

Stochastic Collision Electrochemistry of Single Silver Nanoparticles

Peter A. Defnet, Todd J. Anderson, and Bo Zhang*

Department of Chemistry, University of Washington, Seattle Washington, 98195-1700 United States

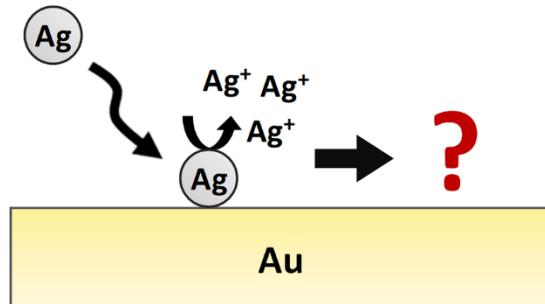
Corresponding Author: zhangb@uw.edu

Phone: (1) 206-543 1767

Fax: (1) 206-685 8665

Abstract. The electrochemical oxidation of single colloidal Ag nanoparticles at an electrode surface has previously been studied as an *in-situ* particle-sizing methodology. However, the discovery of multipeak amperometric behavior in 2017 sparked new interest towards understanding the precise physical mechanism of the manner in which a freely diffusing Ag nanoparticle interacts with the electrode surface. Random walk simulations, unique electrochemical experiments, and correlated optical/spectroscopic techniques have revealed exciting new results regarding the physical and chemical processes occurring upon single nanoparticle collision.

Graphical Abstract:



Key Words:

Single Nanoparticle; Electrochemistry; Collision; Correlated Microscopy; Multipeak

Introduction. Single-entity electrochemistry has gained much attention over the past decade due to the desire to characterize individual objects separate from an ensemble [1,2]. To this end, stochastic collision electrochemistry (SCEC) has been increasingly used as a simple and powerful methodology to study single entities. While SCEC has been extended towards a wide range of materials including nanoparticles (NPs) [3,4], emulsion droplets [5,6], and vesicles [7,8], among others [9], here we focus on the oxidation dynamics of single Ag NPs. An Ag NP diffusing in an electrolyte solution can be oxidized on an ultramicroelectrode (UME) to generate a small but detectable current spike (**Figure 1a**). The specific mechanism guiding the dynamics of the NP-electrode interaction has been a hotly debated topic over the past few years. In this review, we aim to introduce the history of these measurements, their analytical merit, complicating discoveries, and new correlative analytical measurements investigating the single Ag NP oxidation mechanism. We encourage interested readers to explore the cited references for more details, acknowledging the brevity of this article.

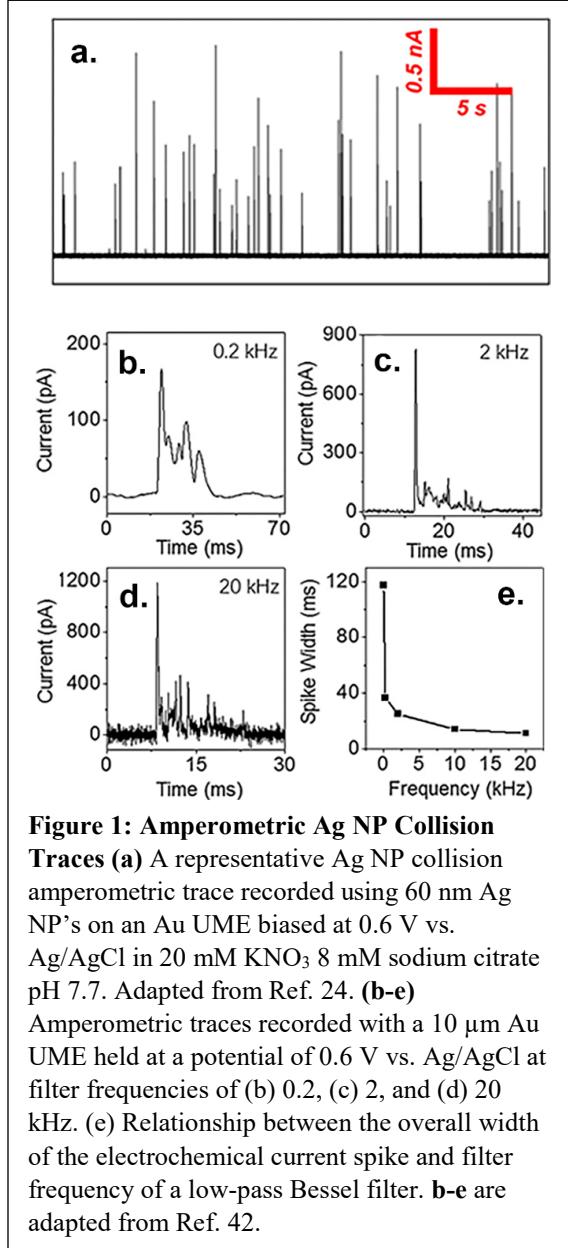


Figure 1: Amperometric Ag NP Collision Traces (a) A representative Ag NP collision amperometric trace recorded using 60 nm Ag NP's on an Au UME biased at 0.6 V vs. Ag/AgCl in 20 mM KNO₃ 8 mM sodium citrate pH 7.7. Adapted from Ref. 24. (b-e) Amperometric traces recorded with a 10 μ m Au UME held at a potential of 0.6 V vs. Ag/AgCl at filter frequencies of (b) 0.2, (c) 2, and (d) 20 kHz. (e) Relationship between the overall width of the electrochemical current spike and filter frequency of a low-pass Bessel filter. b-e are adapted from Ref. 42.

Ag NP Quantitation. In 2011, Compton and coworkers first reported the detection of single colloidal Ag NPs colliding on an UME [10*]. Impacting NPs were claimed to be fully oxidized in single 1-20 ms current spikes [11]. Subsequent studies indicated that the charge integrated from individual oxidative spikes correlated with the expected charge distribution calculated from transmission electron microscopy

(TEM) measurements [12,13]. Thus, Ag NP collision was touted as an *in-situ* quantitation methodology more accurate than dynamic light scattering (DLS) for sizing particles >10 nm in diameter [14] and applicable towards the detection of increasing Ag NP wastewater contamination [15,16]. Many papers were later published exploring the effects of varied conditions including electrolyte concentration [17], electrolyte identity [12], and capping agent[18,19]. Studies were also extended toward the oxidative collision and quantification of other metallic NPs such as Au [20,21] and Cu [22]. Importantly, full Ag NP oxidation was claimed for particle diameters ranging from 10 to 50 nm [12,14], and even upwards of 150 nm in one case [23].

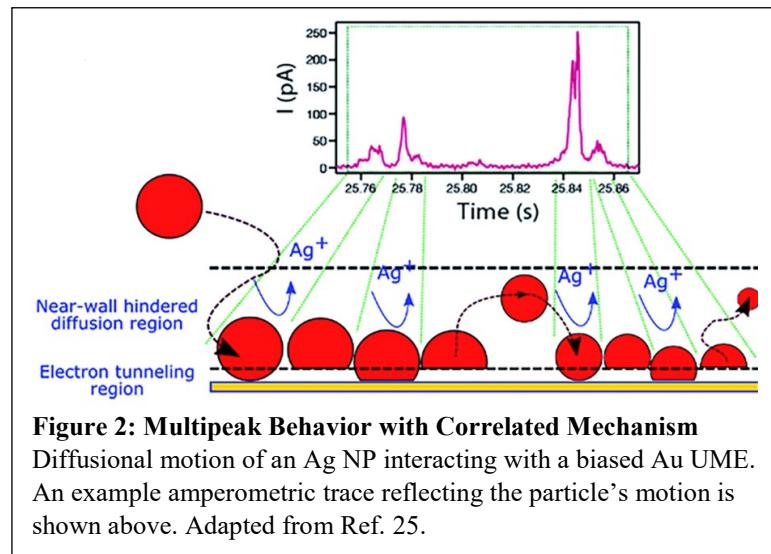
In 2017, however, three papers were published nearly simultaneously by the labs of White and Zhang [24•], Unwin [25•], and Long [26•] that instead observed ‘multiplex’ collision behavior consisting of rapid, successive, small peaks separated by ms spacing. These findings were indicative of a new nano-motion mechanism at the NP-electrode interface distinctly different from Compton’s reported mechanism of full oxidation upon collision. Unwin also reported incomplete oxidation for NPs above 40 nm in diameter, suggesting that larger particles would more likely deviate away from full oxidation. White and Zhang’s work confirmed incomplete oxidation for ~60 nm diameter NPs. The release of these papers raised questions as to why new quantitation limits were observed relative to previous studies.

A significant difference in experimental conditions between the multiplex studies and previous work is in the applied low-pass filtering frequency. The applied low-pass filter relates to the extent to which rapid current changes can be measured [27••]. Higher applied filter frequencies correspondingly increase the temporal resolution of the measurement and therefore can more accurately quantify the number of particle-electrode interactions (see **Figure 1b-d**). Yet, the total charge transferred (and therefore the calculated particle size) [11] is theoretically independent of the applied filtering rate [28], further contributing to the quantitation discrepancy. In 2018, however, work by Compton and coworkers instead showed that filtering rate does indeed indirectly affect the measured amount of charge transferred [29•]. They argue that the baseline noise significantly increases at higher filtering rates, meaning slow and small multiplexes may become indistinguishable from the baseline, thereby leading to less total

quantifiable charge. The authors importantly suggest that higher filtering frequencies (kHz) may be used for nano-motion investigations, but a post-acquisition filtering rate of 100 Hz should be applied for more accurate quantitation due to decreased baseline noise. Ultimately, quantitation of 50 nm Ag NPs is the largest particle size that has been shown to date [12] without assuming full quantitation of aggregate particles [23].

Investigations of the Nano-Motion

Mechanism. The discovery of multipeak behavior sparked a new research interest in the community focused on exploring the fundamental mechanistic dynamics of the NP-electrode interaction. These studies aimed to investigate a more accurate particle collision mechanism,



distinctly separate from the previously accepted ‘hit and fully oxidize’ scheme. While the initial multipeak papers proposed mechanisms dominated by diffusion [25•] (see **Figure 2**) or interfacial forces due to electric fields resulting from NP surface charge or local Ag^+ generation [24•], subsequent studies aimed to validate these ideas. An important study from White and coworkers used lattice random-walk simulations of particle motion coupled with electrochemical kinetic parameters to reproduce the observed multipeak current behavior [30••]. Their simulations quantitatively matched the measured magnitude of peak currents, overall duration of the individual particle-electrode interactions, and the degree of particle oxidation. Interestingly, these simulations considered Einstein diffusion relations and mass-based thermal NP velocity while ignoring the effects of interfacial forces. Their model suggests that a single particle may undergo tens to thousands of nanosecond collisions with the electrode surface before diffusing away. In a follow-up paper, they determined that modern electronic low-noise, high-bandwidth current

amplifiers cannot achieve the temporal resolution necessary to resolve each individual ns duration event [27^{••}]. Instead, modern instruments record averaged overlapping events as the low pass filtering cutoff decreases. Furthermore, a study by Long and coworkers compared experimental data to Poisson-Boltzmann simulations to investigate potential-dependent motion trajectories [31]. Importantly, their results also supported a dynamic motion mechanism.

Following these reports, there was much interest in the community to further explore the mechanism of a single Ag NP interacting with an UME. For example, our lab used nanoband electrodes sized 60, 110, and 180 nm in thickness and observed an increased number of single peak events, suggesting that detectable nano-motion may be limited with the application of thin electrodes [32[•]]. White and coworkers used an adjustable micro-gap between two opposing UMEs with opposite biases to oxidize a colliding particle and subsequently reduce the generated Ag⁺ [33^{••}]. Interestingly, they found that only 50% of the oxidized Ag NP is released as free Ag⁺, suggesting the formation of an insoluble complex such as Ag₂O. The generation of Ag₂O was further validated by our lab by recording a higher frequency of events containing long trailing tails generated using alkaline conditions. The extended decay durations were proposed to be due to electrocatalytic water oxidation across Ag₂O formed at potentials >1 V [34].

Correlated Optical and Spectroscopic Methods. Despite the excellent temporal resolution achievable with amperometry alone, the integration with correlated optical methods can provide added spatial information while correlated spectroscopic measurements can yield further chemical information regarding the NP-electrode interaction. Correlated measurements can aid in revealing key mechanistic insights which are unapproachable with pure electrochemistry such as distinguishing particle dissolution vs. departure, deconvolution of overlapping electrochemical processes, and identification of oxidation products. While these techniques are powerful tools for studying single particles, one drawback is that many of them are also low-throughput and therefore require greater effort to characterize a statistically

relevant quantity of data. Our discussion will be separated into two categories: (1) techniques monitoring NPs immobilized on the electrode surface followed by (2) those investigating freely-diffusing particles.

Dark field microscopy (DFM) has been extensively used to study the oxidation behavior of immobilized Ag NPs. In a 2016 study, Kanoufi and coworkers correlated DFM with electrochemistry and found they were able to distinguish NP aggregates [35]. Interestingly, the aggregates did not fully oxidize, which was thought to be due to poor electrical contact with the electrode. Separately, Willets and coworkers revealed stunning new mechanistic behavior in a similar DFM-electrochemistry study when they noticed Ag_xO_y particles forming on the electrode surface following the oxidation and dissolution of Ag NPs [36^{••}]. They proposed that the large injection of Ag^+ following particle oxidation promoted immediate electrodeposition and aggregation of Ag_xO_y , with observed clusters appearing up to several μm away from the original particle. In another study, Willets and coworkers combined DFM with superlocalization to monitor Ag_2O formation across a single particle with <10 nm spatial precision [37^{••}]. Correlated studies revealed that Ag NPs undergo electrodissolution in either a spatially symmetric or asymmetric manner, likely influenced by the directionality of the surface oxide formation.

Tschulik and coworkers have also uniquely combined DFM with hyperspectral imaging (HSI-DFM) to identify chemical changes during NP oxidation. They demonstrated that AgCl is further oxidized at potentials overlapping with water splitting [38] and were separately able to monitor the chemical transformation from AgSCN to a higher order soluble species in the presence of high SCN^- concentration [39]; the authors emphasize that these processes are only distinguishable with the use of correlated spectroscopy. They have also separately compared the kinetics of Ag NP oxidation in the presence of both NO_3^- and Cl^- electrolytes [40]. It was found that Ag NP oxidation proceeds more slowly in the absence of a precipitating anion such as Cl^- , an observation which they attribute to the thermodynamically unfavorable formation of solvated Ag^+ cations. The authors conclude that the inhibited kinetics may indicate that the oxidation of a single Ag NP during collision experiments occurs over the course of multiple events while the NP remains in contact with the electrode surface.

Collisions between freely diffusing Ag NPs and a positively biased electrode have also been investigated with similar dual optical-electrochemical experiments. For example, surface plasmon resonance microscopy (SPRM) methods monitor the scattered intensity of a plasmonic wave propagating across the surface of a transparent Au electrode. The Tao group introduced the elegant plasmonic electrochemical current microscopy (P-ECM) in which changes in the scattered plasmonic intensity are correlated to NP size and, by extension, oxidation current [41]. Wang and coworkers used a similar SPM method to provide evidence that physical contact between a colliding Ag NP and the detecting electrode may be maintained when multipeak behavior is exhibited [42]. They suggest that thermal motion and microconvection are responsible for the appearance of multiple closely spaced detection events. However, the high SPM noise levels producing uncertainty of ~13 nm and suboptimal temporal resolution achieved in this study (2.5 ms) must also be considered.

Our group has introduced a unique method that enables fluorescence monitoring of colliding Ag NPs confined within a nanoscale electrochemical cell [43*]. By detecting the fluorescence of Ag nanoclusters formed from the photocatalytic decomposition of the Ag_2O oxidation product, we were able to image dynamic collision events of a single Ag NP within the nanocell as it

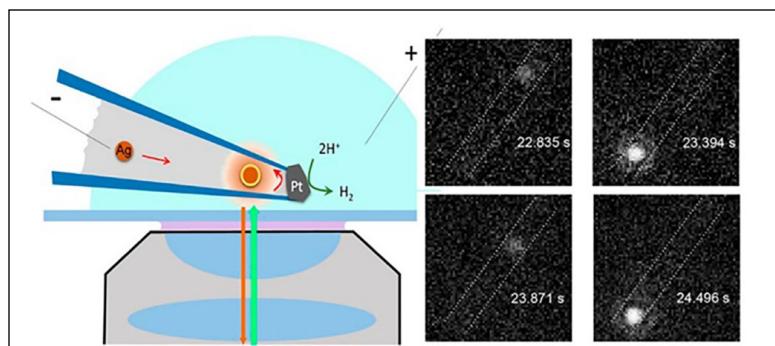


Figure 3: Fluorescence Monitoring of Ag NP Collision: A schematic of the experimental setup used to image single NP collisions in a nanopipette electrochemical cell is shown on the left. A single Ag NP collides on the Pt nanoelectrode surface and is partially oxidized resulting in the formation of Ag_2O . The oxide layer is photodecomposed leading to the formation of fluorescent Ag nanoclusters. The oxidation of Ag inside the nanocell is electrically coupled to the reduction of protons on the external surface of the Pt. A panel of representative fluorescence images of the NP collision process is shown on the right. Adapted from Ref. 43.

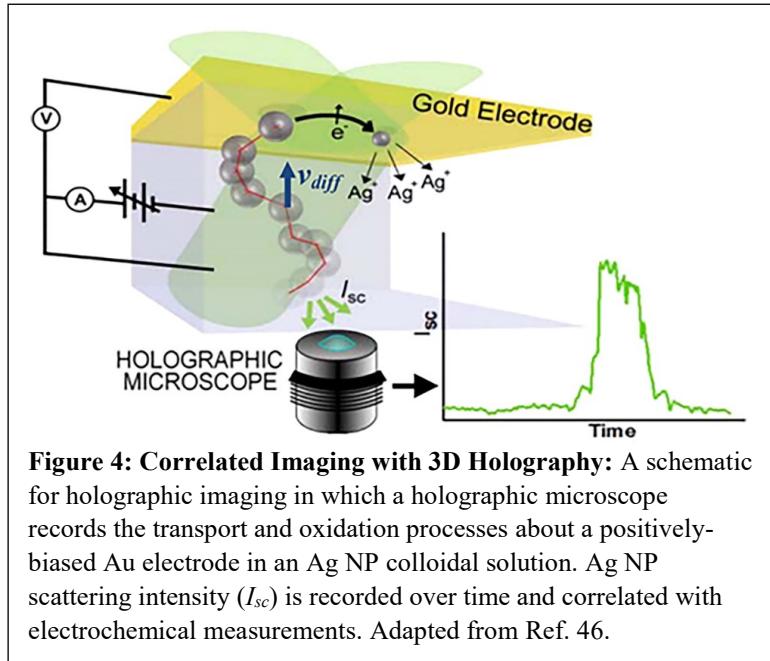
encountered the electrode/solution interface. We attribute the repeated motion of the particle to balanced electrostatic interactions between the NP, Pt electrode, and walls of the quartz nanocell (see **Figure 3**).

3D holography also provides an especially attractive means of tracking NP motion during collision experiments. It measures the z-distance between incident particles and the electrode surface in

addition to traditional 2D NP tracking by collecting interference patterns from the light source. The phase information contained in these interference patterns enables the complete 3D reconstruction of the position of any NP within a volume extending several tens of microns from the electrode surface into the solution [44]. This microscopy technique was jointly used by Kanoufi and Tessier in the first correlated electrochemical and optical detection of Ag NP collisions on an UME [45]. The authors demonstrated that NP oxidation with NO_3^- electrolyte does not commence immediately upon contact with the electrode surface. Two explanations were proposed for these interesting results: the NP may have landed on a region with poor electroactivity, thereby requiring time for it to diffuse to a more active location; or near-wall hindered diffusion slowed the NP movement within <10 nm of the electrode surface and 3D super-resolution holography could not distinguish between a contacting NP and one less than 10 nm away. Separate studies by the same authors have also examined diffusiophoretic transport of Ag NPs to the electrode surface and NP dissolution kinetics (see Figure 4) [46,47].

Conclusion. Overall, we have surveyed the recent literature in which the electrochemical oxidation of single Ag NPs has been investigated. With the aid of ultrafast electrochemical measurements, simulations, and correlated analytical techniques, a more complete understanding of the NP-electrode interaction can be achieved. Many opportunities for further study remain, such as correlated imaging of

single particle motion at the electrode surface with nm resolution while exposed to bulk solution. This phenomenon could be investigated with the use of correlated *in-situ* TEM to enable the observation of a



single particle moving across a biased electrode. Alternatively, new advances in low-noise high-bandwidth current amplifiers may also enable improved amperometric resolution of recorded multipeak events. Such studies would further explore the random-walk collision mechanisms proposed by White and coworkers. Furthermore, the lessons learned in fast temporal recording of single Ag NP collisions may also be extended toward other stochastic collision studies to reveal previously unresolvable physical or chemical mechanistic behaviors. These studies would offer new insights into the fundamentals of the electrode-analyte interface.

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Declaration of Interest: None

Declaration of Competition: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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- Paper of special interest.
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