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Observing Iridium Oxide (IrO_x) Single Nanoparticle Collisions at Ultramicroelectrodes

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Abstract: We describe the electrochemical detection of single iridium oxide nanoparticle (IrO_x NP) collisions on a $NaBH_4$-treated Pt ultramicroelectrode (UME). We observe single NP events through the enhanced current by electrocatalytic water oxidation, when IrO_x contacts the electrode and transiently sticks to it. The overall current transient consists of repeated current spikes that return to the background level, superimposed on a current decay, rather than the staircase response seen where an NP sticks on the UME. Here each event produces a unique current spike (or "blip"). The frequency of the spikes was directly proportional to the particle concentration, and the peak current increased with the applied potential. The observed current is very sensitive to the material and surface state of the measuring electrode; a $NaBH_4$-treated Pt UME was important in obtaining reproducible results.

Metal nanoparticles (NPs) have been of interest in many fields, often because of their large surface-to-volume ratio and size-dependent optical properties.[1] Most research on NPs has focused on ensemble-averaged properties,[2] but there have been investigations of the electrochemical behavior of an immobilized single NP, despite the experimental difficulties of fixing, characterizing, and making measurements at the nm scale.[3]

Studies of the electrochemical behavior of diffusing NPs at an electrode can provide information about the dynamic behavior but are more difficult. Previous reports from our laboratory described single NP collisions with an electrode.[4] These studies utilized the large current amplification that occurs when a platinum (Pt) NP collides and sticks to an inert electrode and a rapid electrocatalytic reaction occurs. In this case, a stepwise current increase ("staircase" response) is seen whenever a Pt NP contacts an electrode surface and sticks to it.

In this paper we report the observation of NP transients where the response is a "blip" or "spike" (vs a "staircase"), demonstrating a shorter residence time (<1 s) at the electrode surface. The background current level remained steady even after multiple collisions and each current spike was transient and reversible. As discussed later, the observed current magnitude implies that the collisions involve transient sticking.

We used NPs of iridium oxide (IrO_x) (diameter 28 ± 4.8 nm, see Figure S1 in the Supporting Information), a known electrocatalyst for water oxidation,[5] to observe the blips. As shown in Figure 1, without IrO_x NPs, the current for water oxidation at a Pt ultramicroelectrode (UME) in an aqueous solution (pH 13) at an applied potential of 0.8 V (vs Ag/AgCl) is small. However, in the presence of IrO_x NPs the current greatly increases. As illustrated in Scheme 1, only when an IrO_x NP is in contact with the electrode surface, does one see an enhanced water oxidation current. On the electrode surface, the electrochemically generated Ir^{VI} state of the NP is thought to act as a redox catalyst for water oxidation, cycling between different Ir oxidation states.[6] When the IrO_x NP leaves the electrode surface or is blocked by impurities or products, the current ceases. This behavior causes the current spike shown in Scheme 1. If the IrO_x NP irreversibly stuck on the electrode after colliding, a stepwise current transient would be obtained as shown in previous papers with Pt NPs.[4a,b]

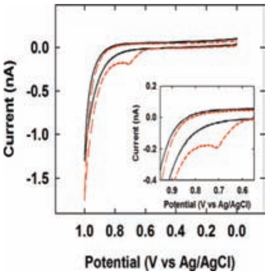

Figure 1. Cyclic voltammograms of water oxidation at Pt UME (radius 5 μm) in pH 13 solution (0.1 M NaOH) containing 0 (black solid) or 12 pM IrO_x NPs (red dashed). Scan rate is 50 mV/s.

Scheme 1. Schematic Illustration of Single IrO_x NP Collision Event and the Current Enhanced by Electrocatalytic Water Oxidation

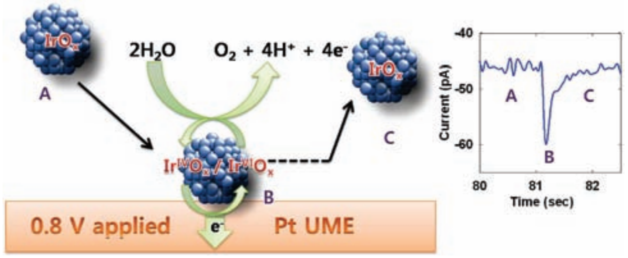

Figure 2 shows typical behavior on injecting a solution of IrO_x NP into the solution containing the UME. The current spikes were quite uniform, although there were some differences in shape and height, which probably indicate differences in the size and shape of the particular NP and differences in the course of the reactions with time.

Normally, the current spike in a single collision showed a very fast increase and a slower decay. The fast increase in current signals the contact of the NP on the electrode surface, while the slow current decay may represent processes while the NP is sticking to the electrode and carrying out the electrode reaction. A local pH change during the reaction, blockage of NP active sites by product or impurities, and NP decomposition and detachment from the surface may be responsible for such transient behavior. The charge passed during a single collision event was roughly $(1-20) \times 10^{-12}$ C (2 to 40 pA height of a current spike). A previous report[6] showed that all Ir sites in ensembles of small (1.6 ± 0.6 nm) IrO_x NPs were active with a turnover frequency (O_2 molecules/Ir site/s) of 8 to 11 s^{-1} at 1.0 V. For our larger (diameter 28 ± 4.8 nm) NPs containing about $(2.9 \pm 1.4) \times 10^5$ Ir sites, assuming a turnover

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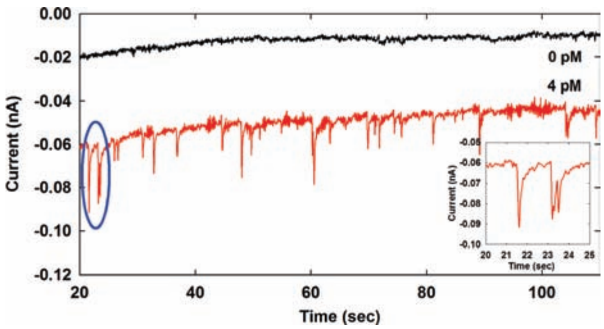

Figure 2. Chronoamperometric curves for single IrO$_x$ NP (radius ∼14 nm) collisions at the NaBH$_4$-treated Pt UME (radius 5 μm) in pH 13 solution (0.1 M NaOH) without (black) and with (red) 4 pM IrO$_x$ NPs. Applied potential is 0.8 V (vs Ag/AgCl). Data acquisition time is 50 ms. The small change in the background current may be caused by a small number of IrO$_x$ NPs adhering to the electrode.

frequency of about 10 s^{-1}, each NP would produce (2.9 ± 1.4) × 10^6 molecules of O$_2$/s (equivalent to about (1.9 ± 0.9) × 10^{-12} C/s), consistent to what is observed.

The collision frequency was proportional to the particle concentration (Figure 3) with a value of 0.07/s at a 1 pM IrO$_x$ NP concentration. In this study, the particles do not stick permanently and thus do not generate a concentration gradient, so the collision frequency cannot be calculated simply from the steady-state diffusion-controlled flux of particles to the UME surface,[7] $f_{p,s}$. However this equation,[4a] $f_{p,s} \approx 4D_pC_pa$, gives a lower limit (D_p is the diffusion coefficient and C_p is the concentration of the particles; a is the radius of the UME disk electrode). The estimated diffusion arrival frequency, 0.21/s (at a 1 pM IrO$_x$ NP concentration), is a little higher than the experimental value, so not all NP arrivals to the electrode surface result in measurable transients.

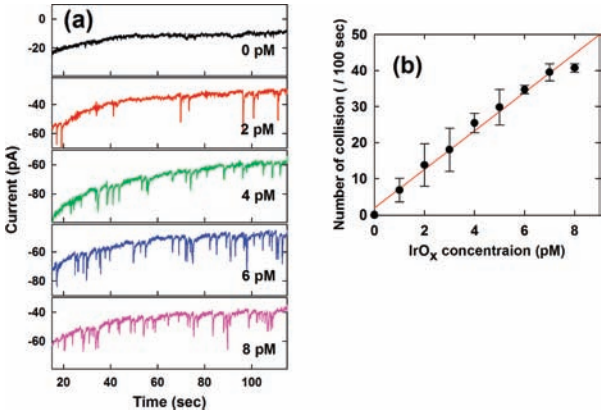

Figure 3. (a) Chronoamperometric curves for single IrO$_x$ NP collisions at the NaBH$_4$ treated Pt UME (radius 5 μm) in pH 13 solution (0.1 M NaOH) containing various concentrations of IrO$_x$ NPs from 0 to 8 pM. Applied potential is 0.8 V (vs Ag/AgCl). Data acquisition time is 50 ms. (b) Correlation between the number of collisions and concentration of IrO$_x$ NPs (for 3 to 5 replicate measurements).

Although no staircase response is seen, even an approximate consideration of the currents observed suggests that some transient sticking of the IrO$_x$ NPs must occur. Adsorption of IrO$_x$ NPs at the Pt UME at open circuit is shown in experiments like those in Figure 1, because the peak height of the voltammogram obtained when a Pt electrode is dipped into an IrOx solution depended on the quiet time before a voltammogram was run. The observed peak current near 0.7 V (vs Ag/AgCl) increased with immersion time before the voltammogram and also with the IrO$_x$ concentration (see Figure S2). However, these open circuit adsorbed NPs were removed when a potential above 0.7 V at pH 13 was applied. The peak disappeared on a second voltammetric scan and only recovered after standing at open circuit. The background current of a chronoamperometric curve at 0.8 V after exposure of the Pt UME at open circuit for different quiet times decreased with time and reached a steady-state value that was almost the same as the one for an IrO$_x$-free solution (with a small offset) (Figure S3). However blips are still observed with a quite steady frequency for at least 2 h. Thus, the recovery to the background current level seems to indicate that the particle leaves the electrode surface after transient sticking, probably because of the oxygen evolution reaction. Thus the current spikes represent the initial collision and then the loss.

In addition, small numbers of NPs remaining on the electrode surface are probably responsible for the current offset of IrO$_x$-containing solution. (See Figures S4 and S5 in the Supporting Information.) Such a current offset was also observed in a previous study.[6]

The shape and frequency of the current transients are affected not only by the NPs but also by the state of the surface of the measuring UME. For example, an untreated bare Pt electrode does not show good reproducibility for chronoamperometric measurements. However, after immersing the Pt UME in a 10 mM aqueous NaBH$_4$ solution for 5 min, more reproducible results are obtained and the frequency of current spikes increased as compared with an untreated electrode (see Figure S6), even though water oxidation at the Pt UME itself did not change very much (see Figure S7). How the NaBH$_4$ activates the Pt electrode surface to the IrO$_x$ NPs collision is still not clear, although the use of a NaBH$_4$ treatment to activate Au or Pt electrodes for other reactions has been reported.[8] However, according to X-ray photoelectron spectroscopy (XPS) analysis (see Figure S8), the IrO$_x$ NP appears to stick better on a NaBH$_4$-treated Pt UME as compared to an untreated one, perhaps because the more-reduced Pt surface is stickier than an untreated one. We also noted the same tendency when a different reducing agent, such as hydrazine, was substituted for the NaBH$_4$.

In conclusion, we describe the electrochemical detection of single IrO$_x$ NP events at the UME. During the collisions, we could observe the current enhanced by electrocatalytic redox cycling. Studies of the collisions of single NPs in the absence of long sticking simplifies the application of this technique in studies of electrocatalysts and in analytical schemes, since each measurement is not affected by earlier NP collisions.

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Supporting Information Available: Experimental details and additional experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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