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Single Entity Electrochemistry and Photoelectrochemistry of Semiconducting Nanoparticles

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Abstract

Semiconducting nanoparticles (SC NPs) are essential in a variety of new technical applications such as optoelectronic devices, sensors, and catalysts. Recent study on the single entity electrochemistry and photoelectrochemistry of SC NPs is a fascinating subject that has grown in popularity in recent years. The nano-impact approach opens up new avenues for researching electron transfer mechanisms at the single particle level and allows for the discovery of intrinsic (photo) electrochemical activities of SC NPs. In this paper, we present a review of recent research on the electrochemistry and photoelectrochemistry of single SC NPs using the nano-impact approach. The first topics covered are the redox reactions and electrocatalysis of single metal oxide semiconductor (MOS) NPs and chalcogenide quantum dots (QDs). Following that, the photoelectrochemistry of single SC NPs such as TiO_2 and ZnO NPs is summarised. The important discoveries and problems for each issue are emphasised, as are our thoughts on future study areas.

***Keywords:* Photoelectrochemistry; Electrocatalysis**

Introduction

Semiconductor nanomaterials are gaining popularity due to their superior physical and chemical properties when compared to bulk counterparts, such as continuous absorption bands, narrow and intense emission spectra, high chemical and photo-bleaching stability, processability, and surface functionality, which make them suitable candidates in single electron devices, sensors, imaging devices, solar cells, nano-electronics, optoelectronic devices, and memorabilia. Understanding the mechanism and kinetics of the essential processes in their applications requires electrochemical and photo-electrochemical research of semiconductor nanoparticles. When studying the (photo) electrochemistry of nanomaterials, macroscopic (ensemble) data are still primarily employed to infer the underlying microscopic processes. However, this is not always obvious or completely represented. Polydispersity, variable particle orientations, the production of the probable agglomerated and uneven "mat" associated with the dropcast process, and other phenomena that make the data difficult to understand may emerge from a huge population of nanoparticles. To get a better mechanistic knowledge of the electrochemical and photo-electrochemical reactivity of nanomaterials, methods for studying electron transfer events on single redox nanomaterials and individual catalytic entities must be developed. The "nano-impact" technique (or particle-electrode impacts) is one of these developing methodologies, which is realising an

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altogether new way of researching nanoparticles, their reactivity, and catalytic capabilities, revolutionising the science of nano-chemistry. The "nano-impact" method, which is caused by Brownian collisions of NPs with an electrode held at a suitable potential, allows NPs to be individually electro-reduced or oxidised, or to mediate (catalyse) charge transfer processes that are not viable on the microelectrode itself under the conditions of study. This powerful electrochemical technique has found great success in providing insights into the fundamental study of nanoparticles: not only basic particle characterization (e.g., sizing, concentration, chemical identity, agglomeration/aggregation state, porosity), but also in-depth understanding at single-particle levels for the mechanisms and dynamics of (photo) electrochemical processes of interest.

Since Lemay's paper in 2004, when the collision of single latex microspheres on (ultramicroelectrode) UMEs was explored, the stochastic electrochemistry "nano-impact" has been born. Early efforts on insulating and metallic NPs include those by Quinn, 2004 and Xiao and Bard, 2007. The impetus for studying semiconducting (SC) NPs stems from a desire to investigate photoelectrochemical currents in SC nanostructures for energy conversion. Since then, single entity investigations on semiconducting materials such as metal oxides and quantum dots have been carried out. The primary purpose of single SC (photo) electrochemistry research is to comprehend the net (photo) electrochemistry catalytic process at the single particle level and to establish the instinct activity-structure link. Furthermore, the mechanistic analysis of individual NPs' (photo) electrochemistry will help to comprehend and eventually govern charge transfer at the nanoscale. Although various publications and reviews summarised single SC photo-electrochemistry, their electrochemical redox behaviour and electro-catalytical activities were not thoroughly described. As a result, the short review's primary goal is to provide insight into the electrochemistry and photoelectrochemistry of single semiconducting nanoparticles.

Electrochemistry of Semiconducting Nanoparticles as a Single Entity

Metal Oxide Nanoparticle Single Entity Electrochemistry

Metal Oxide Semiconductors (MOS) are a popular form of semiconducting material due to its morphological plasticity, chemical stability, physicochemical interfacial qualities, and ability to mix in composite structures. The early electrochemical investigations on MOS often focus on the average behaviour via ensemble measurements at a few mm in diameter macroelectrode, some of which involve the simultaneous contact of suspended colloids with the electrode surface. Heyrovsky, for example, explored polarography and voltammetry of aqueous SnO_2 and TiO_2 suspensions in 1995. Although collision and adsorption of nanoparticles can occur on a macroelectrode, the extremely high collision frequencies and massive background signals associated with the vast electrode surface make it difficult to individually resolve the collision events. The use of a microelectrode reduces both the collision frequency and the baseline noise, resulting in unambiguous resolution of single impact events. Understanding the property and activity of single MOS are garnering increased interest as a result of the development of this nano-impact technology. The electrochemical behaviour of single MOS such as IrO_x, Fe_2O_3, Fe_3O_4, CeO_2, CuO, Co_3O_4, TiO_2, ZnO, and $CoFe_2O_4$ has been studied in recent years using the nano-impact approach. The specific study concerns are primarily concerned with two aspects: electrochemical redox behaviour and electrocatalysis of single MOS, which are described and explained in the following paragraphs. For a direct kind of nano-impact, the nanoparticles are typically fully oxidised (or reduced), allowing for quantitative electrolysis of the nanoparticles. The charge (Coulombs) acquired by integrating the current transients reflects the number of atoms (or molecules) in the nanoparticle, indicating its size (through Faraday's first Law). A huge number of current spikes may be monitored quickly and inexpensively, yielding a particle size distribution. With appropriately sensitive home-built yet affordable equipment, the approach can size nanoparticles as tiny as 5 nm. In addition to sizing nanoparticles, the nano-impact approach may also estimate their concentration by measuring the frequency of observed impacts. Furthermore, the potentials at which current spikes appear are clearly tied to the chemical identity of the nanoparticles, and recent work has demonstrated that it is capable of measuring particle agglomeration/aggregation states as well as particle porosity. Direct nano-impact research on MOS now focus mostly on the redox behaviour of the MOS itself Fe_3O_4, ZnO, and CuO, as well as the MOS surface-bound with electroactive species CeO_2, TiO_2.

Scientists performed cathodic and anodic impact studies on Fe_3O_4 nanoparticles, revealing two separate approaches to electrochemical particle size. Furthermore, individual Fe_3O_4 NPs were studied in the presence and absence of a magnetic field, and a considerable magnetic field-induced aggregation of NPs was detected in the presence of a magnetic field. More intriguingly, dissolution of Fe_3O_4 NPs is severely impeded in a magnetic field; this is most likely owing to the magnetic field gradient force trapping the generated Fe^{2+} ions near the NP surface and so impeding mass-transport driven NP dissolution. Scientists used reductive impact studies to obtain electrochemical sizing for Fe_2O_3 NPs. The initial electron transfer mechanism is discovered to be the rate determining step in the reductive dissolution of nanoparticles, and the interfacial proton concentration has a significant influence on the whole process. A further study confirmed the quick and reversible agglomeration/dis-agglomeration process of Fe_2O_3 NPs, paving the path for future research into the agglomeration equilibrium of mineral nanoparticles in aquatic environments. Perera examined the impact experiments of ZnO nanoparticles (NPs) and achieved the measurement of the ZnO NPs' redox potential. The formal potential is shown to be a substantial function of NP size (1/r), since smaller NPs are less stable than bigger ones and hence more easily reduced. Karunathilake presented on new insights into the reduction kinetics and mass transport of ZnO single entities. Zampardi recently used the nano-impact method to investigate the electrochemical behaviour of single copper oxide nanoparticles in the presence of anionic species (Cl and NO_3) commonly found in real water media to better understand the environmental fate of CuO nanoparticles and correctly assess their toxicity. The feasibility of detecting nanoparticles in real-world medium is proven.

In addition to the redox behaviour of single MOS, the redox behaviour of MOS absorbed with active species has been studied at the single particle level. Sardesai used the nano-impact method to study the decrease of surface bound oxygen species on single CeO_2 NPs as well as the antioxidant activity of CeO_2 NPs in a simple, quick, and low-cost way. Recently, the oxidation and reduction of As^{3+} loaded CeO_2 NPs utilising collision electrochemistry was described, with the greatest spike frequency at pH 8 indicating maximal adsorption capacity. The concentration of As in solution was calculated using the observed charge and peak current, as well as the spike frequency. Furthermore, based on the reduction of the adsorbed dye molecules, the nano-impact is used to investigate the degree of cluster formation of Alizarin Red S modified rutile (TiO_2) nanoparticles. Lin and Compton quantified the adsorbed catechol on single Al_2O_3 particles, and the individual impact spikes caused by catechol oxidation were modelled to estimate the charge diffusion coefficient over the particle surface. More redox active species, such as catechol, anthraquinone, chloranil, and poly (vinyl ferrocene), were also absorbed by alumina particles, and their surface coverages and charge diffusion coefficients were calculated.

The study of single MOS redox behaviour and their absorption of redox active species reveals more precise physiochemical parameters for both the MOS and the adsorbed redox species. In addition to the direct redox reaction of the nanoparticles, mediated (indirect) electron transfer can occur on the surface of hitting nanoparticles. Transient current increases may be detected when catalytically active nanoparticles collide with an inert microelectrode in a solution containing redox molecules due to heightened catalytic activity on nanoparticle surfaces. The current response to these collisions can take one of two main forms: a current spike or a current step, depending on a few complicated elements including the residence duration of the hitting catalytic nanoparticles on the electrode surface and the nanoparticle deactivation time. If the nanoparticle desorption or deactivation is relatively slow in comparison to the experimental time, a "step on" in the current-time response is detected, otherwise a "spike" is achieved. Some important applications of facilitated electron transfer for MOS have been documented, including IrO_x, Fe_2O_3, Co_3O_4, and $CoFe_2O_4$ NPs. The first research on MOS-mediated effects indicated increased current transients from the electrocatalysis of individual impacting IrO_x NPs toward the Oxygen Evolution Process (OER). Instead of a continuous response, a current decline was detected, and the resultant current was shown to be very sensitive to the material and surface condition of the electrode utilise. The current transients from hydrogen peroxide oxidation at a single IrO_x NP, when combined with microscopic research, help to uncover the causes of catalytic NP deactivation and the parameters influencing collision dynamics. Xie recently demonstrated water oxidation on single Co_3O_4 nanoparticles, proposing a process involving hydrogen peroxide as the first oxidation product of electron transfer and subsequent breakdown to create dioxygen. Single particle electrocatalysis identifies the rate-determining step as well as the reaction's limiting kinetics. El Arrassi studied the OER on single $CoFe_2O_4$ NPs and discovered that the current density at single nanoparticle studies may reach several kAm^2. The steady-state current study further shows that the electrocatalytic activity is restricted by the diffusion of generated oxygen away from the particle, revealing fresh insights into the intrinsic activities of nanocatalysts. The nano-impact approach has been used to explore the single entity electrochemistry of MOS, which includes the redox behaviour and electrocatalysis of single MOS. The latter has demonstrated the capacity to expose essential physiochemical features of nanoparticles (sizing, concentration, agglomeration/aggregation state) as well as give a comprehensive knowledge of the mechanisms and dynamics of electrochemical events at the nanoscale. However, additional research into the redox behaviour of single MOS in complex aqueous environments is necessary before realising in-situ electrochemical determination and analysis of solution phase MOS in a real-world setting. To better understand the underlying mechanism and kinetics of the essential processes, single entity electrocatalysis should be extended to additional metal oxide based electro-catalysts.

Single Entity Electrochemistry of Semiconducting Quantum Dots

Semiconducting Quantum Dots (QDs), particularly chalcogenide QDs, have unique optical and electrical features such as limited emission absorption and excellent photo-stability, making them more useful in optoelectronic devices, catalysis, bio-labeling lasers, sensors, LEDs, and photovoltaics. The study of single entity electrochemistry of QDs began lately with the publication of

CdSe/CdS QDs by Alshalfouh, 2019. Electrochemical impact measurements were performed in conjunction with fluorescence correlation spectroscopy (FCS) to better understand the reactivity and dynamics of CdSe/CdS QDs at a Pt microelectrode surface. The latter had a diameter of around 1 m to match the size of the optical observation volume. The oxidation of CdSe/CdS QDs with negatively charged shells was studied using cyclic voltammetry. Significantly, it is discovered that electro-oxidized QDs may still produce light even when the emission lifetime diminishes. Unlike the frequently reported metal NPs in single collision experiments, additional collision events are likely necessary for a tiny QD to undergo a full anodic breakdown, according to this paper. Multiple collision occurrences are necessary for a QD to have a full anodic breakdown, according to this paper. Furthermore, Wang recently showed the intrinsic electrocatalytic activity of single MoS_2 quantum dots (QDs) toward HER. The current responses observed at silver and carbon ultramicroelectrodes (UMEs) were recorded separately. At Ag UMEs, current "spikes" with substantially greater current intensity are found, whereas "steps" are produced at C UMEs, revealing the effect of the substrate-MoS_2 interface on HER activity. The reason for the scarcity of publications on the electrochemistry of single QDs is likely attributable to the following factors: The small size of the QDs (a few nanometers in diameter) makes electrochemical detection with current low-noise potentiostats more difficult; the semiconducting nature of the QDs complicates the electron transfer process more than metal nanoparticles; and the surface chemistry of the QDs imposed uncertainties to the collision process with the electrode surface.

Photoelectrochemistry of Semiconducting Nanoparticles as a Single Entity

Semiconductor photoelectrochemistry is concerned with the conversion of solar energy to electricity or chemical fuels and focuses on photo-driven reactions at solid/liquid interfaces. The principles of SC nanomaterials, such as charge carrier production, separation, transport, and notably interfacial charge transfer at heterogeneous nanoscale interfaces, must be elucidated in order to realise practical energy conversion applications. So far, single entity photoelectrochemistry has been described for colloidal bared and sensitised TiO_2 and ZnO NPs. To measure the stochastic photoelectrochemical currents of individual anatase TiO_2 nanoparticles, Fernando used the nano-impact technique. It was stated that the current phases for NP suspension under illumination in MeCN were not detected, however the steps emerged in MeOH. This is because NPs emit valence-band holes that oxidise MeOH when illuminated. They also explored the photoelectrochemical behaviour of NPs of varying diameters and observed that collisions resulting in a current step may be lower for semiconductor NPs than metal NPs (Fernando, 2013). Furthermore, adding a dye has been shown to boost detection sensitivity. Barakoti. specifically reported the study of dye-sensitized nanoparticles and their agglomerates with stochastic electrochemistry, and under illumination the cathodic steps are observed due to the photo-oxidation of the dye, which injects electrons into the TiO2 NP and yields the oxidised dye molecules at particle surface. Researchers (2018) used a micrometer-thick nanoparticulate TiO_2 coated Au ultramicroelectrode (TiO_2 AuUME) to create an ultrasensitive photoelectrochemical technique for sensing photocurrent from single SC nanoparticles. The addition of di-tetrabutylammonium cis-bis(isothiocyanato) bis(2,2′-bipyridyl-4,4′-dicarbox-ylato) ruthenium(II) (N719) to TiO_2 NPs improves photoelectrochemical current. They observed that electron transport into the nano-particulate TiO2 film occurs when individual N719 TiO_2 nanoparticles collision stochastically with TiO_2 AuUME. The high-resolution photocurrent measurement, when combined with theoretical calculation, allows for the determination of electron transfer of a single N719 TiO_2 nanoparticle as well as the estimate of the electron diffusivity of TiO_2 AuUME.The methodology was then utilised to analyse the photo-electrochemical behaviour of a single N719 ZnO entity on an Au ultramicroelectrode with varying TiO_2 layer thicknesses. The photocatalytic capabilities of N719 at a single ZnO entity were determined, and the effect of film thickness on electron transport behaviour was calculated using modeling. The latter is consistent with the experimental results, demonstrating that single SC NPs photo electrochemistry may be quantified successfully. Light-controlled single nanoparticle collision studies for $PtTiO_2$ NPs with carbon UME and IrO_x NPs with a Nb:TiO_2 (110) rutile single crystal UME were demonstrated by the scientists. $PtTiO_2$ NPs were electrochemically deposited in situ, and their collisions with a carbon UME as a light guide were catalytically enhanced by the Oxygen Evolution Process (OER). Current blips caused by collision occurrences were noticed. Furthermore, photoelectrocatalytic activity of this semiconductor/cocatalyst combination was shown by light-controlled collisions of IrO_x NPs with a Nb TiO_2 (110) rutile single crystal UME. Individual IrO_x NP activity can be deduced from the current spikes. The increased electro-catalytical activity of IrO_x NPs toward OER is linked with larger current spikes for IrO_x NPs than for Pt NPs and $PtTiO_2$ NPs. Overall, research on single SC photoelectrochemistry is currently quite restricted, with just two kinds of MOS nanoparticles studied. The research objects should be expanded so that some broad detection algorithms may be created. Furthermore, additional research on the photocurrent behaviour of single SC NPs with varying characteristics is needed to better understand their inherent performance-structure correlations.

Conclusion

This brief review summarises recent scientific work on the electrochemistry and photoelectrochemistry of single semiconducting nanoparticles. The redox reactions and electrocatalysis of single metal oxide semiconductor NPs and quantum dots by the nano-impact technique are described. The approach permits both the discovery of fundamental physiochemical characteristics of nanoparticles and an in-depth study of the mechanisms and dynamics of (photo) electrochemical processes at single particle levels. However, the nano-impact approach still faces certain general obstacles, such as a lack of a deeper knowledge of the dynamics of NPs during the collision process and how different elements affect it. Due to their semiconducting nature, the substrate-NPs interaction is significantly more critical in the electron transfer process for SC NPs. Influencing elements are anticipated to include electrode materials, surface chemistry of NPs, and media composition, all of which are currently poorly known and must be further explored and explained in the future. Furthermore, research on single SC NP photoelectrochemistry is still in its early stages, and the research objectives should be expanded so that some general detection and analysis strategies can be developed, and the intrinsic (photo) electrochemical activity-structure relationships for more SC NPs can be revealed.