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# Collision electrochemistry: a simple methodology for investigating complex processes

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## Abstract

Despite the apparent simplicity of collision electrochemistry, recent studies have demonstrated that the transient responses often exhibit a high degree of complexity. This complexity originates either from a temporal evolution of the current transient or from the combination of distinct processes occurring simultaneously. Unraveling these current blips and their progression over time allowed revealing various processes such as growth, morphology transformation, complex electrocatalytic mechanisms and simultaneous reactions at the single entity level. However, this level of complexity might lead to misinterpretation if the interfacial interactions are not properly understood. In this review we summarize the recent studies aiming at investigating *operando* the evolution of colloidal solutions and resolving concomitant processes by collision electrochemistry. Next, we discuss studies that report the role of interfacial interactions that could possibly blur the observation of such complex events. To this end, we particularly highlight the advantages of correlative approaches to collect crucial complementary information.

## Key words

Nanoparticles, Collision electrochemistry, Optical microscopy, Solution processes, Concomitant reactions, Interfacial interactions, Electrocatalysis

## Introduction

Single entity electrochemistry is now a well-established field to perform electrochemical investigations of individual objects from the micro down to the nanometer scale, allowing, among others, to explore *operando* dynamic and complex behaviors at the single nanoparticle (NP) level [1,2]. Among the techniques available, collision electrochemistry, also termed as nanoimpact electrochemistry, provides a versatile and powerful means to reveal the intrinsic properties of single entities in ensemble by shrinking the dimensional size of the electrochemical interface to the micro/nanoscale [3,4]. A typical collision electrochemistry experiment involves the mass transport of individual entities towards the electrode surface, followed by interaction or adsorption of these entities with the micron-sized electrode one by one. As a result, transient collisions alter the interfacial charge transfer or interfacial structure, which is tracked by recording the chronoamperometric/chronopotentiometric responses at the electrode. Based on electrochemical signal generation, most collision electrochemistry methods fall in four categories, including blocking [5], electrocatalytic amplification [6], electrolysis [7], and capacitive oscillation [8].

From a fundamental standpoint, this methodology appears to be a distinct departure from steady-state, and shows promise in obtaining a time-series information of single NPs in a complex process, contributing to a better understanding of underlying chemistry. Indeed, since the first reports on collision electrochemistry [5-7], the methodology has been optimized and current/potential fluctuations resulting from the impact of NPs onto the electrode are better understood. The development of

low-noise electrochemical instrumentation with high bandwidth enables the detection of stochastic behaviors of single entities occurring at the ultrafast timescale [9-11]. Since then, collision electrochemistry is extensively used to investigate the properties and the electrocatalytic activity of colloidal NPs and to understand solid/liquid interfaces [12]. Combined with advanced theoretical modeling methods, it also provides insights into the NPs mass transport and interfacial kinetics [13,14]. In addition, the integration of single entity collision electrochemistry with optical techniques contributes to obtaining a complete mechanistic understanding of transient nanoelectrochemistry with high spatial and high temporal resolution [15,16]. It allows for instance to reveal the mass transport of individual NPs and their multi-step reaction through multiple discrete current-time ( $i$ - $t$ ) peaks [17-19]. Collision electrochemistry now opens new possibilities for revealing *operando* the evolution of individual NPs' activity and morphology in solution and for resolving concomitant reactions at the single entity level. The latter are reviewed hereafter, together with important parameters that can influence the transient current responses. We also discuss the added value of combining collision electrochemistry and optics in a correlated approach. Taken together, this methodology extends far beyond simply determining the heterogeneity among NPs but also employs them as probes to interrogate their environment and the forces to which they are subjected.

### Monitoring solution processes

Beyond a fundamental investigation of NP heterogeneities in ensemble, collision electrochemistry shows promise for the *operando* characterization of nanomaterial synthesis in solution [20-27]. This approach integrated with scanning electrochemical microscopy in generation/collection-like mode permits the simultaneous electrosynthesis and measurements of single silver oxide nanocubes ( $\text{Ag}_2\text{O}$  NCs), as schematized in Figure 1A [22]. In this configuration, Ag sacrificial ultramicroelectrode (UME) is used to generate  $\text{Ag}^+$  by electrooxidation while the opposing gold (Au) UME produces  $\text{OH}^-$  and tracks the growth dynamics of  $\text{Ag}_2\text{O}$  NCs, simultaneously. This synchronized analytical technique reveals that electrogeneration kinetics of  $\text{Ag}^+$  controls the growth mode of  $\text{Ag}_2\text{O}$  NCs by supersaturation mechanism. With the aim of mechanistic study of electro-synthetic process of hollow NPs, collision electrochemistry is also applied to the *operando* analysis of anodic transformation and self-terminating electrooxidation of individual Ag NPs in aqueous  $\text{HS}^-$  solution [23,24]. One can speculate the formation kinetics of individual hollow Ag/ $\text{Ag}_2\text{S}$  NPs from the profile of each single collision  $i$ - $t$  transient [24]. These event blips indicate that  $\text{Ag}_2\text{S}$  layer thickness remains independent of the initial NP size.

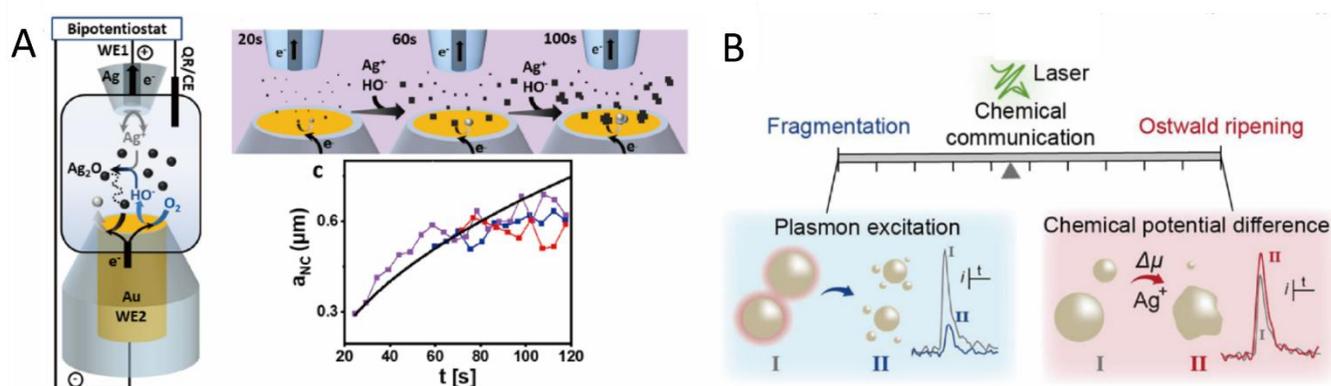


Figure 1. Probing *operando* the temporal evolution of colloidal solutions. (A) Collision electrochemistry integrated with SECM technique for tracking morphology transformation and aggregation at the single NPs level. Reprinted from Ref. [22]. Copyright 2021 Elsevier. (B) *Operando* investigation of interparticle chemical communication in a photochemical process. Reprinted from Ref. [28]. Copyright 2023 Wiley-VCH.

Recently, collision electrochemistry is applied to reveal the interparticle communication that controls the

photochemical synthesis kinetics of a population of Ag NPs, as shown in Figure 1B [28]. This approach opens a new way for understanding the correlation between the heterogeneous behaviors of single NPs and the collective characteristics of global NPs, an emerging topic in nanoelectrochemistry [29-31]. The semi-quantitative statistical analysis of transient events indicates that mass transport determines the chemical potential difference between individual Ag NPs, thereby influencing the morphology transformation path of ensemble over time.

### Resolving concomitant (electro-)catalytic reactions

Collision electrochemistry can also be employed to discriminate the conversion of NPs from their electrocatalytic activity. In one single collision, both steps can be subsequently revealed as exemplified for the AgBr NP reduction and oxygen reduction reaction (ORR) [32], nickel hydroxide NP oxidation and oxygen evolution reaction (OER) [33] and the Ag NP oxidation and OER [34]. In those examples, the current spike can be attributed to the NP conversion and is always followed by a current step corresponding to the NP electrocatalytic activity as illustrated in Figure 2A. To reveal both concomitant transformation and electrocatalytic activity of the NPs, the choice of UME material is demonstrated to be crucial [32]. A deeper analysis of such processes allows extracting size-reactivity relationships [32, 33]. For instance, the turnover frequency (TOF) extracted from the current step height for the OER versus the NP size determined from the current spike corresponding to the oxidation of Ni(OH)<sub>2</sub> to Ni(OOH) allows evidencing a decrease of TOF with an increase of the NPs radius as shown in Figure 2B. The trend, based on the analysis of several hundreds of NPs, is in good agreement with previous results obtained at individual Ni(OH)<sub>2</sub> NPs immobilized on nanoelectrodes [35]. In these examples, a good accuracy between the size of the NPs determined by the collision experiment and postmortem electron microscopy analysis is noted. However in the case of the combined Ag oxidation/OER processes, a mismatch is observed due to a possible occurrence of both reactions (conversion and electrocatalysis) within the current spike [34]. The authors also demonstrated that a protective layer of polyvinyl pyrrolidone (PVP) covering the Ag NPs decrease the contribution of the OER in the current spike compared to citrate-capped NPs.

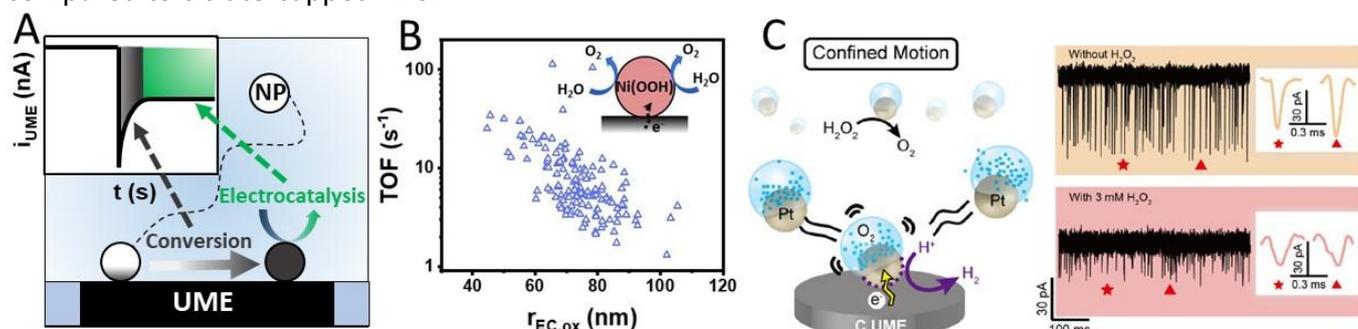


Figure 2. (A) Illustration of the typical behavior of concomitant transformation and electrocatalytic activity of NPs. Adapted from Ref [32]. Copyright 2022 Wiley VCH. (B) Turnover frequency (TOF) of the OER at individual Ni(OH)<sub>2</sub> NPs as a function of their electrochemical radius. Reprinted from Ref. [33]. Copyright 2023 American Chemical Society. (C) Methodology used for studying the collision of single Pt NPs for the HER during the catalytic decomposition of H<sub>2</sub>O<sub>2</sub>. Reprinted from Ref. [40]. Copyright 2023 American Chemical Society.

NPs collision experiments are also powerful to decipher complex electrocatalytic schemes, including methanol oxidation and hydrogen evolution reaction (HER). Analyzing the current transients recorded with high temporal resolution and at different potentials allow evidencing the different reaction steps [36-38]. The hydrogen adsorption during the HER is quantified [37], and the possible competition of electrocatalytically active UME is highlighted. Particularly, it is proposed that the production of molecular hydrogen issued from the HER triggered at the UME surface can spontaneously form adsorbed hydrogen on Pt NPs' surface before collision [38]. The "redox" state of the NPs in the solution

phase then could play a role on the NPs reactivity. The alteration of the NPs potential in the presence of iodine in a hydrogen-saturated solution leads to bipolar collision transients because the NPs subsequently act as a reducer and as an oxidant [39]. The current transient presents typical reductive step followed by oxidative one upon the collision of the Pt NPs at the UME surface. This behavior is attributed respectively to the hydrogen adsorption from water reduction and the catalytic oxidation of  $H_2$  in solution due to a rapid switch in the NPs' potential. Besides, NPs collision experiments are also used to evidence other competing reactions such as  $O_2$  and  $H_2O_2$  [38] or the spontaneous chemical decomposition of  $H_2O_2$  and the HER [40]. In the latter example, it is proposed to go one-step beyond, employing the collision electrochemistry to indirectly probe  $O_2$  nanobubbles formation issued from the decomposition of  $H_2O_2$  at the surface of individual Pt NPs. As depicted in Figure 2C, the nanobubble partially blocks the active surface of the NPs and disturb the HER current transient response upon their collision. From both experimental measurements and theoretical calculations, the size of the nanobubbles and oxygen gas density are quantified, providing new insights into the gas accumulation mechanism at individual NPs.

### Unlocking and distinguishing interface interactions

An important aspect in collision electrochemistry involves the dynamic interactions between individual particles and the electrode. This interfacial interaction has the capacity to influence stochastic mass transport and charge transfer, thereby shaping the transient current response profile [41]. For instance, collision electrochemistry coupled with theoretical calculations showed that the interaction of Ag NPs and the UME controls the interfacial kinetics [42]. In comparison to carbon (C) UME, Au UME amplifies the strength of interaction that is attributed to the more negative adsorption energy observed for individual Ag NPs on the Au UME. This strong interaction contributes to the electrooxidation of Ag NPs, thus the observation of transient current blips characterized by large current amplitude and short duration. To enhance such adsorptive interaction between NPs and the electrode interface, alkaline media was used. It allowed for a complete dissolution of individual Ag NPs by confining the stochastic motion of NPs within the tunneling region of the Au UME. The role of the NP/electrode interactions is also demonstrated to strongly influence the HER efficiency of  $MoS_2$  Quantum Dots, as illustrated in Figure 3A [43]. It shows that HER performance is significantly enhanced on Ag UME compared to C UME, resulting in a very high catalytic efficiency of  $MoS_2$  QDs. Further DFT calculations suggest that this enhancement is due to an increase in the Gibbs free energy of  $MoS_2$ -Ag interaction.

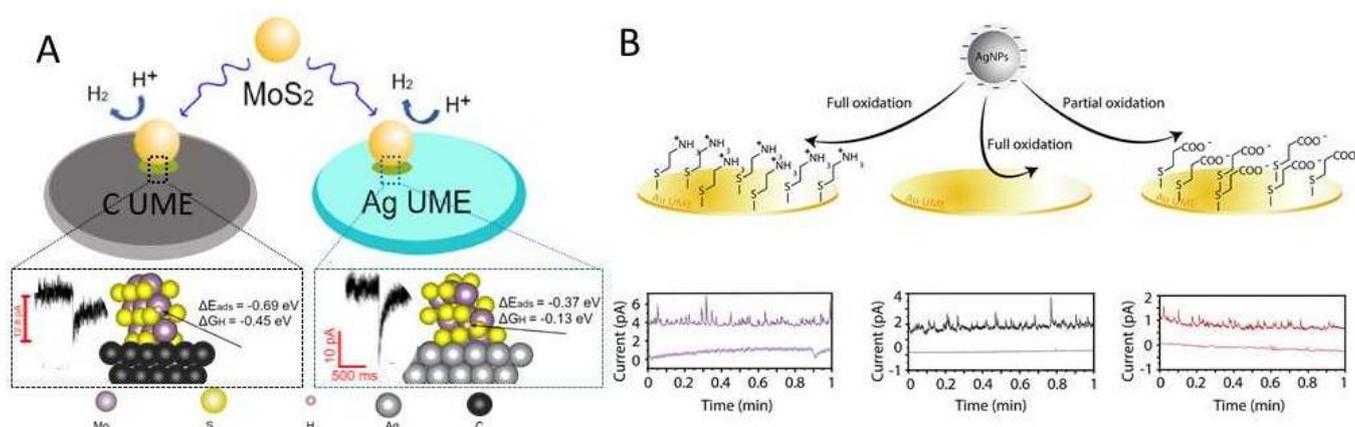


Figure 3. Interfacial interactions. (A) Enhancement of the HER efficiency of  $MoS_2$  Quantum Dots on Ag UME compared to that on C UME. Adapted from Ref. [43]. Copyright 2021 American Chemical Society. (B) The effect of charged SAMs on the electrooxidation kinetics of single Ag NPs. Reprinted from Ref. [45]. Copyright 2023 American Chemical Society.

Additionally, modifying the electrode with self-assembled monolayers (SAMs) allows controlling the electrooxidation dynamics at the electrochemical interface by tuning electrostatic interactions [44], as

shown in Figure 3B [45]. For instance, the incorporation of negatively charged SAMs on the Au UME surface leads to repulsive electrostatic interactions between the Ag NPs and the electrode. This significantly hinders both the collisions frequency and electron transfer. The interfacial dynamics in collision electrochemistry can also be tuned by the formation of Ag-S coordinate bond between a single Ag NP and the ultrathin layer of polysulfide on the Au UME [46]. The sulfurous layer deposited on the Au UME surface acts as an adhesive force for attracting individual large-size Ag NPs. The layer alleviates the stochastic motion trajectory of individual colliding Ag NPs, promoting the electrooxidation of Ag NPs to form Ag<sub>2</sub>S when bulk sodium thiosulfate is present in solution. The high interfacial electrooxidation rate of individual colliding Ag NPs allows the observation of increase in both collision frequency and current amplitude.

### Tracking dynamic processes with correlated approaches

To unambiguously interpret the current transient signals associated to the collision events, one emerging solution is to couple the electrochemical detection with a complementary visualization technique such as optical microscopies. They are often simple to implement with various configurations and viewing modes enabling the entire UME to be imaged in real time [47].

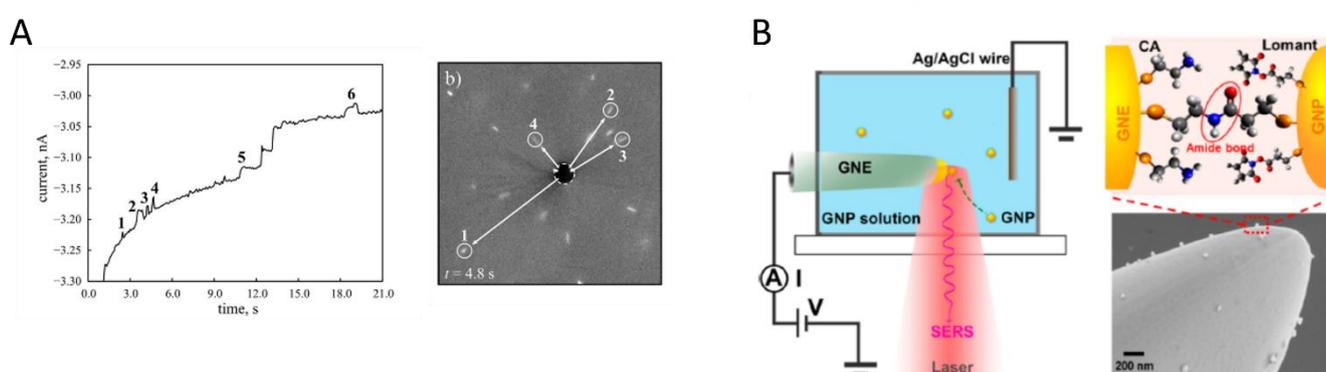


Figure 4. Optical tracking of particles colliding with a biased electrode and correlated results. (A) Optical evidence of electroosmosis flow induced by a faradaic reaction at an UME causing current spikes. Reprinted from Ref. [49]. Copyright 2020 American Chemical Society. (B) Methodology for following dynamically by correlated time-resolved SERS spectroscopy the formation and stability of molecular junctions during NP collisions. Reprinted from Ref. [57]. Copyright 2021 American Chemical Society.

Since the seminal work of Fosdick et al [48], who employed fluorescence microscopy to monitor the electromigration of microbeads at a Pt UME, two independent recent studies correlating microscopy images and blocking impact transients have confirmed the importance of electroosmotic fluxes in collision electrochemistry experiments [49,50]. In Figure 4A, the particle optical tracking in low supporting electrolyte concentration reveals the electroosmotic flow resulting from the application of the electric field to the insulating glass of the UME during the oxidation of ferrocenemethanol [49]. It results in spike-shaped transients such as those shown in Figure 4A superimposed to step-like transients.

In addition to electrode/particle surface charges, electrolyte concentration, etc., the geometry of the NPs also plays a role. Indeed, a complete understanding of dynamic particle-electrode interactions appears particularly challenging when particles exhibit asymmetrical geometry. This is typically the case for graphene nanoplatelets for which an additional optical visualization is required. It has been observed that current spikes can originate from the electrical connection of single conductive graphene nanoplatelets to the UME followed by their reorientation at the polarized interface [51]. In addition, positive current steps are recorded when the nanoplatelets are seen lying both onto the UME and the insulating glass, thus increasing the electroactive area. Negative current steps arise when the nanoplatelets do not form electrical contact with the UME and partially block the diffusion layer [52].

Besides, collisions of micro-motors are demonstrated to be complexified by the driving force linked to the consumption of a fuel. In this situation, optical tracking can be used to evaluate the velocity and kinetic energy of the colliding motors as function of fuel concentration [53]. In addition, the faradaic reaction of the NP arriving at the biased interface can also modify its motion which in turn influences the current responses. This is true for the cathodic conversion of silver halide NPs which occurs step by step with local release of ions which propel the NP. Like for nano-motors, the motion dynamic is revealed optically and correlated to the current response [54,55].

Finally, a recent interesting application of collision electrochemistry coupled with Raman analyses is the study of dynamic molecular junctions [56]. If nanometer-sized electrode and NPs are properly functionalized, collisions of the latter can lead to the transient or permanent creation of molecular bonds between two synthons. The molecular junctions can then be revealed electrochemically through the increase in current and by fluctuation in Raman scattering intensity, exalted due to the appearance of a hot spot (intense and localized electro-magnetic field) in the nanoscale gap between the electrode and the NP if the latter exhibit plasmonic properties. The methodology is illustrated in the example of Figure 4B for the monitoring of aminolysis reaction between ester and amine groups [57].

### **Conclusions and perspectives**

We highlight the capability of collision electrochemistry to provide valuable insights into solution processes and quantitative analyses of intricate electrocatalytic schemes at the single NP level. Collision electrochemistry enables the real-time characterization of nanomaterial (electro)synthesis and is currently applied for investigating NPs agglomeration in sensing applications [58,59]. Moreover, the technique has been employed to decipher complex electrocatalytic mechanisms, unraveling the intricacies connecting the conversion of NPs with their electrocatalytic activity. This approach that aims at establishing clear structure-reactivity relationships, seems promising to investigate ions insertion associated with NPs conversion [60]. However, it is crucial to acknowledge that such experiments are significantly influenced by NPs/UME interactions. Recent fundamental studies have enriched our understanding of NPs' electrochemical reactivity and mass transport, highlighting the substantial impact of UME material/functionalization and experimental parameters, such as the pH of the solution. By synergistically combining collision electrochemistry with optical monitoring, it is also possible to further correlate transient faradaic signals with NPs/electrode interactions, revealing the effects of electroosmotic fluxes, the influence of particle geometry or enabling the exploration of single molecular junctions. Such interactions could be of major importance in many other collision electrochemistry experiments as it is very recently revealed with micro/nanodroplet [61,62].

However, extracting new relevant information can require high-level data processing, and advanced statistical analyses as collisions experiments usually generates large datasets [63]. New approaches are being developed in related fields of research such as for nanopores [64,65] and should now be applied to collision experiments. As an alternative to classical analyses, unsupervised machine learning and template matching approaches appear promising for increasing the speed and accuracy of the analyses while automating the process and avoiding human bias [66]. Note that these analyses are generic and also applies to optical microscopy and could therefore be of interest for correlated approaches [30,67].

### **Declaration of competing interest**

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.

### **Data availability**

No data was used for the research described in the article.

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