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Analysis of Diffusion-Controlled Stochastic Events of Iridium Oxide Single Nanoparticle Collisions by Scanning Electrochemical Microscopy

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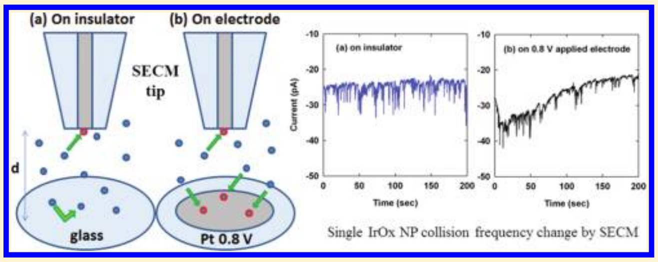
S Supporting Information

ABSTRACT: We investigated the electrochemical detection of single iridium oxide nanoparticle (IrO_x NP) collisions at the $NaBH_4$-treated Pt ultramicroelectrode (UME) in a scanning electrochemical microscope (SECM) over an insulating surface. The NP collision events were monitored by observing the electrocatalytic water oxidation reaction at potentials where it does not take place on the Pt UME. These collisions occurred stochastically, resulting in a transient response ("blip") for each collision. The frequency of the collisions is proportional to the flux of NPs to the UME tip, and thus equivalent to the SECM current. A plot of collision frequency versus distance followed the theoretical approach curve behavior for negative feedback for a high concentration of mediator, demonstrating that the collisions were diffusion-controlled and that single-particle measurements of mass transport are equivalent to ensemble ones. When the SECM was operated with a Pt substrate at the same potential as the tip, the behavior followed that expected of the shielding mode. These studies and additional ones result in a model where the IrO_x NP collision on the Pt UME is adsorptive, with oxygen produced by the catalyzed water oxidation causing a current decay. This results in a blip current response, with the current decay diminished in the presence of the oxygen scavenger, sulfite ion. Random walk and theoretical bulk simulations agreed with the proposed mechanism of IrO_x NP collision, adsorption, and subsequent deactivation.



■ INTRODUCTION

We report here scanning electrochemical microscopy (SECM) studies of the collisions of individual iridium oxide nanoparticles (IrO_x NPs) with the ultramicroelectrode (UME) tip, where the collision frequency replaces the SECM current as a measure of the response. The results show that stochastic events governed by random walk (RW) processes follow the same negative feedback behavior as the Fick's law-governed current at higher concentrations. This constitutes, in a sense, a demonstration that the time average of the observed particle motion is equivalent to the ensemble average behavior. These measurements also provide further insight into the mechanism of IrO_x NP collisions at an UME.

We have previously developed and investigated an electrochemical method to observe single NP collisions with an electrode. Observation of these events is based on the large current amplification that occurs when an electrocatalytic NP (e.g., IrO_x) collides with an UME that is much less active than the NP for a reaction of interest, such as water oxidation—oxygen evolution reaction (OER), and a rapid electrocatalytic reaction occurs. Recently, with IrO_x NPs and the OER electrocatalyzed by IrO_x,[1] we observed a transient or "blip" response for each collision. This was different than the step or "staircase" response that was obtained in earlier studies with the Pt NP/hydrazine oxidation system.[2] The staircase current increase can be explained by a model in which the NPs collide and stick irreversibly on the electrode surface. However, the blip current responses can occur when the rate of the reaction at the NP rapidly decreases because of deactivation of the NP surface or a shorter NP sticking time on the UME. Here, the sticking time will depend on the nature of the UME surface and the nature of the NP surface, which are functions of variables like the NP capping agent and adsorbents in the solution. For example, the electrocatalytic reaction can be deactivated by adsorption of species on the active sites that block them from carrying out the electrocatalysis; deactivation can also be caused by decomposition of the NP.

If the NPs stick and are deactivated, a concentration gradient will form at the UME surface that can be expressed as a diffusion-controlled collision frequency. This is analogous to the diffusion of a species that undergoes a chemically irreversible electron-transfer reaction at the electrode.

In principle one can explain the IrO_x NP collision mechanism by analysis of the frequency of the collisions. If the NP sticks on a disk UME surface, the collision frequency

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will be proportional to the disk electrode radius, r_d, by a RW process, equivalent for a continuous process to Fick's law.[3] The step frequency, f_p (particles s^{-1}), is thus given by

$$f_p^{ads} = -4D_p r_d c_p^{bulk} \tag{1}$$

where D_p is the diffusion coefficient of the particle. On the other hand, if the NP is not irreversibly adsorbed or deactivated and simply collides and comes off of the electrode, the frequency will be proportional to the area of electrode. In this case, the frequency, f_p (particles s^{-1}), is

$$f_p^{ela} = -\pi r_d^2 k_{ads} c_p^{pca} \tag{2}$$

where k_{ads} (cm s^{-1}) is the rate constant for adsorption and C_p^{pca} is the time-averaged concentration of NPs at the electrode surface (or plane of closest approach). RW simulations have been used for treating electrochemical reactions[4] but not, to our knowledge, for examining elastic or transient adsorption cases where the simulated results satisfy the theoretically obtained eqs 1 and 2. As shown in our previous study,[5] the frequency is proportional to the radius of the electrode for the diffusion-controlled case and to the area of the electrode for the elastic collision case.

However, we reported that it was difficult to distinguish whether the adsorption of NP on the electrode surface is long-term or transient. Even for elastic collisions at low concentrations, the collisions bin as bunches of collisions,[5] and the frequency of the bunches, as opposed to the individual collisions, was found to be proportional to the radius of electrode, not the area. That is, at low concentrations, the arrival of a particle at the electrode surface depends upon RW diffusion, but once at the electrode surface, the particle will undergo many collisions until it diffuses away. However, in this case, no macroscopic concentration gradient forms. In any event, the response could not be used to determine the nature of blip current response.

Another way one can prove the mechanism of permanent adsorption (sticking) is to determine the time dependence of the frequency. This is equivalent to considering the decay of current, e.g., as in a Cottrell plot, with time. In this case, it is the collision frequency that decreases as a function of time, as governed by Fick's law, when the NP is irreversibly adsorbed on the electrode surface, with continued diffusion of NPs from the bulk solution. The small frequency change of NP collision is difficult to detect because the concentration change is quite small during the experimental time domain, NP collisions are stochastic events, and in some cases the particles can change over extended time periods, e.g., aggregate. Since this experiment is performed with a very low concentration of NPs (picomolar), their movement must be considered by a RW model rather than by Fick's law, because the inter-NP distance is large and the concentration gradient is too small to detect.

One can also demonstrate the existence of diffusion-controlled behavior at steady state in the SECM, because the tip−substrate distance, d, is directly related to the diffusion time. Here we study the collision frequency as a function of distance between the electrode and an insulating substrate, where negative feedback occurs. We could also use an active substrate at the same potential as the tip, which can cause a shielding effect by consuming the IrO_x NPs on both electrodes. Theoretical approach RW simulations were carried out and compared with experimental results. Finally, an oxygen scavenger and alternative sacrificial donor, sulfite ion, was employed to identify whether the reaction product, oxygen, is responsible for the deactivation.

Note that Peterson and Cliffel[6] used thiol-monolayer-protected gold nanoclusters as a mediator with the SECM; however, this was at a much higher NP concentration, resulting in microampere-level currents in recorded approach curves. Their work, however, demonstrated the use of NPs as mediators in the SECM.

■ EXPERIMENTAL SECTION

Reagents. Potassium hexachloroiridium(IV) (K_2IrCl_6) was obtained from Johnson Matthey Inc. (Ward Hill, MA). All buffer salts and other inorganic chemicals were obtained from Sigma or Aldrich, unless otherwise stated. All chemicals were used as received. Ultrapure water (>18 MΩ, Millipore) was used in all experiments. Platinum (99.99%) wires, 10 μm diameter, from Goodfellow (Devon, PA) were used to fabricate the UME and SECM tips.

Preparation of Metal Nanoparticles. Iridium oxide (IrO_x) colloid (diameter 28 ± 4.8 nm) was prepared according to the procedure reported elsewhere.[1,7]

Preparation of UMEs and SECM Tips. UMEs (10 μm Pt) were prepared with platinum wires sealed in molten soft glass following the general procedures developed in our laboratory.[8] The metal wire was connected to a Ni-Cr lead with silver epoxy, and the electrode was polished, finally with 0.05 μm alumina, until a mirror surface was obtained. The projected surface area and the quality of UMEs were checked by voltammetry of ferrocene methanol oxidation in an aqueous solution. Platinum UMEs were used to fabricate the SECM tips by procedures described elsewhere;[8] the tips used in this study had the ratio between the insulator thickness and the radius of the microdisk electrode (RG) < 10. All electrodes were polished prior to use with alumina (0.05 μm) paste on microcloth pads (Buehler, Lake Bluff, IL).

Instrumentation. SECM and other electrochemical measurements were done in a CHI900 SECM station (CH Instruments, Austin, TX). The electrochemical experiment was performed using a CH Instruments model 660 potentiostat with the three-electrode cell placed in a Faraday cage. The electrochemical cell consisted of an UME or SECM tip working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. The data acquisition time in all experiments was 50 ms. The procedures in the measurements followed previous reports.[1,5] The stock solution of NPs was of micromolar concentration, and a few microliters of this was injected into the larger (10 mL) volume to obtain the reported concentrations of NPs.

Random Walk Simulation. The frequency of the observed blip responses in SECM was simulated with a C-language program under the same conditions as previously reported.[5] For the purpose of validating the general approach, simulations were carried out both for irreversible adsorption and for elastic collisions. For the simulation, we took a box (500 μm × 500 μm × d; d = 1, 2, 4, 5, 6, 8, 10, 12, 14, 15, 16, 18, 20, 40, 50, 60, 80, and 100 μm) on each side, where d represents the distance between tip and substrate. A tip electrode of 10 μm diameter was located centrally on the bottom of the box. Depending on the height of the box, d, from 250 to 25 000 particles were positioned in the box to maintain the particle concentration constant at 1 particle/1000 $\mu m^3 \approx 1.66$ pM.

The treatment of how the particle diffuses to the electrode follows that of the RW/collision model according to the approach described in our previous paper.[5]

All simulations were carried out at least 90 times for a given set of variables and the data averaged to produce the results shown.

■ RESULTS

SECM Negative Feedback Experiment. We investigated the blip current response with IrO_x NP collisions.[1,5] Analysis of collision frequency can be a key to solve the mechanism of IrO_x NP collision because the frequency is changed depending on the extent of adhesion during a collision. If the NPs stick irreversibly on the electrode surface, the electrode acts as a sink for particle diffusion and the collision frequency is totally diffusion-controlled. Moreover, depending on the current response, it can be identified as irreversible adsorption (as manifested by a step in the catalytic current) or as adsorption accompanied by irreversible deactivation, as manifested by a step followed by decay in the current. In this case, the frequency will be proportional to the radius of the electrode.

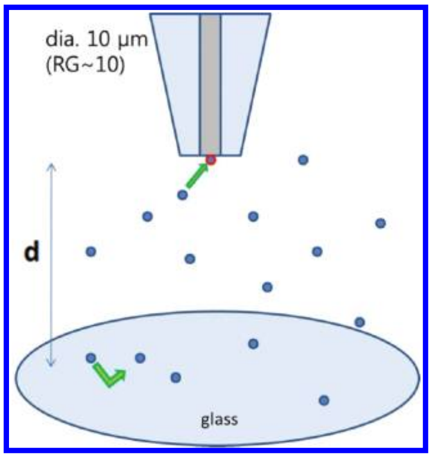
If the blip response is caused by a more elastic collision, with the NP ultimately desorbed, a concentration gradient of the type discussed above is not formed. Therefore, the average concentration gradient of the NPs during the overall experimental time would be zero, and a diffusion-limited flux cannot be used to calculate the collision frequency. In this case the RW[9] of individual NPs must be considered to model the response, and the frequency will be proportional to the area of the electrode, not the radius.

Experimentally, the frequency of the blip response by IrO_x NP collision was proportional to the concentration of NPs, the UME radius (not the area), and the reciprocal of solution viscosities.[5] Therefore, the frequency of blip response could be described by a diffusion-controlled movement of the particles to the electrode. However, even if the frequency is proportional to the radius of electrode and not to the area, the collision may be "elastic", not diffusion-controlled, because, as shown in the previous study,[5] the "elastic" collisions were binned as bunches at a very low concentration. This bunching comes from the limitation of data sampling time of the instruments employed to measure the current, because the collisional movement should be faster than the data sampling time in the potentiostat. Accordingly, the frequency of the collision bunches, where a bunch may represent a blip, also scales linearly with the electrode radius. To conclude, the frequency analysis focusing on the proportionality of the radius or area of the electrode in previous study was insufficient to identify the blip response.

Another way to investigate whether the IrO_x NP adsorbed on the $NaBH_4$-treated Pt UME (see Supporting Information) is to trace the concentration change (or frequency change) of NP as a function of time during the experiment. Even when the collision is clearly adsorptive, it is hard to detect the collision frequency change as a function of time because the initial concentration of NP is too low and the frequency is not changed much after several stochastic collision events. To overcome this difficulty in detecting the NPs concentration changes, we turned to measurements with the SECM.

To identify the nature of blip current response, the frequency was investigated in the thin layer between tip and substrate in the SECM as shown in Scheme 1. The current typically decreases as a function of distance from the tip to insulating surface as the tip approaches it (termed "negative feedback"); this is diffusion-controlled. We thus expect the collision frequency to decrease during the recording of an approach curve if it is controlled by RW. At the same time, if the collision is "elastic", not controlled by diffusion, the frequency will be independent of the distance between the tip and the surface. The red solid line in Figure 1 shows an approach curve by SECM typical, for example, of a ferrocene methanol solution with the tip over an insulating glass surface. This is typical negative feedback of SECM. The red squares and blue triangles in Figure 1 are results of RW simulation at different distances for 300 s: red squares represent the case when the NPs collide and stick for a long time, and blue triangle represent the case when the NPs collide elastically and bounce off the electrode surface. The normalized frequencies show the expected tendency. One shows diffusion-controlled behavior, and the other shows independence of cell thickness. Lastly, the black circles in Figure 1 are the experimentally obtained average frequencies of IrO_x NP collisions over 300 s at different

Scheme 1. Schematic Illustration of the Analysis of IrO_x NP Collision Frequency on the Glass (Insulating Surface) Using 0.8 V (vs Ag/AgCl) Applied Pt Tip Electrode of SECM (Tip Radius = 5 μm, RG ≈ 10)



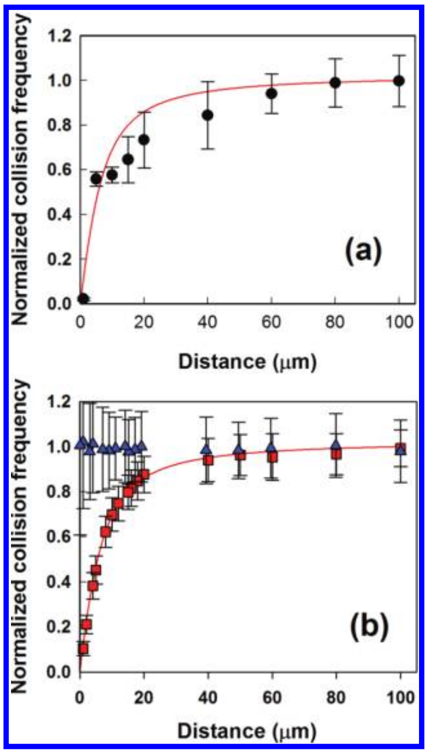
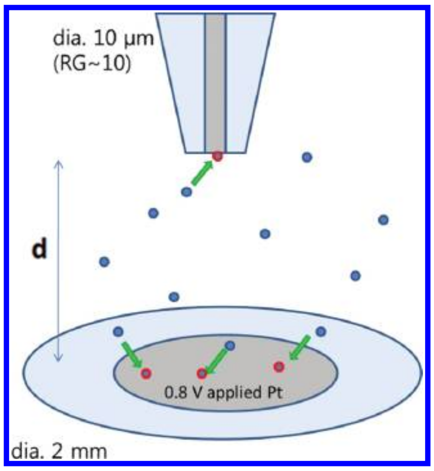


Figure 1. (a) Experimental (black circles) and (b) simulated (red squares for sticky collision and blue triangles for nonsticky collision) normalized collision frequency as a function of distance between a tip and insulating surface. The red line is theoretical approach curve. The tip radius is 5 μm, and RG ≈ 10. Total data collection time is 300 s. The applied E on the tip is 0.8 V (vs Ag/AgCl), and the pH is 13. The normalization is done with respect to collision frequency in bulk solution. Data acquisition time in experiment is 50 ms. The error bars show the standard deviation (experiments, 5 replicate measurements; simulation, 90 replicate measurements). Particle concentration is 2 pM. In the simulation, D_p was taken as 1.75×10^{-7} cm^2/s.

distances. It agrees well with the diffusion-controlled model and the RW simulation (red squares in Figure 1) and an approach curve governed by Fick's law (red solid line in Figure 1). The agreement for these three is very interesting and indicates that the collision of IrO_x NP onto the Pt electrode is highly adsorptive. The blip current response has to be caused by an irreversible deactivation following collision.

SECM Shielding Experiment. One can also carry out a shielding experiment by SECM, where the substrate and tip are held at potentials where both cause the same reaction of the investigated species. In this case the species is depleted even more than with simple negative feedback, so the shielding approach curve lies well beneath the negative feedback one.[10] Thus, in the IrO_x NP experiment, one can introduce another adsorptive drain on the substrate side of a thin layer, and if the oxidation reaction is irreversible, one should see a much faster decrease of NP concentration and hence the current. The collision frequency of IrO_x NP was investigated with a Pt disk electrode (radius ~1 mm) that was much larger than the tip, as shown in Scheme 2. As shown in Figure 2, when the Pt substrate was held at 0.8 V (vs Ag/AgCl), the collision frequency decreased much faster than negative feedback because most of the NPs collided and adsorbed on the larger Pt electrode opposite the tip (black circles in Figure 2), generating a typical SECM shielding approach curve. A RW simulation also showed the same tendency (red squares in Figure 2), demonstrating again that the stochastic calculation is equivalent to the ensemble diffusion calculation by Fick's law.[8] With this condition, as the concentration change becomes large, the collision frequency change as a function of time, equivalent to the tip current, can be investigated. The frequency change at the tip electrode as a function of time is shown in Figure 3. When we applied 0.8 V (vs Ag/AgCl) to both the substrate and tip electrodes, the frequency decreased faster as a function of time. When a potential at which the NPs are unreactive was applied on the substrate electrode, 0 V (vs Ag/AgCl), with 0.8 V (vs Ag/AgCl) on the tip electrode as shown in Figure 3b, the frequency decreased, but slower than when the substrate was at 0.8 V (vs Ag/AgCl). This indicates that some of the NPs can adsorb on the Pt UME at this potential (Supporting Information Figure S1), but most of the deactivation is caused by electron transfer at 0.8 V (vs Ag/AgCl). The RW simulated result represented in Figure 3c shows the same tendency as the experimental data (Figure 3a).

Scheme 2. Schematic Illustration of the Analysis of IrO_x NP Collision Frequency on the 0 or 0.8 V (vs Ag/AgCl) Applied Bigger Pt Disk Electrode (Radius ≈ 1 mm) Using 0.8 V (vs Ag/AgCl) Applied Pt Tip Electrode of SECM (Tip Radius = 5 μm, RG ≈ 10)



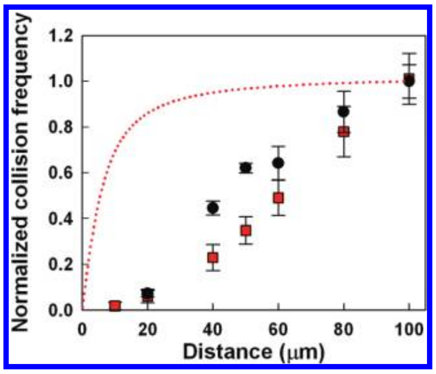


Figure 2. Experimental (black circle) and simulated (red square) normalized collision frequency as a function of distance between a tip and 0.8 V (vs Ag/AgCl) applied Pt disk electrode (radius ~1 mm). The red line is theoretical approaching curve on insulating surface. The tip radius is 5 μm, and RG ≈ 10. Total data collection time is 300 s. The applied E on the tip is 0.8 V (vs Ag/AgCl), and the pH is 13. The normalization is done with respect to collision frequency in bulk solution. Data acquisition time in experiment is 50 ms. The error bar is standard deviation (experiments, 5 replicate measurements; simulation, 90 replicate measurements). Particle concentration is 2 pM. In simulation, D_p was taken as 1.75×10^{-7} cm^2/s.

Adsorption and Deactivation of IrO_x. We also observed the adsorption of IrO_x NPs on a Pt electrode and the loss of their activity when 0.8 V was applied through additional experiments. In a background cyclic voltammogram of bare Pt electrode immersed for an incubation time of about 1−5 min in an IrO_x NP-containing solution, we could observe a peak at about 0.7 V that was not present in a scan before the NPs were added (Figures S1 and S2). We ascribe this peak mainly to the adsorption of smaller IrO_x NPs that can rapidly diffuse to the electrode and adsorb. The peak disappears on a second scan taken immediately after the first (Figure S1). As shown in Figure S2, the peak appears only when the UME is immersed in an IrO_x NP-containing solution, and the peak current increases as a function of incubation time and NP concentration until it attains a steady saturation level. This indicates that IrO_x NPs that are too small to produce clear blips adsorb on the Pt UME and are deactivated when a potential at which water oxidation starts is applied. The rate of deactivation is higher at more positive potentials. Therefore, the deactivation process seems strongly associated with the reaction itself, so we can rule out deactivation by impurity adsorption, which may play a role in other NP collision experiments. Moreover, it is unlikely we would see the rather uniform current decay at every current response if the decay were caused by adventitious impurities. Therefore, formation of reaction products, e.g., proton or oxygen, may be responsible for the deactivation.

For example, proton production in the OER could change the local pH with an increase of local overpotential for the reaction. To test this, IrO_x NP collisions were investigated at different pHs with different buffer solutions. Just as with the pH 13 NaOH solution, a pH 7 or 8 phosphate-buffered saline (PBS) solution produced the same shape of blip current response (Figure S3a). However, we did not observe current spikes in the pH 9 or 10 Tris buffer (Figure S3b). Therefore, the current response seems to be more sensitive to the

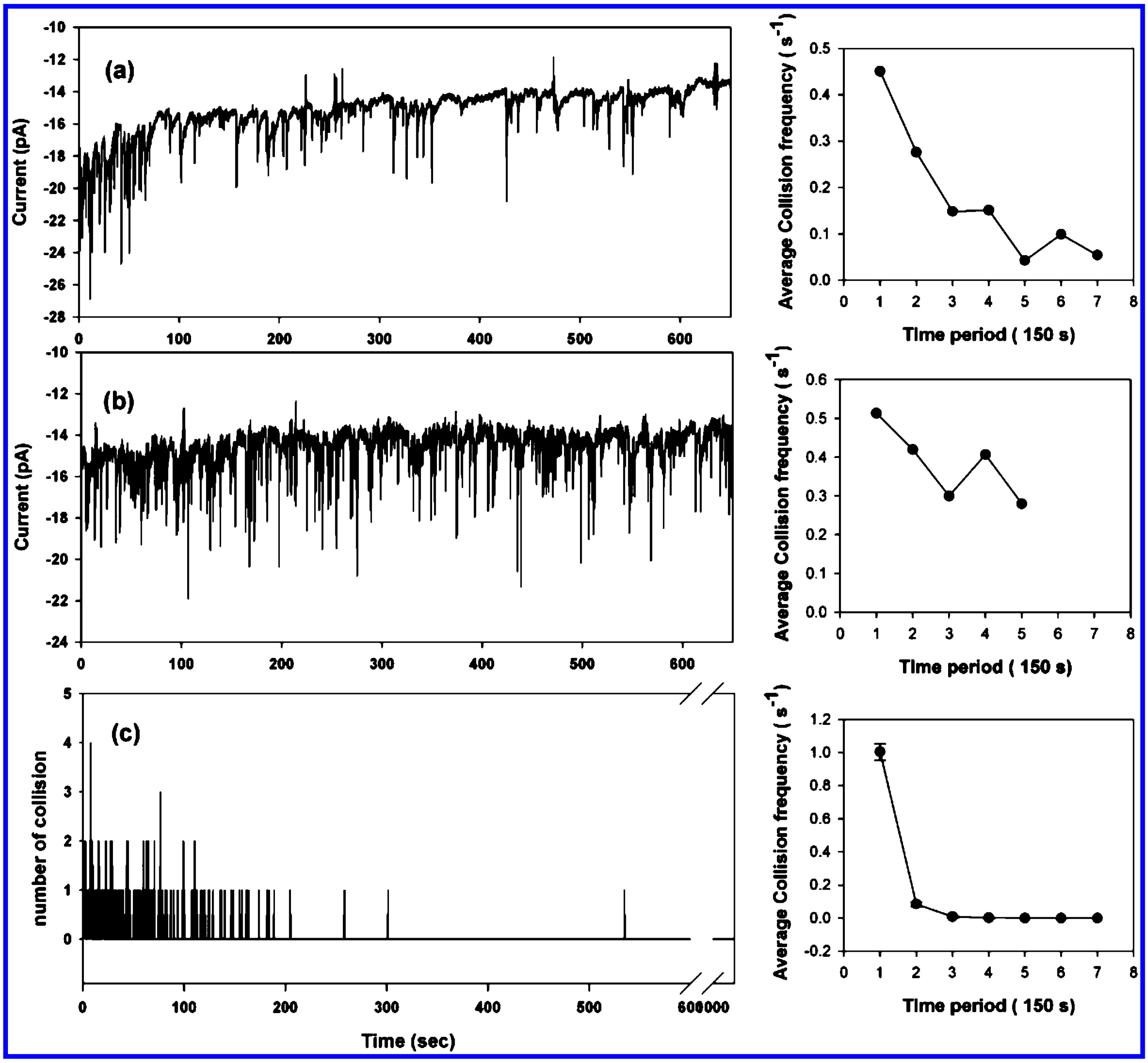


Figure 3. Experimentally obtained current transient of 0.8 V applied Pt tip electrode over a Pt disk substrate electrode (radius ~1 mm) held at (a) 0.8 or (b) 0.0 V vs Ag/AgCl. The distance between tip and substrate is 50 μm. The tip radius is 5 μm, and RG ≈ 10. (c) Simulation result of blip response as a function of time on the 0.8 V applied Pt disk electrode. The number of collisions is acquired every 50 ms. Particle concentration is 2 pM.

electrolyte than to the pH of the solution, suggesting that a local pH change caused by electrogenerated protons probably does not cause deactivation.

The frequency and shape of collision peaks is a function of the NP size, applied potential, and electrolyte concentration (Figures S4−S6). Especially in 75 mM PBS (pH 7), the peak shape changed significantly with corresponding applied potential. It was broader at a lower potential (1.1 V vs Ag/AgCl) and narrower at a higher potential (1.3 V vs Ag/AgCl) (Figure 4a), suggesting that the deactivation process is related to the kinetics of the electrochemical reaction. The sharp current response at 1.3 V (vs Ag/AgCl), i.e., a fast increase and fast decrease of current, implies that the electrochemical reaction is much faster at higher potential; however, the deactivation also happened more rapidly. Actually, the average amount of charge transferred per peak was about the same as with the peak at 1.1 V (vs Ag/AgCl): about 4.0 pC at both potentials. That indicates the current decay, i.e., the deactivation of the NP, is related to the amount of charge transferred, with the amount for the total deactivation independent of electrochemical reaction kinetics. Thus, the deactivation is related to the amount of reaction product, because when the electrochemical reaction is fast, the products are also produced rapidly.

To test the role of oxygen, the alternative reaction product to proton, in the deactivation, we added an oxygen scavenger, sulfite ion, into the electrochemical cell. When we added 1.5 mM sodium sulfite to the solution, the peak became broader, especially at 1.1 V (vs Ag/AgCl), where the current transient showed more of a staircase response, characteristic of collisions and adsorption of stable particles (Figure 4b).[2] The oxygen scavenger, sulfite ion, also acts an alternative electron donor and delays the deactivation process by oxygen. If sulfite only reacted with oxygen, a more dramatic change to a stepwise

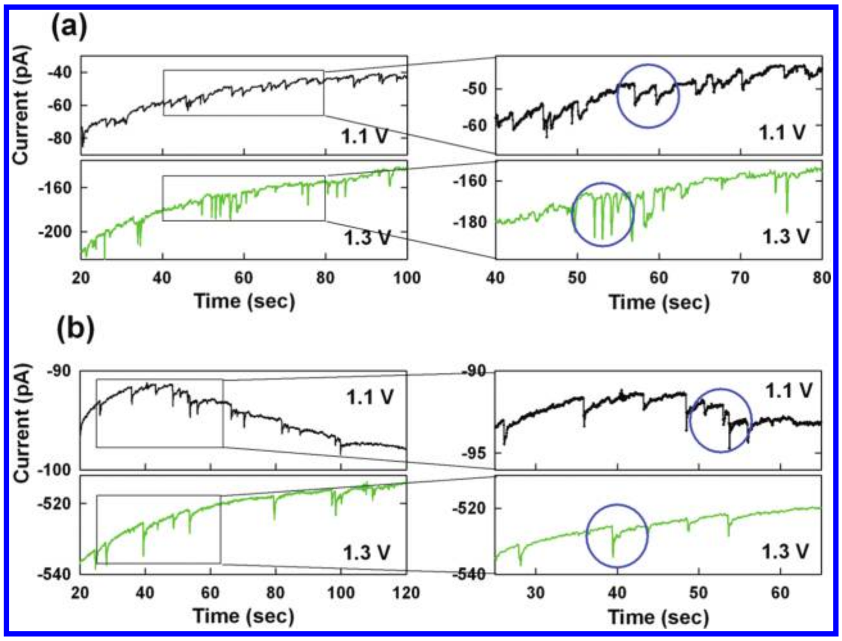


Figure 4. IrO_x NP collision in a pH 7 phosphate buffer (75 mM) at a 1.1 or 1.3 V applied (vs Ag/AgCl) Pt UME (radius 5 μm) (a) without and (b) with 1.5 mM sodium sulfite. The buffer solution contains 4 pM IrO_x NPs, and data acquisition time is 50 ms.

increase might be expected, but the sulfite itself can oxidize on the Pt UME, so the background current has a large offset, and this made it harder to observe the NP collision peaks. Nevertheless, we could see the peak broadened and the baseline changed (Figure 4b). The baseline changed even more with higher IrO_x NP concentrations (Figure S7).

Thus, we can explain the blip response of an IrO_x NP collision with an UME by the NP adsorbing and then deactivating during the OER, probably by formation of the reaction product, oxygen. The relatively slow current decay can be attributed to the aggregated structure of an IrO_x NP rather than a single compact sphere (Figure S8). Coverage by oxygen could block the electron transfer and result in a current decay. However, it takes some time for the oxygen to penetrate inside the aggregated structure of IrO_x NP.

When we added sulfite ion, not only the peak shape but also the peak frequency changed and became larger than in a sulfite-free solution. This is probably an effect of small NPs, because the structure of IrO_x NP is not a single sphere but rather an aggregation of smaller ones, so that there are always small NPs in the solution, which can be seen by TEM. However, these small NPs do not produce discernible collision signals.[1] In the presence of sulfite the collision signal is amplified more than just with the OER and the NPs have more time to transfer detectable charge before they are deactivated. This results in many small peaks.

The possibility of detachment of deactivated NPs from the electrode surface was also investigated, since the deactivation step may eventually be followed by the detachment of NPs from the electrode. If the deactivated NPs are detached and reactivated by the oxygen scavenger or cause reaction directly with it, the collision frequency will be recovered. But the SECM experiments in the presence of sulfite ion also showed the same diffusion-controlled behavior (Figure S9). Thus, the deactivated NP probably remains adsorbed on the electrode surface or is irreversibly deactivated.

■ CONCLUSIONS

We have studied single NP collisions with an UME tip by SECM. When the NPs stick to the electrode and remain active, they produce a stepwise current increase; we ascribe the frequency of staircase response to a diffusion-controlled movement of the particles to the electrode. Collisions of NPs that involve transient sticking or deactivation produce a blip response that can be investigated by frequency analysis in the thin layer between the tip and substrate in the SECM. The frequency change follows the diffusion-controlled movement of NPs and agrees with the simulated result by a random walk model and theoretical calculation by Fick's first law. The results demonstrate that single NP collision responses can be recorded with the SECM and these provide information about the nature of the NP interaction. For IrO_x NP collisions this involves transient adsorption followed by deactivation by the electrocatalytic OER reaction product, oxygen.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional figures and results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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