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Andrew D Pendergast, Christophe Renault, Jeffrey E Dick. Correlated Optical–Electrochemical Measurements Reveal Bidirectional Current Steps for Graphene Nanoplatelet Collisions at Ultramicroelectrodes. *Analytical Chemistry*, 2021, 93 (5), pp.2898-2906. 10.1021/acs.analchem.0c04409 . hal-04551865

HAL Id: hal-04551865

<https://hal.science/hal-04551865>

Submitted on 18 Apr 2024

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Correlating Electrochemistry and Optical Microscopy Reveals Unexpected Collisions of Asymmetric Single Entities

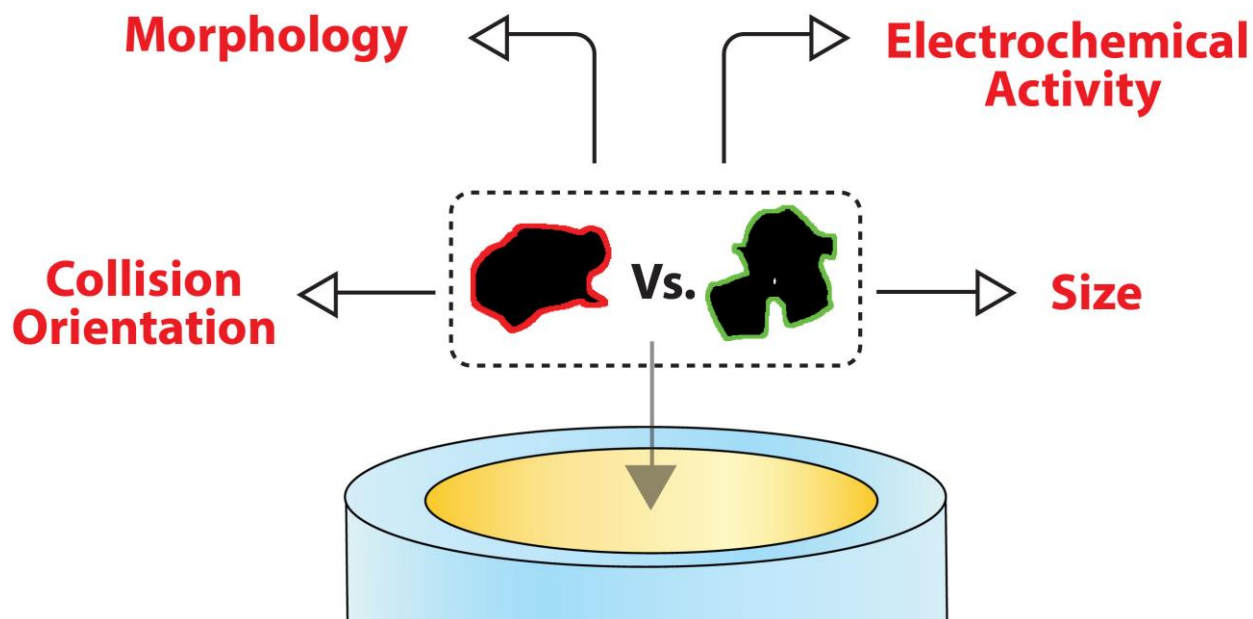
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Abstract: Synthetic methods for nanoparticle formation yield a heterogeneous population of nanoparticles, making techniques to study chemico-physical properties of single nanoparticles invaluable when studying reactivity. While single entity electrochemical experiments have been well documented for symmetric objects including spherical metal nanoparticles, emulsion droplets, and cells, asymmetric objects provide an additional challenge due to enhanced degrees of freedom in the orientation of the object during the collision. Recently, graphene has emerged as a prominent electrode material due to a combination of high charge density capabilities, mechanical stability, and biocompatibility with applications ranging from in-vivo sensing to industrial energy conversion reactions. Graphene nanoplatelets (GNPs) are a quasi-two-dimensional conductive nanomaterial with two dimensions in the micron scale and one in the nanometer scale, functionally acting as a planar material. Upon collision with an electrode surface in the presence of ferrocenemethanol, an outer sphere redox mediator, a wide range of current responses are observed that are not observed for symmetric objects. Here, we present correlated electrochemistry and optical microscopy to simultaneously probe chemical and spatial information at the single entity level towards a complete understanding of collision dynamics at the nanoscale for graphene nanoplatelets. From these measurements, changes in the steady state current for the oxidation of ferrocenemethanol can be directly related to changes in the electrode surface area upon GNP collision, providing insight on the geometry of the single-entity | electrode interface that would be otherwise inaccessible without the two combined techniques. Additionally, this correlated technique permits deconvolution of complex current responses, revealing coupled transient events in the range of tens of seconds.

Keywords: Single entity, collision electrochemistry, graphene nanoplatelet, Correlated measurement

Single entity electrochemistry has emerged in recent years as a powerful tool to characterize populations one-entity-at-a-time by a variety of amperometric and voltammetric collision techniques. Since Lemay's seminal work studying single latex nanoparticle collisions on ultramicroelectrodes the field has matured to include a range of single entity populations including metallic nanoparticles, emulsion droplets, biological vesicles, and single living cells.¹⁻⁶ Conventionally, populations of single entities are suspended in a continuous electrolyte phase and diffuse or migrate towards an electrode surface held at a constant potential. After a single entity stochastically collides with the electrode surface, a transient current response is recorded, relating the size and location of the colliding entity with an electrochemical signal in a number of blocking or amplification strategies with a monotonic current response.^{7, 8} By analyzing a large number of collision events, statistical models can be developed to characterize a given population, revealing differences in size, electrocatalytic activity, and other physicochemical properties between single entities. Collision electrochemistry offers unparalleled sensitivity, allowing characterization of complex populations with unit limit of detection to deconvolute population heterogeneities to reveal structure/function relationships one-entity-by-one.⁹⁻¹¹ Graphene has emerged in recent years as an important electrocatalytic material; offering high electrical conductivity, low thermal conductivity, mechanical stability, and extensive opportunities for chemical modification.¹²⁻¹⁴ As a two-dimensional material, graphene nanoplatelets offer a unique system to couple these advantageous properties of bulk graphene with the enhanced surface-area-to-volume ratio of nanoparticles.¹⁵ While single entity collision measurements have been extended to a wide range of materials, the quasi-two-dimensional geometries of graphene nanoplatelets complicates conventional amperometric detection.

Importantly, the signal response for the collision of a single entity can be highly dependent on the location of a given collision, such as in the case of a blocking-type experiment with an insulating particle population. In a blocking experiment, a redox mediator is continuously reduced or oxidized at the electrode surface, and an insulating nanoparticle is allowed to collide with the ultramicroelectrode surface.¹⁶ The change in current due to the irreversible collision depends not only on the size of the blocking entity, but also on the location of the collision relative to the electrode edge.¹⁷ For inlaid disk ultramicroelectrodes, the collision of a blocking entity near the edge of the electrode will provide a higher magnitude current decrease compared to an identical collision at the center of the electrode due to enhanced analyte flux at the electrode edge. Fosdick and coworkers first demonstrated this edge effect, colliding fluorescently-labelled polystyrene beads in a blocking-type experiment to reveal differences in the collision response as a function of the distance away from the electrode center.¹⁷ COMSOL Multiphysics was also used to successfully model this response. Recently, work by Deng and coworkers has proposed hemispherical ultramicroelectrodes as a technique to overcome this edge effect with a constant current-density at all points on the electrode surface, however, these electrodes necessitate mercury ultramicroelectrodes which may be unsuitable for studies of oxidative processes.¹⁸ While these experiments have yielded much information of reactivity at the nanoscale, they have all employed symmetric nanoparticles. The quantification of reactivity of asymmetric nanoparticles provides new challenges in terms of understanding how these nanoparticles collide with an ultramicroelectrode surface. Previously, current transients for colliding graphene nanoplatelets have been attributed to capacitive charging at microwire electrodes,¹⁹ however, limited spatial resolution for single colliding entities can be acquired from solely from electrochemical collisions. Here, we propose a coupled amperometric and dark-field microscopy approach to probe single entity collisions of complex populations demonstrating characteristics of both current amplification and blocking type responses within the context of a graphene nanoplatelet (GNP) model system.

In classical spherical single entity collision experiments using catalytic amplification, current blocking, analyte delivery, or single nanoparticle dissolution strategies, the shape of a single collision transient is generally conserved with the magnitude varying as a function of the specific characteristics of the colliding object. For example, amperometric collisions of attoliter toluene-in-water emulsion droplets loaded with an outer sphere redox mediator, such as ferrocene, at potentials sufficient to oxidize ferrocene to ferrocenium reveal consistent anodic current blips corresponding to the rapid electrolysis of the redox probe upon collision.²⁰ For these symmetric spherical single entities, the current transient is irrespective of the rotation of the colliding entity relative to the electrode surface and directionality is conserved throughout a given population. However, for systems of geometrically asymmetric single entities, such as quasi-two-dimensional GNPs with significant size and morphology heterogeneity, a wide range of current transients that electrochemical impact analysis is insufficient to describe, necessitating additional characterization of the collision event.

One method to advance towards complete transient resolution in a single entity collision experiment is to couple electrochemical collision measurements with microscopic techniques. By combining the excellent temporal resolution of electrochemistry on ultramicroelectrodes with the spatial resolution of microscopic techniques, a single collision event can be characterized simultaneously in terms of the chemical and physical dynamics of the system. A representative experimental schematic is presented in **Figure 1A**, wherein a population of conductive GNPs is suspended in an aqueous

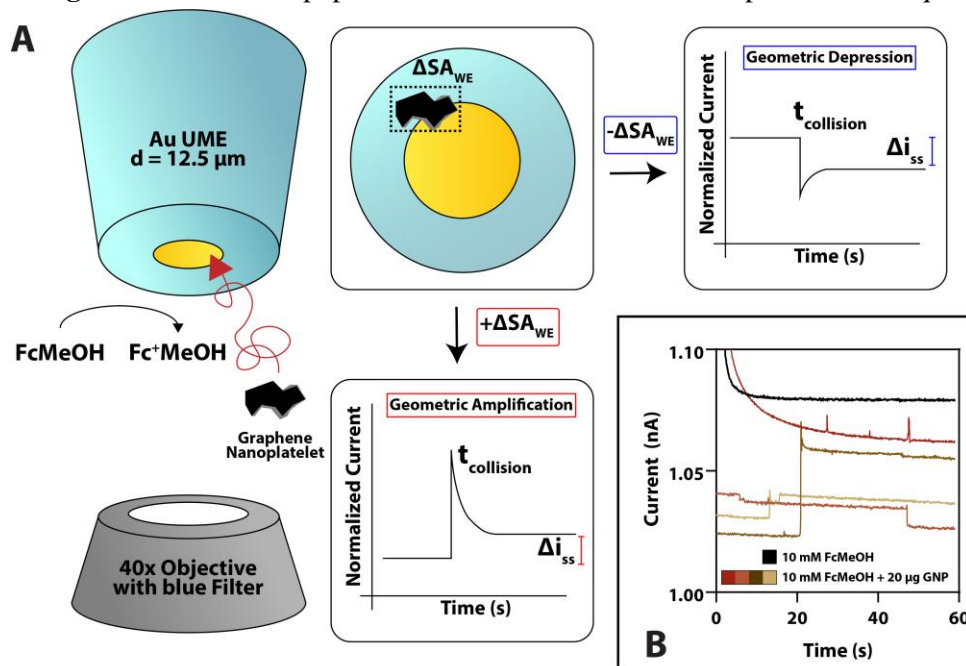


Figure 1. Experimental Schematic | (A). Representative experimental schematic demonstrating ferrocenemethanol oxidation on a Au ultramicroelectrode with graphene nanoplatelets migrating through the bulk aqueous phase and stochastically colliding at the ultramicroelectrode surface. Following collision events, either positive or negative current steps are observed, corresponding to an increase or decrease in the electroactive surface area as represented schematically above. (B). In the presence of 20 μg GNPs suspended in 1 mM FcMeOH, a number of unique collision events are observed in the current-time trace, demonstrating events corresponding to current amplification and attenuation within the same entity population, necessitating correlated detection to differentiate collision dynamics for single entities one by one.

continuous phase with an outer sphere redox mediator, ferrocenemethanol, and allowed to migrate under an electric field to collide with a Au ultramicroelectrode. Following collision at the electrode surface, a wide range of current responses are recorded. A current step increase event, with a positive change in the electroactive surface area of the system, corresponds to the collision of a GNP near the electrode edge with a segment of the platelet extending onto the insulating glass surface of the ultramicroelectrode. In these geometric amplification events, the GNP acts as an extension of the electrochemically active surface area for oxidation of ferrocenemethanol, manifesting in a step-increase in current baseline

proportional to the increased conductive surface area. Conversely, current blockade type events can additionally be observed near the electrode edge, manifesting as a decrease in the electrochemically active surface area of the electrode and a decreased anodic current proportional to a partial blocking of ferrocenemethanol flux to the electrode surface. While blip-type events are observed, analysis of these collision events is convoluted between particle size, location, and collision orientation, necessitating advanced analytical techniques to describe the transient behavior. All three of these collision motifs are observed during the collision of 20 μg graphene nanoplatelets in the presence of 1 mM ferrocenemethanol, as observed in **Figure 1B**. Importantly, in the absence of suspended GNPs, no current response is recorded beyond the baseline oxidation of ferrocenemethanol.

For both geometric amplification and geometric depression type collision events, coupled amperometry and dark-field microscopy allows the real-time correlation of electrochemical and spatial signals at the single entity level. In **Figure 2A.i**, a dark-field micrograph of an electrode surface with an adsorbed GNP is presented with a corresponding background-subtracted and contrast-filtered image to highlight the GNP presence. From this image, a relative change in the electrode surface area can be extracted by summing the initial electrode area and the area of the GNP extending onto the insulating glass at the ultramicroelectrode edge. This change in electrochemically active surface area, Δa , can be related to the change in steady-state current, Δi_{ss} , as presented in **Figure 2A.ii**. Additionally, the collision dynamics can be resolved from video microscopy as presented in **Figure 2A.iii-v** corresponding to frames captured during the collision event. From these images, the electrode surface is initially characterized at a pre-collision steady state, corresponding to a GNP diffusing or migrating near the electrode surface without perturbing the diffusional layer of ferrocenemethanol (**Figure 2A.iii**). Subsequently, the GNP is observed to collide at the electrode at an initial position (**Figure 2A.iv**) and subsequently reorient to a static position (**Figure 2A.v**) with a new steady-state current as a result of geometric amplification. Similar analysis of blocking-type responses reveals an apparent decrease in electrode surface area following a collision, as seen in **Figure 2B.i** with the presence of a GNP near the edge of the electrode and a correlated change in current in **Figure 2B.ii**. Additionally, the dynamics of a blocking collision can be extracted from video microscopy, as presented in **Figure 2B.iii-v**

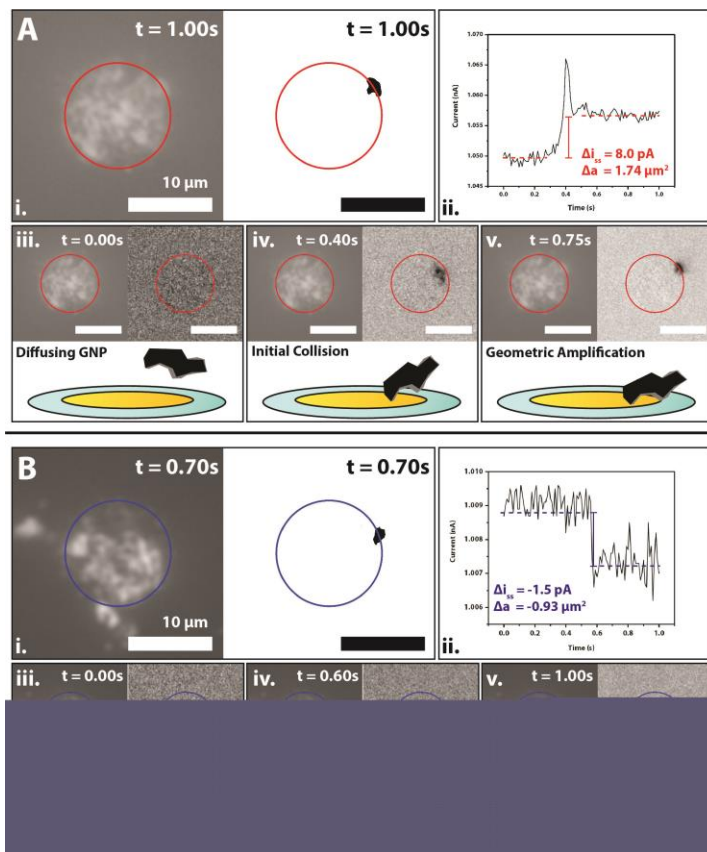


Figure 2. Simple Correlated Collision Events | (A) Representative geometric amplification event with coupled graphene nanoplatelet optical measurement (**i**) and current step increase (**ii**). From dark-field microscopy, the nanoplatelet is observed to migrate towards the electrode surface, collide, and reorient to a static position (**iii-v**) with a new steady state current corresponding to an increased electrode surface area. **(B)** Representative geometric depression event with coupled optical measurement (**i**) and amperometry (**ii**). During depression type events, the nanoplatelet partially blocks redox mediator flux to the electrode surface, suggesting either collision on the surrounding glass or poor electrical connection with the underlying electrode. A proposed mechanism is represented schematically for a collision on the glass substrate and subsequent partial flux blocking (**iii-v**). All scale bars are

corresponding to the baseline electrode surface, the initial GNP collision, and the partial electrode flux blockage respectively.

For a population of GNP collisions including both geometric amplification and geometric depression events, the relative change in steady-state current cannot be solely described by the size of the colliding GNP as presented in **Figure 3A**. As a quasi-two-dimensional material, the geometric contribution of an adsorbed GNP can be modelled as that of a plane on the electrode surface. In the case of both geometric amplification and geometric depression events, the location and size of the static GNP following collision can be extracted, revealing preferential collision at or near the electrode edge as presented in **Figure 3B**. Interestingly, geometric depression events are observed at the edge of the electrode both with and without overhang onto the glass insulating substrate. For these depression events, the first class of depression events can be rationalized in terms of colliding onto the glass insulating layer and subsequently laying above the electrode surface without any direct electrical connection. In this case, a partial flux blockage would be expected, resulting in a decreased current magnitude proportional to the orientation of the GNP on the glass substrate. The second type of depression event, wherein a GNP collides directly on the electrode surface with a correlated decrease in current magnitude, suggests a poor electrical connection between the GNP and electrode surface due to surface defects, electrode fouling, or poor GNP conductivity, however, the exact mechanism is not yet understood. When correlated measurement reveals a collision with a positive or negative current step in addition to an increase or decrease in the surface area of the electrode system, the change in current (δ_I) and the change in electrode surface area (δ_{SA}) can be evaluated as:

$$\delta_I = \frac{i_{ss,bare+GNP} - i_{ss,bare}}{i_{ss,bare}}$$

and

$$\delta_{SA} = \frac{SA_{bare+GNP} - SA_{bare}}{SA_{bare}}$$

Where $i_{ss,bare}$ and SA_{bare} are the steady state current and surface area prior to GNP collision and $i_{ss,bare+GNP}$ and $SA_{bare+GNP}$ are the steady state current and surface area following collision. From these values, a collision correlation factor, α , can be evaluated as:

$$\alpha = \frac{\delta_I}{\delta_{SA}}$$

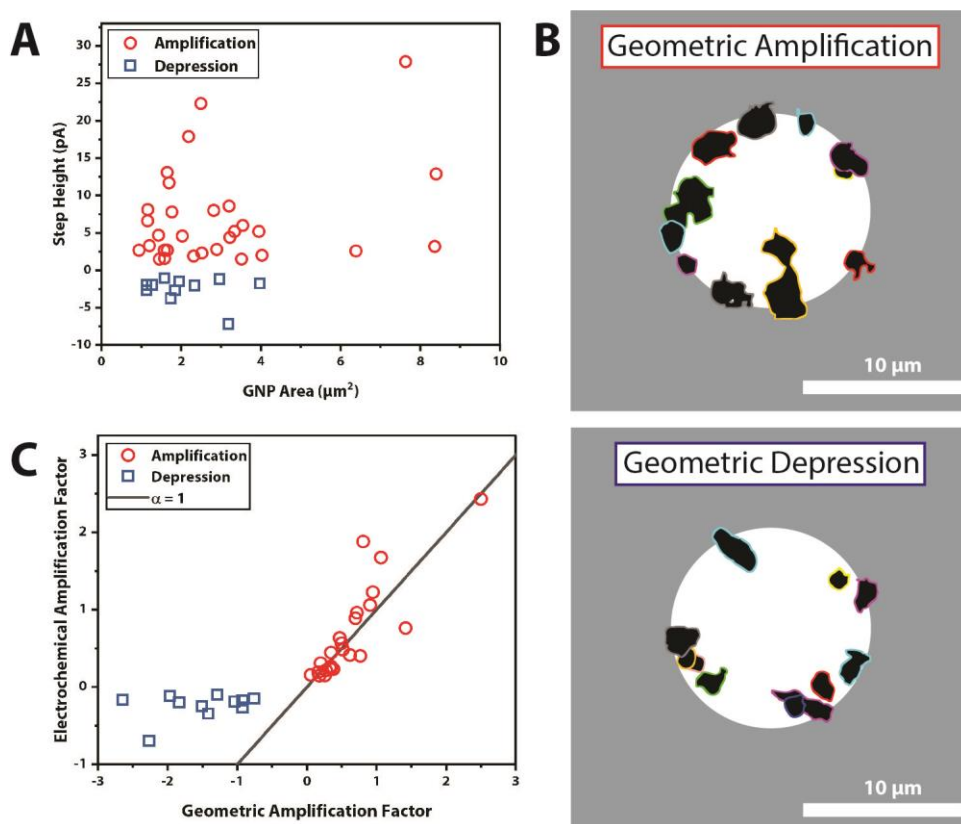


Figure 3. Effect of Collision Location on Electrochemical Response | (A) Analysis of colliding graphene nanoplatelet geometry and correlated steady-state current change for amplification and blocking events, revealing a range of nanoplatelet sizes producing similar current responses, limiting quantitation. (B) Representative collision overlays and geometric amplification and depression type events, revealing a preference for collisions near the edge of the electrode. (C) Correlating changes in steady state current and apparent electroactive surface area reveals a good correlation for amplification step-type events, however, geometric blocking-type events demonstrate only partial flux blockade, indicating incomplete attachment to the electrode surface.

From this evaluation, the relative increases in both steady state current and surface area during geometric amplification type events follows a predicted relationship of direct proportionality ($\delta = 1$) as observed in **Figure 3C**. Thus, for the case of a colliding amplifying GNP, the adsorbed GNP can be inferred to lay on the electrode surface and enhance surface area by extending onto the glass insulating substrate and allowing increased total redox mediator flux. Conversely, geometric depression type events reveal a wide range of collision correlation factors with decreased current blocking compared to the predicted values, suggesting that the underlying electrode surface experiences hindered mass transport of redox mediator, but still contributes to the overall electrode current. By correlating amperometry and video microscopy, the current response for single colliding amplifying GNPs can be directly quantified with respect to the size of the colliding entity and the morphology of the electroactive surface following collision.

Beyond quantitative determination of GNP-electrode interactions during a collision event, correlated electrochemical and optical microscopy allows deconvolution of complex transient responses that would be difficult solely through electrochemistry. While elementary step and blip type responses were observed for the collision of a single GNP, correlated measurement allows unambiguous decoupling of changes in the electrochemical signal and on the electrode surface. For example, from the amperometric transient presented in **Figure 4A**, two step events are observed: first corresponding to a

geometric amplification to a new steady-state current around 7 seconds and subsequently a geometric depression to a second steady-state current around 50 seconds. *A priori*, these two current responses would appear unrelated, as expected in classical collision electrochemistry, however, with correlated video microscopy,

these two responses can be resolved to a single GNP that initially collides and subsequently detaches from the electrode surface. This collision-attachment-detachment can be resolved with correlated microscopy to reveal a static platelet on the electrode surface spontaneously detaching and migrating back into solution.

Additionally, the power of correlated measurements allows characterization of complex collision transients that may involve reorientation processes, as presented in **Figure 4B** with an initial collision and current step followed by a second current step on the timescale of seconds. In the absence of correlated microscopy, there is ambiguity regarding the origin of a two-step signal, potentially leading to the divergent conclusion that there are either two collision events or one collision event that changes over time. Upon analysis, the correlated dark-field microscopy reveals that the coupled step behavior can be attributed to a single colliding platelet subsequently reorienting on the surface to change the electroactive surface area following the collision event. As stochastic collision electrochemical measurements are predicated on the assumption that a single collision produces a single response, this correlated technique offers a powerful method to directly relate electrochemical response to the physical interaction of the colliding entity on the electrode surface.

Herein, electrochemistry and dark field microscopy are coupled to characterize single entity collisions using a quasi-two-dimensional heterogeneous population of graphene nanoplatelets. As these planar entities produce a range of

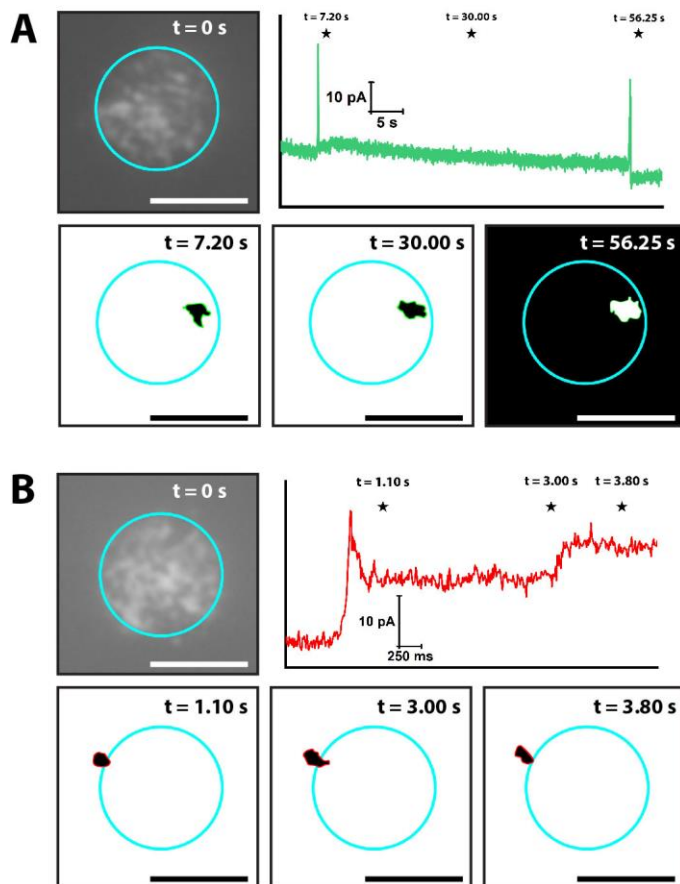


Figure 4. Dynamic Collision Transients Reveal Post-Collision Reorientation | (A) Representative complex transient behavior with an initial positive current-step and a subsequent negative current-step following approximately 50 seconds. From optical micrographs, the colliding graphene nanoplatelet is observed as static on the electrode surface following collision after which the platelet spontaneously detaches, manifesting in a negative current step of similar magnitude. The optical micrograph at $t = 56.25$ seconds corresponds to the physical detachment of the high contrast platelet on the electrode surface, manifesting as an apparent void zone. (B) Representative multi-step current transient response with steps separated by approximately two seconds. During the collision event, the graphene nanoplatelet is observed to initially collide on the electrode surface to extend beyond the underlying electrode and subsequently reorient to further extend,, increasing the electroactive surface area and thereby total

current responses upon collision with an electrode surface in the presence of an outer sphere redox mediator, electrochemistry alone is insufficient to deconvolute the effects of particle size and collision location on the resultant current response. Correlated amperometry and dark field microscopy allow facile determination of GNP-electrode collision geometries to begin probing populations of asymmetric nanoentities one-by-one. By directly quantifying the size of a colliding GNP and the additional contribution to the electrochemically active surface area of the electrode system, geometric amplification type events are well described in terms of enhanced analyte flux when the GNP collides near the edge of the electrode and extends onto the insulating glass substrate while remaining electrically connected. Additionally, these correlated measurements allow rapid and unambiguous determination of collision dynamics for more complex transient responses representing two or more elementary transient steps. In the context of single entity analysis, this technique offers a means to probe asymmetric entities including nanoparticles, other platelet systems, and living cells with excellent spatiotemporal resolution, potentially allowing complex studies on single entity interactions at the nanoscale.

Conflict of Interest Statement:

The authors declare no competing interests.

Acknowledgments

JED gratefully acknowledges the University of North Carolina at Chapel Hill for start-up funds, which supported this work. CR gratefully acknowledges

Author Contributions

All authors have given approval to the final version of this manuscript.

Supporting Information

Online supporting information is available at: . 1) Materials and Methods, 2) Ultramicroelectrode Characterization, 3) Transients in Absence of Redox Mediator, 4) Graphene Nanoplatelet Collision Transients at Varying Potentials, 5) Optical Micrographs of Adsorbed Graphene Nanoplatelet, 6) Micrograph Processing, 7) Supplementary Video Index

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