colloidal solutions of polydispersed NPs were studied about two decades ago by Heyrovský.[3] Even though the electrochemistry of the individual NPs was neither accessed nor studied in these early works, it was deduced from the electrochemical response that the voltammogram (*i.e.*, a plot of current *vs* voltage) of the colloids was actually the sum of individual reduction events of those particles of different sizes.[3] Other studies by Heyrovský *et al.* involved metal oxide semiconducting NPs, such as TiO_2, SnO_2, or Fe_2O_3, where signals were generated by the electrocatalytic proton reduction to hydrogen at the electrode surface upon impact.[5,6] Later studies by the same authors investigated the electrochemical behaviors of metallic (Al, Fe, Ni, Cu, Mo, and W) NPs covered by thin layers of their corresponding hydroxides.[7] They observed significant spikes in the voltammograms and attributed them to the distinct impacts of individual NPs (or their clusters) on the surface of a mercury electrode. Even though Heyrovský did not eventually study the impact of individual NPs, he reported two phenomena in his work that are used today in order to track individual impacts of NPs on the electrode surface; that is, one can (i) indirectly observe an event of impact if the NP material is able to catalyze the redox reaction of a selected electrochemical probe present in the solution (*i.e.*, hydrazine oxidation or hydrogen evolution) or (ii) directly oxidize/reduce the NP as it approaches the surface of the electrode (Figure 2).

Indirect Detection of Individual Impacting Nanoparticles. The indirect visualization of individual NPs was first implemented by Xiao and Bard.[8] Such visualization was based on a setup

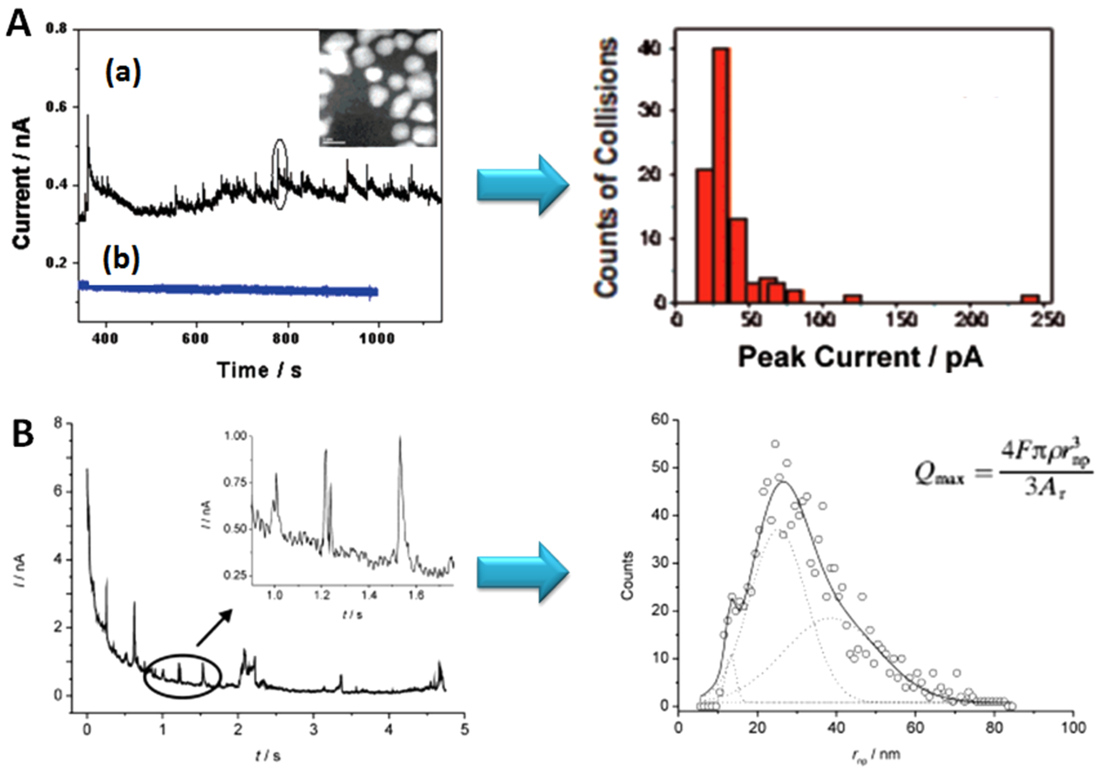

Figure 2. Two fundamentally different ways of detecting individual impacting nanoparticles (NPs) at the electrode surfaces. (A) Indirect detection *via* electrocatalytic reduction/oxidation of signaling molecules in the solution. On the left panel is shown the current transients at a carbon fiber electrode in the absence (blue) and presence (black) of Pt citrate NPs. Signaling redox reaction is reduction of H^+ presented in the buffer upon impact of Pt NP to H_2. Right panel: Statistics of number of collisions *versus* their peak currents. Reprinted from ref 8. Copyright 2007 American Chemical Society. (B) Direct electrochemical detection and characterization of Ag NPs in aqueous solution. Left panel: Chronoamperometric profiles showing oxidative Faradaic collisions of Ag NPs in citrate solution. The inset shows detailed impact spikes. Right panel: Distribution of NP radii inferred from Q by equation (inset) with deconvolution. Reprinted with permission from ref 12. Copyright 2011 Wiley-VCH Verlag GmbH & Co.

that primarily traced the generated current by signaling molecules dissolved in a solution. While the detection electrode is not catalytic toward the oxidation/reduction of the signaling molecules, the material of the impacting nanoparticle is catalytic (Figure 2A). As previously mentioned, this strategy was first conceptualized in Heyrovský's work. The first experimental study was carried out at a carbon electrode indirectly detecting individual impacting Pt NPs *via* the reduction of signaling H^+ to H_2, in which Pt is an excellent electrocatalyst.[8] The frequency of the impacts was related to the concentration of the NPs, while the concentration of the signaling molecules influenced the amplitude of the catalytic signals. In later work, the same authors attempted to correlate the size of the impacting NPs. This concept was subsequently extended to other types of NP materials and their corresponding signaling molecules, for example, by exploiting the oxidation of water or N_2H_4.[9,10] Typical NP materials that can be detected with this method are Pt, Au, or IrO_x NPs.[9] Note that individual NP catalytic signals typically last for ~1 s, and therefore, it is easy to reach the saturation point of the resolution of the method. In some cases where the NPs stick to the surface of the electrode, "staircase" signals are obtained instead of "spike" signals since the stuck NPs generate electrocatalytic currents consistently.[11] As such, even though the indirect detection of individual impacting NPs is popular, it often suffers from the indirect and unclear correlation between the NPs' size distribution and the obtained signal intensity.

Direct Detection of Impacting Nanoparticles. Instead of detecting nanoparticles indirectly by their electrocatalytic effect on an otherwise noncatalytic electrode surface, Compton and coworkers brought to life an important concept of direct electrochemical detection of metal and metal oxide nanoparticles. The first work was based on the oxidation of impacting individual Ag NPs at an electrode surface;[12] colloidal silver nanoparticles were oxidized upon their diffusion-driven impact on the electrode surface, producing "spikes" from which the calculated electric charge can determine the number of atoms and thus the size of the impacted NP (Figure 2B). The electrochemical detection method is much faster than the indirect "electrocatalytic" detection, as it lasts in the range of 1–10 ms. It has been shown theoretically that impacted NPs are completely oxidized during that short period of collisions and that partial oxidation is very unlikely.[13] The method can be expanded to any metal or metal oxide NPs capable of undergoing redox reactions on the electrode surface, such as Ag, Ni, Fe_2O_3, *etc.*[14,15] More importantly, based on the potential at which the redox reaction takes place, one not only can determine the size of the impacting individual NP (from the area of the "spike") and concentration of the NPs in the colloid (from the frequency of the "spikes") but also can infer the material of which the NP is composed. The work by Compton's group has further shed light on the fact that it is possible to detect directly both individual impacting metal or metal oxide nanoparticles and polymer nanoparticles.[16] Such insights opened up the field of electrochemical detection of individual impacting nanoparticles to a wide spectrum of materials. In the work by Compton's group published in this issue of *ACS Nano*, the scope of detection is further extended to carbon C_{60} nanoclusters in non-aqueous media.[2] These C_{60} nanoclusters undergo electrochemical reduction at determined electrode potentials upon impact with the electrode surface (Figure 1). This is a significant milestone because the voltammetry for the direct impact of individual carbon nanoparticles (carbon nanotubes, graphite, graphene, and graphene oxide) on an electrode surface has not previously been reported. This work is of great importance because detection of carbon particles is generally regarded as challenging.[17]

OUTLOOK AND FUTURE DIRECTIONS

The work by Stuart *et al.*[2] opens up the possibility of studying a variety of carbon nanomaterials, such as graphene nanoparticles and quantum dots; electrochemically studying the diffusion of the colloidal nanoparticles in different solvents; and carrying out the analytical determination of these nanoparticles. Given the increasing widespread release of metallic and carbon nanomaterials into the environment due to their incorporation in commercial products, the immediate detection capability of electrochemical methods in performing highly automated, cost-effective, and rapid screening has provided hope for the development of a much needed point-of-care environmental monitoring system.[18] The next logical step forward would be to implement the detection of individual impacting nanoparticles in microfluidic systems, where so far only groups of the impacting nanoparticles have been targeted.[19] A direct electrochemical monitoring for the motions of autonomous metallic micro/nanomotors is another area where this technique can show great potential.[20]

Conflict of Interest: The authors declare no competing financial interest.

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