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PAPER

Stochastic electrochemistry with electrocatalytic nanoparticles at inert ultramicroelectrodes—theory and experiments†‡

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Collisions of several kinds of metal or metal oxide single nanoparticles (NPs) with a less catalytic electrode surface have been observed through amplification of the current by electrocatalysis. Two general types of current response, a current staircase or a current blip (or spike) are seen with particle collisions. The current responses were caused by random individual events as a function of time rather than the usual continuous current caused by an ensemble of a large number of events. The treatment of stochastic electrochemistry like single NP collisions is different from the usual model for ensemble-based electrochemical behaviour. Models for the observed responses are discussed, including simulations, and the frequency of the steps or blips investigated for several systems experimentally.

Introduction

Stochastic electrochemistry involves electrochemical studies where the current or charge associated with random individual events is observed at an electrode surface as a function of time, concentration, and electrode size, rather than the usual virtually continuous responses associated with an ensemble of a large number of events. The mathematical approach required to treat stochastic electrochemical processes is clearly different from the partial differential equation one that is widely used for modeling electrochemical behavior. However, even when individual current steps or pulses can be observed, the average of a large number of those events must conform to the predictions of ensemble (*i.e.*, non-stochastic) theory. By studying electrochemical systems involving individual events, in a manner analogous to that presently used for spectroscopic studies of single molecules and single particles,[1,2] we hope to obtain a deeper insight into the details of processes than is available from ensemble (macroscopic) studies where the behavior is averaged over a large number of events. Stochastic electrochemical techniques may also lead to new applications,

such as ultrasensitive analytical schemes and new approaches to probing the nature of events at electrode surfaces.

Several stochastic systems have been studied based on electrocatalytic particles, *e.g.* metal or metal oxide nanoparticles (NPs).[3–7] In this technique the current response associated with a single NP (typically 2 to 30 nm diameter) can be observed by taking advantage of the fact that a heterogeneous electrocatalytic reaction of interest will not occur at an appropriately selected "inert" electrode surface; the same inert surface can, however, carry out an electron transfer to a proximal or adsorbed electrocatalytically active NP to drive the reaction. In certain cases, for example when the NP is irreversibly adsorbed, this provides sufficient amplification for the multi-electron electrocatalytic processes to be seen as an individual event. Representative responses are shown in Fig. 1. Two general types of responses are seen: (a) a current staircase[3–5] or (b) a current blip (or spike) response[6,7] superimposed on a background current from the electrode. The

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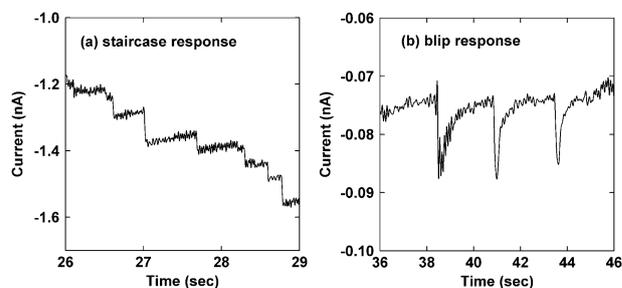

Fig. 1 Typical responses of single NP collisions: (a) staircase response of Pt NP/Au UME/hydrazine oxidation system[4,5] (b) blip response of IrOx NP/Pt UME/water oxidation system.[6]

current staircase response occurs when particles stick to the electrode for a time that is long compared to the duration of the overall experiment, so one sees the stepwise accumulation of individual and independently active particles on the electrode surface. Blip responses occur when any sticking time of the NP on the electrode is shorter. Clearly the nature of the electrode surface as a result of various pretreatments is important, as is the nature of the NP surface as a function of capping agent and ionic adsorption, in determining the observed behavior. Processes that deactivate the electro-catalytic reaction, for example by blocking the active sites on the NP, may also be important factors that control the nature of the responses.

As shown in Table 1, these kinds of responses with several different ultramicroelectrode (UME) materials, NPs, and electrocatalytic reactions, have been demonstrated. In all cases the diameter of the electrode is typically much larger than the NP diameter, and the concentration of the NP in solution is selected so that the probability of simultaneous events (*e.g.* two NPs interacting with the electrode at the same time) is very small. Moreover, studies are conducted for sufficiently short times that the area of the electrode affected by the multiple irreversible sticking collisions of particles is small relative to the total area, so that the NP-free area of the UME remains fairly constant and the probability of more than one layer of NPs is negligible.

The main approaches, so far, for characterizing the responses have been (i) the frequency of events at the electrode; (ii) the magnitude of the currents in each event; and (iii) the details of the shape of the current *vs.* time response as functions of experimental variables, such as particle concentration, UME size, reactant concentration, UME potential, and surface pretreatment of the electrodes and NPs. This paper is mainly devoted to experimental and theoretical approaches to finding models that can elucidate the observed frequency responses quantitatively or, at least, semiquantitatively. Such models may be useful in improving our understanding of the behavior of species at or near the surface of an electrode. This is accomplished in the following sections by discussing some stochastic models for diffusion and reaction, and by experimental studies. We leave discussions of the current magnitudes of the responses and the details of their shape to future papers on this work.

Theoretical model and simulation

A Staircase response-sticking model: diffusion limited flux of particles to the electrode

As discussed in earlier papers,[3,4] in the staircase response, the NPs appear to stick irreversibly on the electrode surface.

Therefore, at a sufficiently extreme potential a diffusion-limited flux of particles can be assumed with irreversible adsorption (as manifested by a step in the catalytic current) or by adsorption accompanied by irreversible deactivation, as manifested by a step followed by a decay in current. In either case the electrode acts as a sink for particle diffusion with a Dirichlet boundary condition,[8] $c_p^{pca} = 0$, where c_p^{pca} is the time averaged concentration of NPs at the electrode surface (or plane of closest approach) and c_p^{bulk} is the average bulk concentration of particles (particles cm^{-3}). The step frequency, f_p (particles s^{-1}), is:

$$f_p = 4D_p r_d c_p^{bulk} \qquad (1)$$

where D_p is the diffusion coefficient of the particle and r_d is the radius of the disk electrode. If adsorption is not sufficiently fast, more general expressions can be used to describe mixed kinetic and diffusion control:

$$f_p = 4D_p r_d (c_p^{bulk} - c_p^{pca}) \qquad (2)$$

and

$$f_p = \pi r_d^2 k_{ads} c_p^{pca} \qquad (3)$$

where k_{ads} (cm s^{-1}) is the rate constant for adsorption and r_d is the radius of the UME. The stochastic character of k_{ads} will be a function of k_{coll} (rate constant for collision of particles on the electrode, in cm s^{-1}) and p_{ads}, the probability that any given collision leads to adsorption. Thus on average

$$k_{ads} = p_{ads} k_{coll} \qquad (4)$$

With this conceptual model, adsorption cannot occur unless there has been a collision, however every collision will not lead to adsorption or an observable event. A slightly different way of thinking about this is to assume that adsorption occurs only at particular surface sites, *e.g.* particular structural defects on the electrode surface or places with surface adsorbates that promote adsorption of the NP. A collision is still required, but the probability, p_{ads}, will also be a function of the location on the surface. Combining eqn (1)–(4) gives:

$$f_p = 4D_p r_d (c_p^{bulk} - c_p^{pca}) = 4D_p r_d \left(c_p^{bulk} - \frac{f_p}{\pi r_d^2 k_{ads}} \right) \qquad (5)$$

Then

$$f_p = \frac{4D_p r_d c_p^{bulk}}{1 + \frac{4D_p}{\pi r_d k_{ads}}} \qquad (6)$$

When the k_{ads} is large, the maximum collision frequency, eqn (1) results and when the sticking frequency, k_{ads}, is

Table 1 Different stochastic electrochemistry experiments reported

Electrode	NP	Electrocat. reaction	Solution conditions	Resp.[a]	Ref.
C	Pt	$H^+ \rightarrow H_2$	50 mM H_2 citrate$^-$	ST	3
C, Au	Pt	$N_2H_4 \rightarrow N_2$	10 mM N_2H_4, pH 7.5	ST	4,5
Pt	IrO_x	$H_2O \rightarrow O_2$	0.1 M NaOH	BL	6
PtO_x	Au	$BH_4^- \rightarrow BO_2^-$	0.1 M NaOH	BL	7

[a] Type of response: ST = staircase; BL = blip or spike.

small $\left(k_{ads} \ll \frac{4D_p}{\pi r_d}\right)$, eqn (6) reduces to eqn (3) with c_p^{pca} replaced by c_p^{bulk}.

In the experimental studies, the observed step frequency depends on the electrode materials and surface modification. Applying this equation for Pt NP/Au, C electrode system, we could estimate a value for k_{ads} from the experiment. If the response was due to the sticking and deactivation of NPs, this approach could also be applied.

B Blip response

1 Random walk model. 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. In this case a different model is needed, where the details of the model depend upon the NP residence time on the electrode. An alternative is that the particle sticks to the electrode, but is much more rapidly deactivated than cases where steps are seen.

If we assume that there is no change in the nature of the particle at the electrode caused by deactivation or reaction, the blip response requires repeated transient sticking, but not permanent sticking. 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 random walk of individual NPs must be considered for understanding the response. As is well known from the random walk model, the NP is moving through the medium in all directions with the same absolute instantaneous kinetic velocity as in vacuum, v_{RMS}. Einstein[9] showed that the root-mean-square velocity (really the speed) of a particle in a liquid is expressed by the expression from kinetic molecular theory

$$v_{RMS} = \sqrt{\frac{3k_B T}{m}} \qquad (7)$$

where k_B (1.3803×10^{-23} J K^{-1}) is Boltzmann's constant, T (K) is the temperature Kelvin, and m is the particle mass.

We can use this same v_{RMS} to define the average random-walk speed

$$v_{RMS} = \frac{\delta}{\tau} \qquad (8)$$

where τ is the step period and δ is the step length for the random walk. Eqn (8) is true not only in gas phase but also in liquid phase with different τ and δ. Note that the particle is always moving, but is changing directions upon collisions with solvent molecules in a solution phase.

For particles in solution, the average collision frequency, $\overline{f_{coll}}$ (collisions s^{-1}) with surface area, A, and particle concentration, C_p, is:

$$\overline{f_{coll}} = \frac{1}{4} v_{RMS} A C_p = \frac{A C_p}{4} \sqrt{\frac{3k_B T}{m}} = \frac{\delta}{4\tau} A C_p \qquad (9)$$

The factor of 4 arises when it is assumed that the only particles that can collide with the surface are those that are within a distance δ of the surface[10] and that the random walk can take place in any (4π) direction. This is same as the collision frequency of a molecule in the gas phase.

The diffusion coefficient, D, is also a function of τ and δ:

$$D = \frac{\overline{\delta^2}}{6\tau} \qquad (10)$$

However, the $\overline{f_{coll}}$ is not the frequency of the blip response, because it represents the number of particles colliding with the electrode without any adsorption and measurable electron transfer. During the random walk motion, once a particle reaches the electrode surface by diffusion, it will undergo many collisions with the electrode. At a high concentration of NPs, many NPs will be colliding with the electrode continuously, so the average collision number will be essentially constant with time. However, at a very low concentration of NPs, the collisions with the electrode only occur when a particle has diffused to the vicinity of the electrode. Thus at low concentrations, there will be relatively long intervals (compared to τ) when no collisions are observed. However the average collision frequency is still given by eqn (9). Thus there will be a bunching of collisions, each bunch statistically separated from one another, where adsorption or electron transfer can only occur during the period of collisions. It is important to note the difference between the individual multiple collisions that occur with a very high frequency and the blips. The blip frequency will then be approximated by the frequency of bunches (when they can be identified). This bunching will produce the stochastic response observed and we show an approach to simulating this behavior in section 3 below.

2 Nonsticking model and estimation that the currents may be too small to see without transient adsorption. One can attempt to explain the blip responses by considering that the charge transfer to the NPs can occur without any adsorption and desorption through direct electron tunneling when the NP is located within a small distance from the electrode.

Heterogeneous electron transfer can occur over a distance, x, between the electrode and the redox center and the probability of electron transfer, p_{ET}, is approximated by a tunneling expression:[11]

$$p_{ET} \propto \exp\left[-\frac{x}{d}\right] \qquad (11)$$

in which d is a distance of the order of 10^{-8} cm. Based on this, we make the approximation that electron transfer between the base electrode (area a) and the particle is facile when the particle is within a distance, d (e.g., $\sim 10^{-8}$ cm), from the electrode and that there is no electron transfer at larger d (e.g., $d > 10^{-8}$ cm).[11]

The probability, p_n, that the volume ad will be occupied by n particles at any instant is defined by the Poisson expression:[12]

$$p_n = \frac{\gamma^n}{n!} \exp[-\gamma] \qquad (12)$$

Where

$$\gamma = adc_p^{bulk} \qquad (13)$$

For the experimental conditions of interest in the present work $\gamma \ll 1$ and

$$p_0 \approx 1; \; p_1 \underset{\gamma \ll 1}{=} \gamma; \; p_2 \underset{\gamma \ll 1}{=} \frac{\gamma^2}{2}; \; \cdots p_n \underset{\gamma \ll 1}{=} \frac{\gamma^n}{n!} \qquad (14)$$

If i_d (A) is the current associated with the particle when it is within the active volume, ad, then the average current, i_{avg}, will be defined by:

$$i_{avg} = \sum_{n=0}^{n_{max}} n p_n i_d \qquad (15)$$

When $\gamma \ll 1$ the dominant value of $n p_n$ obtains when $n = 1$ and the average theoretical current, $i_{avg,theory}$, will be

$$i_{avg,theory} \underset{\gamma \ll 1}{\cong} \gamma i_d \qquad (16)$$

An implicit assumption in this analysis is that there is no concentration polarization of the particle(s) in solution. If there is concentration polarization, then $c_p^{pca} \ll c_p^{bulk}$.

We can estimate i_d and γ from $i_d = 4\pi(\ln 2)nFDCr$ and eqn (13) using actual experimental variables, $e.g.$ 2 nA and 10^{-5}. Therefore, the value of $i_{avg,theory}$, $< 10^{-14}$ A, as deduced from eqn (16), is much smaller than the experimentally observed $i_{avg,exptl}$, $\sim 10^{-11}$ A, so that adsorption is required to rationalize the observed blip responses. If the NP adsorbs during a collision and the residence time is appropriate, it can produce a blip response. The average frequency of the blip response, f_b, will be

$$\overline{f_b} \propto p_{ads} \cdot \overline{f_{coll}} \qquad (17)$$

where p_{ads} is the probability of adsorption during a collision. If the rate of desorption is slow, the response will be a staircase one and the frequency will be controlled by the diffusion-limited flux as described in eqn (1). The kinetics of desorption may be important in understanding the shape of an individual blip, but not for estimating the blip frequency.

3 Simulation of random walk

Methodology. To understand better the frequency of the observed blip responses, a simulation written in C-language was carried out. Random walk simulations have been used in consideration of electrochemical reactions,[13] but not, to our knowledge, for examining elastic or transient adsorption cases. For the purpose of validating the general approach, simulations were carried out both for irreversible adsorption, where the analysis of section A applies, and for elastic collisions. For the simulation, we took a box (cube) 100 μm on each side as shown in Fig. 2. An electrode of 10 μm diameter was located centrally on the bottom of the box. Initially, one thousand of particles were randomly positioned in the box. The particle concentration was thus $1000/(100 \text{ μm})^3 \approx 1.66$ pM.

The treatment of how the particle diffuses to the electrode follows that of the random walk/collision model according to the following rules:[14]

(1) Each particle steps to the right or to the left of the x-axis once every τ seconds, moving at velocity $\pm \nu_x$ a distance, δ_x. At the same time, a particle moves along the y- and z-axis in the same way. For simplicity, we treat τ and $\delta_x = \delta_y = \delta_z$ as constants.

(Actually, particles move diagonally a distance of $\delta = \sqrt{3}\delta_x$.) In practice, these parameters depend on the size of the particle, the structure of the liquid, and the absolute temperature, T.

(2) The probability of going to the right at each step is 1/2, and the probability of going to the left at each step is 1/2.

Particles, by interacting with the molecules of water, are not a function of what happened on the previous leg of their trajectory. Successive steps are statistically independent. The walk is not biased.

(3) In a sticking response, the particle is removed when it arrives at the electrode. In a blip response, the particle bounces from the electrode.

(4) Each particle moves independently of other particles (*i.e.* they do not interact with one another). When it collides with the boundary of the box, it bounces back into the box, so that the flux out of the box is zero. We optimized the total simulation time, the size of box, and step time, τ, so that the diffusion layer does not exceed the box dimension. The collisions at the bottom face (xy-plane) represent collisions with the electrode and the glass insulator of the UME.

For the simulation, we require values for the parameters such as τ and δ_x. One can use v_{RMS} and D with eqn (8) and (10) to estimate the minimum values of τ and δ:

$$\tau = \frac{6D}{v_{RMS}^2} = \frac{\delta^2/\tau}{\delta^2/\tau^2} \qquad (18)$$

and

$$\delta = \frac{6D}{v_{RMS}} = \frac{\delta^2/\tau}{\delta/\tau} \qquad (19)$$

The calculated value for τ and $\delta_x = \delta/\sqrt{3}$ were about 1 ns and 0.19 nm respectively, taking $D = 1.75 \times 10^{-7}$ cm^2 s^{-1} and $v_{RMS} = 33.7$ cm s^{-1} (at $T = 296$ K, $m = 1.1 \times 10^{-16}$ g) for IrO$_x$ NPs. However these small values cannot be used, because the simulation time would be too long to carry out for the experimental times needed. Therefore, a 1 ms of step period was selected, with a step length, δ_x determined as 0.19 μm from the D-value.

The simulation parameters, $e.g.$, step size or total time, were adjusted to the selected box size to avoid artifacts that arise when the diffusion layer grows larger than the box dimension. As shown in the ESI† Fig. S1(a), the simulated collision frequencies for the irreversible sticking case depended on the size of the simulation domain taken. If these were small (<70 μm), the frequency was smaller than the theoretical value (from eqn (1)). The simulated frequency increased over this range with the size of the box, and became constant at the calculated value for a box size of 70 to 100 μm. The smaller value of sticking response appears to be caused by the thickness of the diffusion layer becoming larger than the size of the box taken. During the simulation, the diffusion layer grows and finally reaches the end of the box. At this time, the collision frequency decreases, making it smaller than the mass transfer controlled value. Thus, from this comparison we assume that we can simulate the behavior with a 1 ms step time and could use this number rather than the 1 ns steps, even for the transient adsorption case.
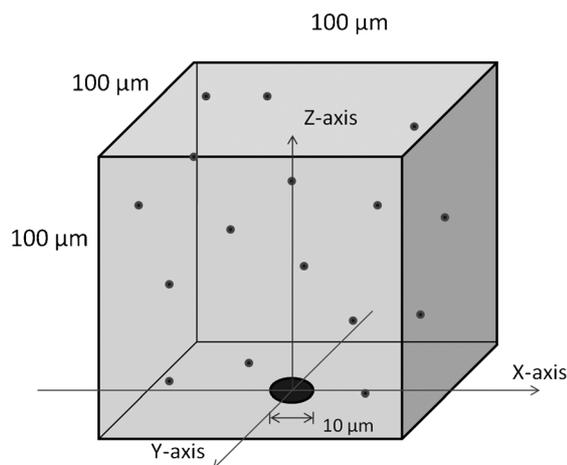
Fig. 2 Schematic representation of simulation domain.

For the blip collision, the total concentration within a box remains fixed and does not change with the size of the box. In other words, the initial number of particles in a box was different for different box sizes for the same particle concentration. For example, only one particle is used with the 10 μm box, compared to one thousand particles for 100 μm box. The simulated frequency, ESI† Fig. S1(b), also shows an effect of the box size, where the smaller collision frequency seems to be caused by the existence of fewer particles in a small box at a given concentration. However here too, the frequency value became essentially constant for domains above about 70 μm size and converged on the value calculated from eqn (9). A 100 μm size box was selected for all further simulations.

Not only the size of the box, but also taking a total simulation time that is too short or too long can produce an artifact. The diffusion layer grows with time, and the simulation has to be finished before the diffusion layer reaches the end of the box. This artifact for a long time only affects the sticking response, but not the blip response. A 50 s total simulation time seems to be appropriate as shown by the results in ESI† Fig. S2.

The simulation results only report the collision frequency of an elastic collision, which is not the experimentally obtained blip frequency. For high concentrations of species interacting with an electrode, the occurrence of collisions is quite uniform with time. However with the very low concentrations involved in the experiments here, collisions only occur when a particle has diffused to the electrode surface. At this time it will undergo many collisions and then can diffuse away. Thus the collisions occur in bunches; this can be seen in the simulations, as shown in Fig. 3. Transient adsorption and electron transfer occurs during these bunches and these result in the blips. To obtain the frequency of the blips, one was assigned to each bunch group, as shown in Fig. 4. While there is some arbitrariness in deciding the grouping, the trend and relative frequency as a function of different variables, like concentration and electrode size, can be recognized. The procedure used to decide on the number of bunches was to group (bin) the observed collisions in a 50 ms time window (the experimental data acquisition time in most experiments) and then bin these within a 250 ms window. Changing the

latter window to 100 or 500 ms resulted in only about a ±10% change in the frequency.

We should emphasize that the shape of the blips shown in Fig. 4 only are functions of the number of collisions in a bunch and are not meant to represent the current–time behavior; only the blip frequency is relevant. Of course, a better model would involve kinetic parameters for adsorption and desorption and electron transfer. This would allow not only a better estimate of the collision frequency, but also the magnitudes of the blip current and the shape of the response.

Simulation results. All simulations were carried out at least one hundred times at a given set of variables and the data averaged to produce results shown in Fig. 5 through 7 (as well as Fig. S1 and S2 in the ESI†). First, the simulations were carried out with different values of τ and δ_x. By changing these, the D and v_{RMS}-values can be varied. Then the collision frequencies at different v_{RMS}, c_p, and r_d were obtained and compared with theoretical and experimental ones. Fig. 5 shows how v_{RMS} affects the collision frequency, when D is fixed at 1.75×10^{-7} cm^2 s^{-1}. The collision frequency was independent of the v_{RMS}-value for a sticking collision (a), however, as expected, it linearly correlated with v_{RMS} for blip collisions (b). These results agree with the theoretical eqns (a) (1) and (b) (9). From the results, we could extrapolate the collision frequency to the actual value for the estimated particle size and the temperature, $v_{RMS} = 33.7$ cm s^{-1}.

The extrapolation fit the theoretical value, 6650 s^{-1}, obtained from eqn (9), suggesting that the use of an artificial v_{RMS} to estimate frequencies is justified. Fig. 6 shows the dependence of collision frequency on concentration. In both cases, sticking and elastic collisions, a linear relation with concentration results. Fig. 7 illustrates the collision frequency as a function of electrode size.

The collision frequency increased proportionally to the radius of electrode in a sticking collision, but with the square of the radius (*i.e.* with the area) in an elastic collision. Note however that, as shown in Fig. 4(b), the frequency of the bunches of collisions, which represent the blips, also scales linearly with the electrode radius. The results for the sticking collisions show that the random walk simulation of individual particles fit well with the equations derived by the diffusion-limited control, and lend confidence to the blip simulations done under the same conditions.

Experimental

Reagents

Potassium hexachloroiridium(IV) (K$_2$IrCl$_6$) was obtained from Johnson Matthey Inc. (Ward Hill, MA). Hexachloroplatinic acid (H$_2$PtCl$_6$) and tetrachloroauric acid (HAuCl$_4$) were obtained from Alfa Aesar (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.

Preparation of metal nanoparticles (NPs)

The platinum NP solution was prepared by mixing 60 mL of a 2 mM aqueous H$_2$PtCl$_6$ solution with 3 mL of 50 mM aqueous
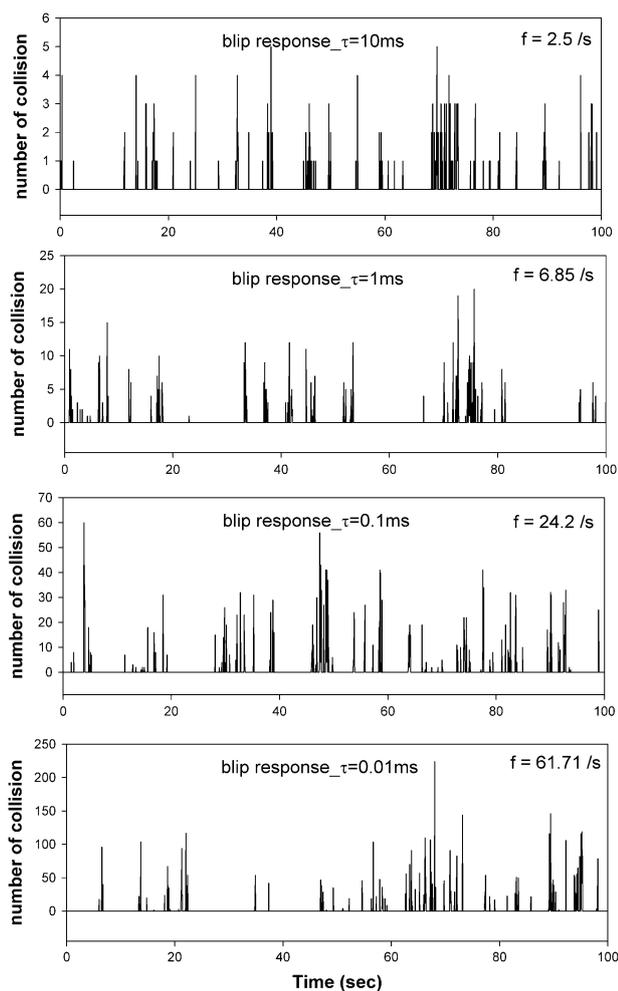
Fig. 3 Simulation results of blip response as a function of time at various v_{RMS}. A different step period (τ) was used to change v_{RMS} and the step length (δ_x) was determined from the $D = 1.75 \times 10^{-7}$ cm^2 s^{-1}. The number of collisions was acquired every 50 ms. Particle concentration, 1.6 pM; domain size, 100 µm; electrode radius, 5 µm.

Fig. 4 (a) Simulation results of blip response as a function of time for different electrode radii. The step period (τ) and step length (δ_x) are 1 ms and 0.19 µm, consistent with $D = 1.75 \times 10^{-7}$ cm^2 s^{-1}. (b) Bunch frequency as a function of radii of electrode. The number of collisions was binned for 250 ms.

sodium citrate solution under vigorous stirring, 7 mL of 120 mM aqueous NaBH$_4$ solution was added dropwise. The solution was kept stirring for another half hour.

Iridium oxide (IrO$_x$) colloid (diameter 28 ± 4.8 nm) was prepared according to the procedure reported elsewhere.[16] K$_2$IrCl$_6$ (6 mg) was added to 10 mL of an aqueous solution containing sodium citrate (3.4 mM). The red-brown solution was adjusted to pH 7.5 with a 0.01 M NaOH solution and then heated to 100 °C in an oil bath with constant stirring. After heating for 30 min, the solution was cooled to room temperature and the NaOH solution was added to adjust the pH to 7.5. The addition of NaOH solution at room temperature, followed by heating at 100 °C for 30 min was repeated until the pH had stabilized at 7.5. The solution was kept at 100 °C for 2 h with oxygen bubbling through the solution. The color of the solution became deep blue.

The gold NP solution was prepared by first boiling 35 mL of a 0.4 mM aqueous HAuCl$_4$ solution. A 1.3 mL aliquot of 1% sodium citrate solution was injected under stirring. The solution was kept boiling for another 15 to 30 min. The solution obtained was ruby in color.
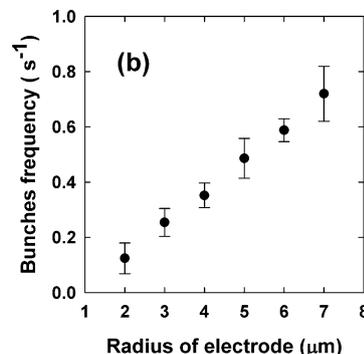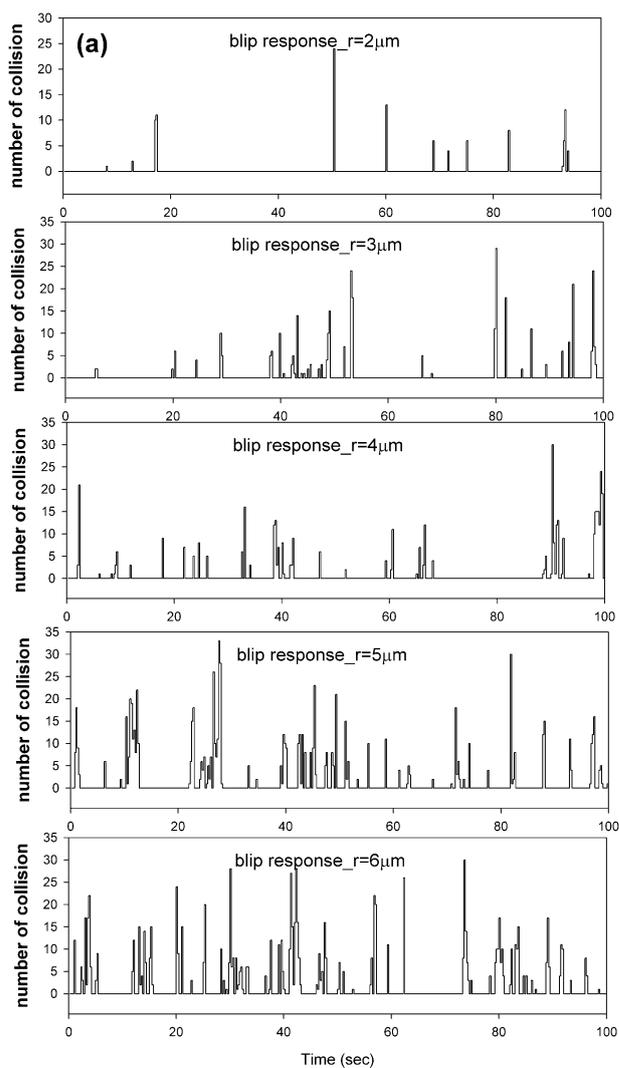
Preparation of ultramicroelectrode (UME)

UMEs (10 µm diameter C, Au, and Pt; 25 µm diameter Au and Pt) were prepared with carbon fiber, Au, and Pt microwires sealed in molten soft glass following the general procedures developed in our lab. The metal wire was connected to a Ni–Cr
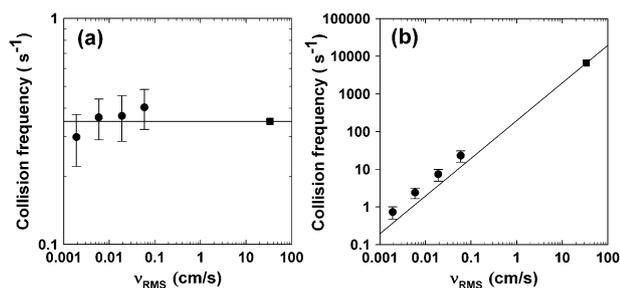
Fig. 5 Simulated collision frequency at various v_{RMS} in case of (a) sticking and (b) blip collisions. The D was fixed at 1.75×10^{-7} cm^2 s^{-1}. Particle concentration, 1.6 pM; radius of UME, 5 μm. Total simulation time was 50 s. The size of the domain was 100 μm. The solid line is theoretical value calculated by eqns (a) (1) and (b) (9). The square is a point from the actual value of v_{RMS} at 296 K.
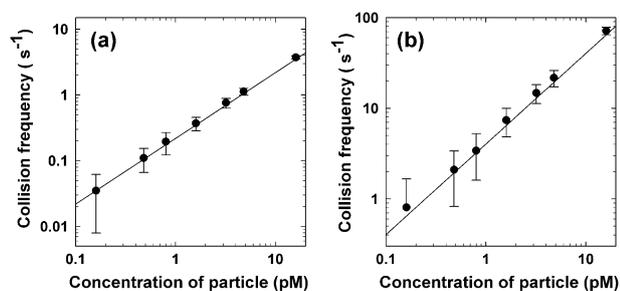

Fig. 6 Simulated collision frequency at various particle concentrations for (a) sticking and (b) blip collisions. Step period (τ), 1 ms; step length (δ_x), 0.19 μm (consistent with a NP diffusion coefficient, D of 1.75×10^{-7} cm^2 s^{-1}); radius of UME, 5 μm. Total simulation time was 50 s. The size of domain was 100 μm. The solid line is theoretical value calculated by eqns (a) (1) and (b) (9).
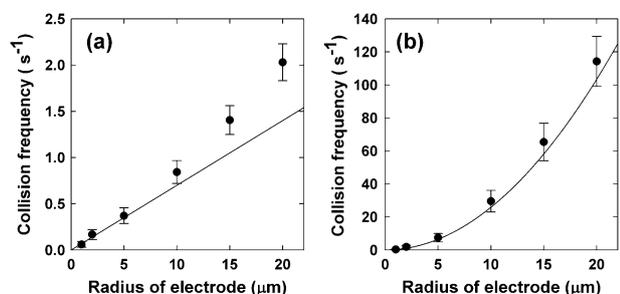

Fig. 7 Simulated collision frequency for various sizes of electrode for (a) sticking and (b) blip collisions. Particle concentration, 1.6 pM; step period (τ), 1 ms; step length (δ_x), 0.19 μm (consistent with a NP $D = 1.75 \times 10^{-7}$ cm^2 s^{-1}). Total simulation time was 50 s. The size of domain was 100 μm. The solid line is the theoretical value calculated by eqns (a) (1) and (b) (9).

lead with silver epoxy, 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. The very small electrodes (Pt, ~8 nm and ~72 nm in diameter) were prepared by a previously reported method.[15]

Viscosity of solution

The viscosity of the solution was varied by adjusting the ratio of water and glycerol: (v water/v glycerol) 9.5:0.5, 9.0:1.0, 8.5:1.5, and 8.0:2.0. All solutions contained 0.1 M NaOH as the only electrolyte.

Instrumentation

The electrochemical experiment was performed using a CHI model 660 potentiostat (CH Instruments, Austin, TX) with the three electrode cell placed in a Faraday cage. The electrochemical cell consisted of an UME (Pt, Au, and C), a Pt wire counter-electrode and an Ag/AgCl reference electrode.

Results

A Platinum NP /Au or C UME/hydrazine oxidation

In previous studies, we obtained a staircase response of sticking collisions with citrate-produced Pt NPs with Au or C UMEs.[3–5] The hydrazine oxidation behavior is significantly different on Pt, Au, and C electrodes. Thus, the collision and adhesion of a Pt NP on a less active Au or C electrode leads to a large current amplification. Fig. 8(b) shows the currents at a Au UME at 0.1 V before and after addition of Pt NPs (citrate stabilized, average diameter ~3.6 nm). The initial noise observed from 5 to 15 s was caused by the opening and closing of the Faraday cage during Pt NP injection. After that, the current increased stepwise (magnitude of 40 to 65 pA each step, rise-time about 40 to 100 μs) and remained at a steady value until the next collision. The step frequency can be estimated by the diffusion-limited steady-state flux, J, to an UME given by

$$J = 4D_pC_p/\pi r_d \tag{20}$$
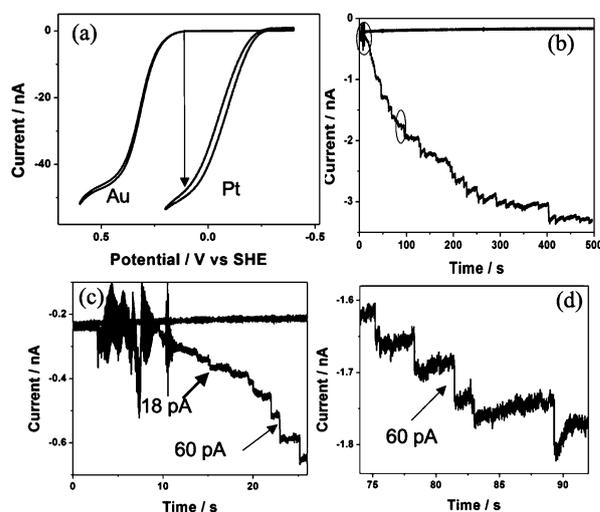
$$f_p = J \cdot A = 4DCr \tag{21}$$

Fig. 8 (a) Hydrazine oxidation at Au and Pt UMEs. Scan rate, 50 mV s^{-1}. (b) Current transient recorded at Au UME before and after Pt NP solution was injected. (c) Zoom of the initial part of (b), and (d) an intermediate part. Pt NP solution concentration, ~36 pM; particle size, ~3.6 nm; UME diameter, 10 μm; solution 10 mM hydrazine, 50 mM PBS buffer, pH ~7.5. Reprinted by permission of the ACS.

As mentioned in the theory section, all NPs are assumed to collide and stick at the electrode, with the total coverage being very small. The calculated f_p from eqn (21) is 0.2 pM^{-1} s^{-1} for $D = 1 \times 10^{-7}$ cm^2 s^{-1} and $r = 5$ µm. Experimentally, the peak frequency increased with increasing concentration of the Pt NPs (Fig. 9) with an average f_p of about 0.012 to 0.02 pM^{-1} s^{-1}. Since f_p is 10 times smaller than the theoretical value implies that not all of the collisions result in particle sticking, *i.e.* the k_{ads} is small for this system; the calculated k_{ads} from the experiment is of the order of 3×10^{-5} cm s^{-1} (eqn (6)).

To study factors influencing the probability of NP sticking, different electrode materials and treatments, different NP capping agents (*e.g.* thiol molecules), and UME surface modification (*e.g.* with a self-assembled monolayer (SAM)) were carried out. For example, treating the C UME with piranha solution resulted in about a five times higher sticking frequency.[4] The frequency decreased when a long chain alkyl thiol SAM was used as a capping group on the particle. Electrode surface modification with a SAM affected the frequency of collisions and for long chain SAMs, totally blocked them.[5] These results indicate that the collision frequency is very sensitive to k_{ads} and could also be a function of the location on the surface and the interaction between electrode surface and the NP.

B Iridium oxide (IrO$_x$) NP/Pt or Au UME/water (OH$^-$) oxidation

We observe a blip response at the IrO$_x$ NP/Pt electrode system.[6] IrO$_x$ is a known electrocatalyst for water oxidation,[16] showing better electrocatalysis than Pt at 0.8 V *vs.* Ag/AgCl in alkaline solution. When we added IrO$_x$ NPs (diameter 28 ± 4.8 nm) into an electrochemical cell with 0.8 V applied to a Pt electrode, current spikes were obtained signaling IrO$_x$ NP collisions with the electrode. Each current spike showed a fast increase and a slower decay as shown in Fig. 1(b).

To test the blip simulation results, experiments were carried out under different conditions. First, as shown previously,[6] the collision frequency was proportional to the concentration of NPs. Fig. 10 shows the linear correlation between frequency and concentration of NPs over the range 1 to 8 pM. The frequencies found at concentrations below 1 pM were irregular and difficult to define, since at this concentration on the average less than one NP is located within ∼10 µm from the electrode. In this case, the collisions are rare and seeing a signal in the experimental time domain has a small probability. At a higher concentration, ∼1.66 pM, there is an average of one particle within 10 µm from the electrode and the collision frequency can be examined by a stochastic model. Second, with different size UMEs, diameters ∼72 nm, 10 µm, and 25 µm, the normalized frequency increased proportionally to the UME radius (not the area) (Fig. 11). No useful signals (data not shown) were found with a ∼8 nm diameter electrode. This variation with electrode size is consistent with the simulation results of Fig. 4, where diffusion rather than collision is the limiting factor in current production. The frequency was also tested with different solution viscosities. The diffusion coefficient of NPs is inversely proportional to viscosity according to the Einstein–Stokes equation, so Fig. 12 can be considered as a correlation between the diffusion coefficient and collision frequency.

C Au NPs /Pt-PtO$_x$ UME/ BH$_4^-$ oxidation

Another example that shows a blip response involves Au NPs and an electrochemically grown PtO$_x$ layer on a Pt UME, observed with the amplification by NaBH$_4$ oxidation in basic solution.[7] This system also shows a linear dependence of the frequency of collisions with the concentration of Au NPs (ESI† Fig. S3) with a frequency of about 0.01 s^{-1}pM^{-1}. As shown in ESI† Fig. S4, for UME radii of 5 µm and 12.5 µm, the number of collisions over the same time interval also increased by about a factor of 2.5.

Conclusions

We have described observations of interactions of single NPs with an UME. When the NPs stick to the electrode and produce a stepwise current increase, the frequency of staircase response could be described by a diffusion-controlled movement of the particles to the electrode. Collisions of NPs that involve transient sticking produce a blip response that can be simulated by a random walk model. The observed frequency also suggests diffusion control. Models that address the size and shape of the current transients in this case are
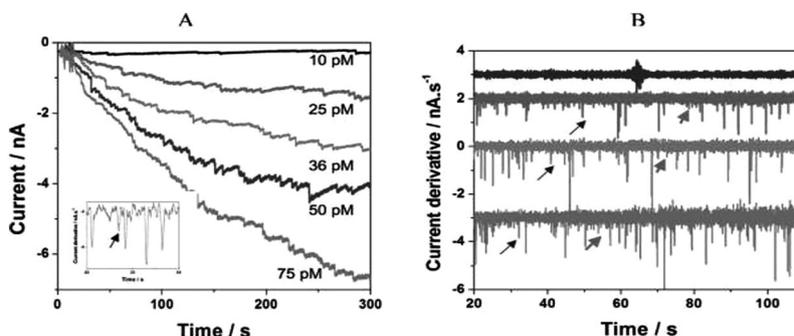

Fig. 9 Pt NP/Au UME/hydrazine system. (A) Current transients recorded at different Pt NP concentrations and (B) corresponding first-order derivatives. The top curve in (B) is the current transient recorded in the absence of MNPs. Traces are offset from zero for clarity. The left arrows point to spikes, which give rise to current steps above 20 pA, and the right arrows to current steps less than 20 pA. Particle size, ∼3.6 nm; 5 µm radius of Au UME; 15 mM hydrazine, 50 mM PBS buffer, pH 7.5. Reprinted by permission of the ACS.
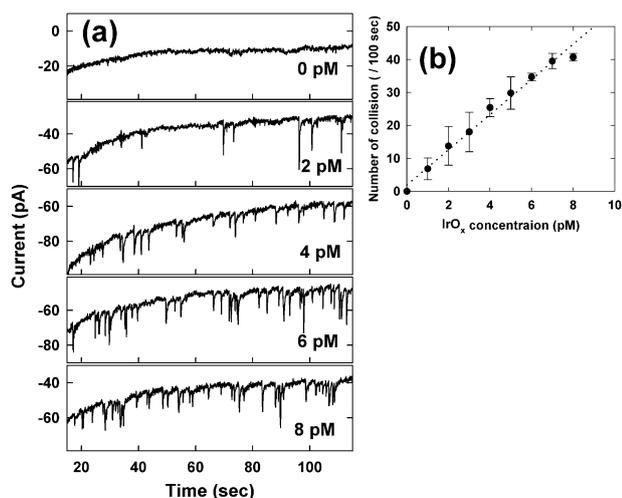
Fig. 10 IrO$_x$ NP/Pt UME/water oxidation system. (a) Chrono-amperometric curves for single IrO$_x$ NP collisions at the NaBH$_4$ treated Pt UME (radius 5 μm) in pH 13 solution (0.1 M NaOH) containing different concentrations of IrO$_x$ NPs from 0 to 8 pM. Applied potential, 0.8 V $vs.$ Ag/AgCl; data acquisition time, 50 ms. (b) Collision frequency as a function of IrO$_x$ NP concentration (for 3 to 5 replicate measurements) Reprinted by permission of the ACS.
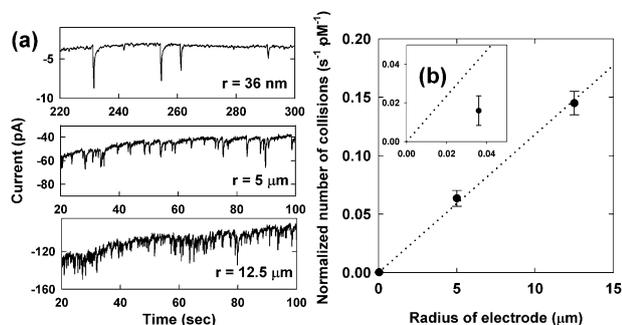

Fig. 11 IrO$_x$ NP/Pt UME/water oxidation system. (a) Chrono-amperometric curves for single IrO$_x$ NP at different size NaBH$_4$-treated Pt UMEs (radius of 36 nm, 5 μm, and 12.5 μm) in pH 13 solution (0.1 M NaOH). IrO$_x$ NPs concentration was 360 pM, 4 pM, and 8 pM respectively. Applied potential, 0.8 V $vs.$ Ag/AgCl; data acquisition time, 50 ms. (b) Collision frequency $vs.$ electrode radius. (for 3 to 5 replicate measurements).

under way and should provide a more detailed understanding of the blip process.
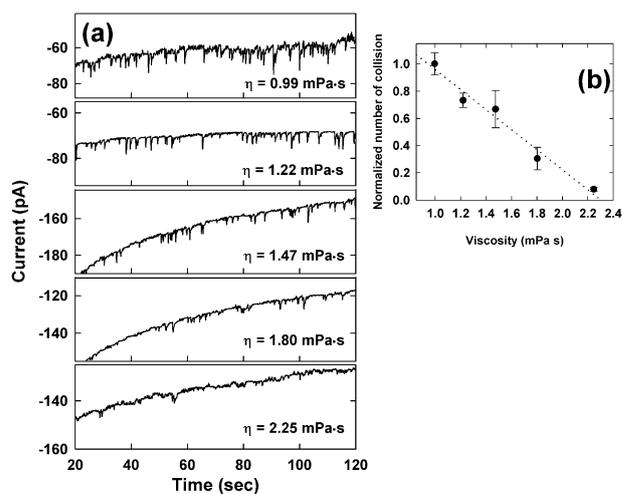
Acknowledgements

Fig. 12 IrO$_x$ NP/Pt UME/water oxidation system. (a) Chrono-amperometric curves for single IrO$_x$ NP collisions at a NaBH$_4$-treated Pt UME (radius 5 μm) in a pH 13 (0.1 M NaOH) solution. Applied potential, 0.8 V $vs.$ Ag/AgCl data acquisition time, 50 ms. (b) Collision frequency as a function of solution viscosity. (for 3 to 5 replicate measurements).

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