

Observation of Electrocatalytic Amplification of Iridium Oxide (IrO_x) Single Nanoparticle Collision on Copper Ultramicroelectrodes

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Recently, the observation of the electrocatalytic behavior of individual nanoparticles (NPs) by electrochemical amplification method has been reported. For example, the Iridium oxide (IrO_x) NP collision on the Pt UME was observed *via* electrocatalytic water oxidation. However, the bare Pt UME had poor reproducibility for the observation of NP collision signal and required an inconvenient surface pre-treatment for the usage. In this manuscript, we have been investigated other metal electrode such as Cu UME for the reproducible data analysis and convenient use. The IrO_x NP collision was successively observed on the bare Cu UME and the reproducibility in collision frequency was improved comparing with previous case using the NaBH₄ pre-treated Pt UME. Also, the adhesion coefficient between NP and the Cu UME was studied for better understanding of the single NP collision system.

Key Words : Single nanoparticle collision, Iridium oxide, Electrochemical amplification, Cu ultramicroelectrode

Introduction

Recently, Bard's group observed single nanoparticle collisions at an ultramicroelectrode (UME) using an electrochemical amplification method.¹⁻⁴ A system consists of a nanoparticle (NP) and UME, and an electrocatalytic reaction is required for the observation of single nanoparticle collisions on the UME by electrochemical amplification method. The materials for the NP and UME should have different electrocatalytic activities for the reaction. If the NP shows better electrocatalytic activity than the UME at an appropriate potential window, the electrochemically amplified current could be observable when the NP collided on the UME. For examples, the Pt NP was better electrocatalyst than the Au UME for the hydrazine oxidation and the IrO_x NP showed better electrocatalytic activity than the Pt UME for the water oxidation at an appropriate conditions. Therefore, Pt NP collision on the Au UME^{1,2} and IrO_x NP collision on the Pt UME³ have previously been reported by this method.

The single NP collision on the UME is recorded as a current transient. Interestingly, the two cases show different current responses: a staircase response and a blip response, respectively.^{4,5} In the case of staircase response, the NPs adhere to the electrode surface and continues to catalyze the electrocatalytic reaction. The Pt NP collision on the Au UME shows the staircase current increase. On the other hand, the blip response obtained by the IrO_x NP collision on the Pt UME is a little complicated. In this case, the NP seems to adhere to the electrode surface similar to the staircase response but has a following deactivation process. The reason for the deactivation process of IrO_x NP is unclear at this moment. But it is possibly due to the oxygen bubble,

which is one of the reaction products, and can cause additional overpotential that maintains the continuous electrocatalytic reaction.^{6,7}

As mentioned, the current responses of single NP collision event depend on many variables: not only the mechanism of electrocatalytic reaction mentioned above, but also the interaction between NP and UME, the surfactant of NP, the electrolyte, or applied potential *etc.* So it is interesting to note that the frequency, amplitude, or shape of the current response of single NP collision also depend on the material of the UME. Actually, the single IrO_x NP collision was first observed on the NaBH₄ pre-treated Pt UME. The current transient signal of the IrO_x NP collision on bare Pt UME was poorly reproducible. This seems to depend on the amount of Pt oxide layer on the Pt UME. Therefore, reduction pre-treatment using NaBH₄ is required for better reproducibility. Not only Pt UME but also other materials able to make UME had been tried for this application. On the Au UME, the current transient signal could be observed, but is also not very reproducible and it was not observed on the C fiber UME.³⁻⁵ As like this, the observation of NP collision is very sensitive to the UME material and treatment.

In this paper, we investigated a new UME material (Cu) for a preferable IrO_x NP collision system and also to reduce the need for the inconvenient Pt UME pre-treatment. The Cu UME shows a lower background current than Pt UME and gives more reproducible results for the IrO_x NP collision experiment without the need for any pre-treatment. The current transient by NP collision and frequency change as a function of NP concentration are compared with the case of Pt UME. In addition, the adhesion coefficient between NP and UME was estimated for a better understanding of the single NP collision system.

Experimental

Reagent. Potassium hexachloroiridium (IV) (K_2IrCl_6) was obtained from Johnson Matthey Catalog Company Inc. (Ward Hill, USA). All buffer salts and other inorganic chemicals were obtained from Sigma or Aldrich. All chemicals were used as received unless otherwise stated. Ultrapure water ($> 18 M\Omega$, Millipore) was used in all experiments.

Preparation of Metal Nanoparticles (NPs). Iridium oxide (IrO_x) colloid (diameter ~ 30.1 nm) was prepared according to the procedure reported elsewhere.^{8,9} K_2IrCl_6 (6 mg, 1.2 mM) was added to 10 mL of an aqueous solution containing sodium citrate (10 mg, 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 to 7.5. The solution was maintained at 100 °C for 2 h with oxygen bubbling through the solution. The color of the solution became deep blue.

Preparation of Ultramicroelectrode (UME). Cu and Pt UMEs were prepared using the following method. Briefly, 7.5 μm radius Cu wire or 5 μm radius Pt wire was sealed in glass after rinsing with methanol and water. The electrode was then polished with alumina powder water suspension to a mirror face. The surface area was checked with standard redox electrochemistry of ferrocene methanol.

Electrochemical Cell and Technique. The solution of the electrochemical cell contained only 0.1 M NaOH without any other electrolyte. The cyclic voltammetry was performed at a 50 mV/s scan rate in pH 13 solution. The chronoamperometric curves were obtained at a data acquisition time of 50 ms. The noise signal was increased at a lower data acquisition time and we found that 50 ms is the optimal data acquisition time for high signal to noise ratio.

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

Results and Discussion

The reproducible observation of a single IrO_x NP collision

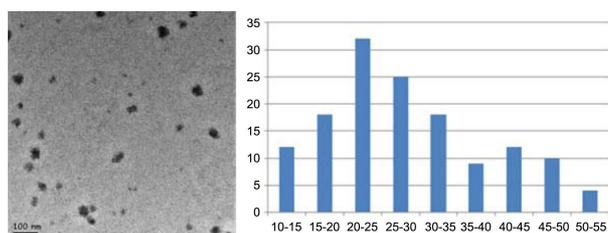


Figure 1. TEM image of IrO_x NPs and its size distribution.

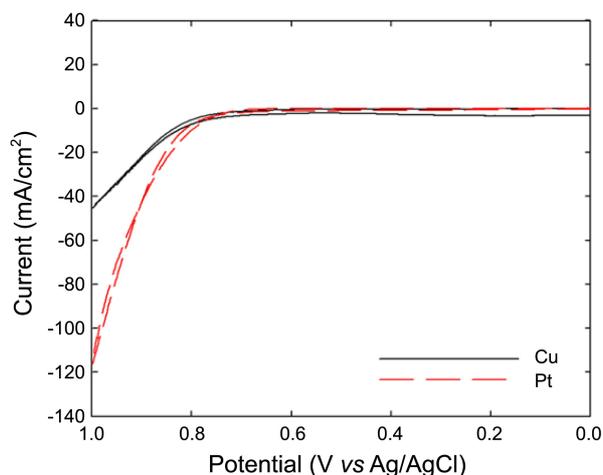


Figure 2. Electrochemical oxidation of water at a Pt (red) and Cu (black) UME in a pH 13 solution. Scan rate is 50 mV/s. The size of UMEs is 10 μm (dia.) for Pt, and 15 μm (dia.) for Cu.

was done by the Pt UME after pre-treatment in $NaBH_4$ solution.³ The additional step makes the experiment more complicated and inconvenient.

Therefore, we investigated other UMEs that can be used more conveniently for the IrO_x NP collision experiment and studied the relation between current transient and the material of UMEs for better understanding of single NP collision on the UME.

Due to the difficulties in the fabrication of UME, only limited materials are available for the UME preparation. In this work, we had prepared Cu as a new UME material for the NP collision observation. The Cu is not widely used as an electrode material in the three electrode system comparing to the noble metals such as Au or Pt due to its higher activity than these. The easy oxidation of Cu itself also became a problem to obtain stable potential windows for electrochemical measurement. However in the alkaline solution with ligand free as just like the solution used in this experiment, the Cu electrode behaves as a stable and reproducible electrochemical surface.^{10,11} This seems due to the Cu oxide layer on the surface protects the surface from further available reactions.

As shown in Figure 2, electrocatalytic ability of Cu and Pt UME for the water oxidation were tested by cyclic voltammetry. Cu UME shows less electrocatalytic behavior than Pt UME, resulting in a low background current. Its onset potential is similar to that of the Pt UME, but the background current and catalytic current were lower. Consequently, Cu UME is acceptable for the NP collision experiment because it shows a lower background current than Pt UME.

To study whether the electrocatalytic activity of IrO_x NP still remains after landing on the Cu UME, the cyclic voltammogram of the Cu UME in a solution containing IrO_x NP is compared with that in a solution without the IrO_x NP. Figure 3 shows that the additional peak around 0.7 V (vs. Ag/AgCl) appeared after exposing in a solution with the IrO_x NP for 300 seconds. This peak is due to the water oxidation reaction by the adsorbed IrO_x on UME. Notably,

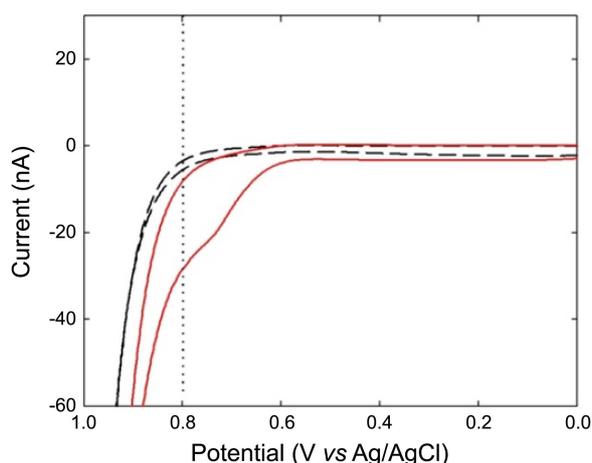


Figure 3. Electrochemical oxidation of water at a Cu UME in a pH 13 solution containing 0 (black dashed) or 11.6 pM IrO_x NPs (red solid). Scan rate is 50 mV/s.

water oxidized by IrO_x on the Cu UME was obtained. The onset potential for water oxidation by IrO_x NPs is lower than that of the Cu UME electrode, at about 0.6 V as reported in a previous study.³ Consequently, we can determine a holding potential for chronoamperometric observation of single NP collision as 0.8 V for the system consisting of Pt NP and Cu UME for the water oxidation. The holding potential indicates where the electrocatalytic reaction occurs by NP and does not occur by UME.

The Cu UME itself does not catalyze water oxidation at 0.8 V, as shown in Figure 2. Therefore, we cannot observe any current transient, except the background current, by the UME without injecting the IrO_x NP into the electrolyte solution. After the synthesized IrO_x NPs were injected in an electrochemical cell containing 0.8 V applied Cu UME, the water oxidation is electrocatalyzed and the current transient is observed whenever the IrO_x NPs collide with the Cu UME. The current increased temporarily by NP collision onto the electrode and reduced back to the background level as shown in Figure 4.

Figure 4 shows typical behavior when a small drop of IrO_x

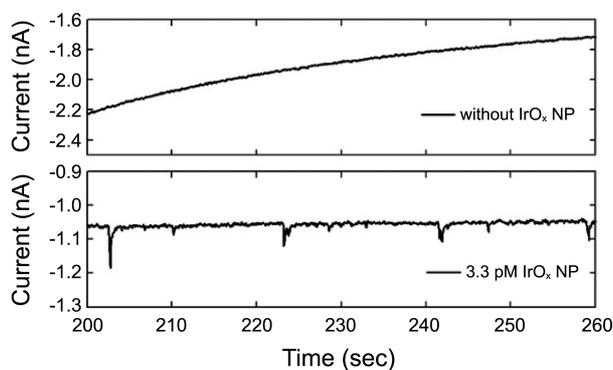


Figure 4. Chronoamperometric curves for single IrO_x NP collisions at the Cu UME in pH 13 solution (0.1 M NaOH) without and with 3.3 pM IrO_x NPs. Applied potential is 0.8 V (*vs* Ag/AgCl). Data acquisition time is 50 ms.

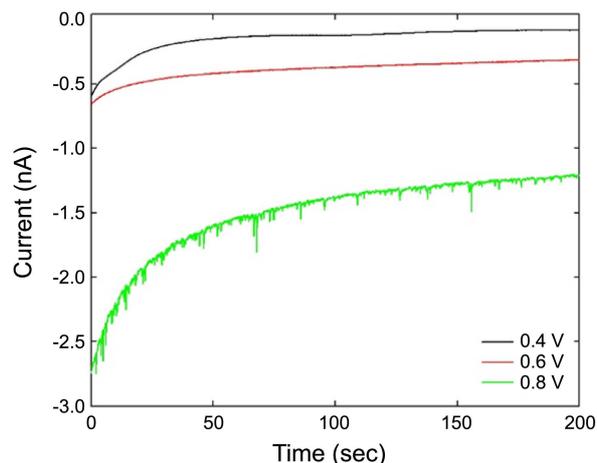


Figure 5. Chronoamperometric curves for single IrO_x NP collisions at the Cu UME in pH 13 solution (0.1 M NaOH) containing 11.6 pM IrO_x NPs with different applied potentials from 0.4 V to 0.8 V. Data acquisition time is 50 ms.

NP was injected into the solution containing the Cu UME. The current spikes were quite uniform, although some differences in shape and height were observed, which probably indicates differences in the size and shape of the particular NP.

To investigate whether the current transient is due to the electrocatalytic water oxidation by IrO_x NPs rather than to the direct oxidation of NP itself or another reaction, the chronoamperometric feature was studied by changing the applied potential from 0.4 V to 0.8 V. Figure 5 shows the chronoamperometric curves in an electrolyte solution containing IrO_x NPs with various applied potentials. In the cases where 0.6 V or 0.4 V are applied, the current transient is not obtained by chronoamperometry. The current transient was observed only in the case where 0.8 V is applied, as a result of IrO_x collision on the Cu UME. Considering that the onset potential of IrO_x NP for the water oxidation is about 0.6 V, the current transient is responsible for the IrO_x NP. There-

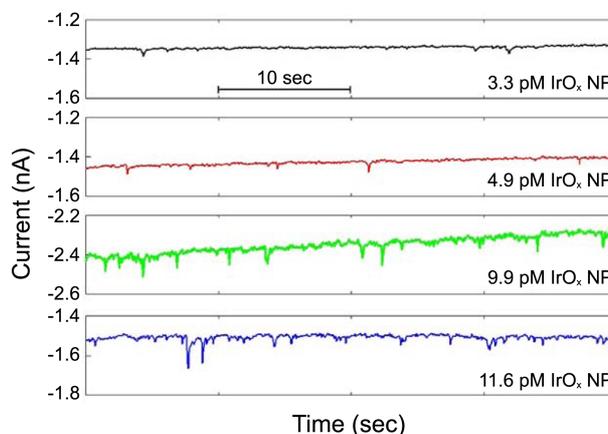


Figure 6. Chronoamperometric curves for single IrO_x NP collisions at the Cu UME in pH 13 solution (0.1 M NaOH) containing various concentrations of IrO_x NPs from 3.3 to 11.6 pM. Applied potential is 0.8 V (*vs* Ag/AgCl). Data acquisition time is 50 ms.

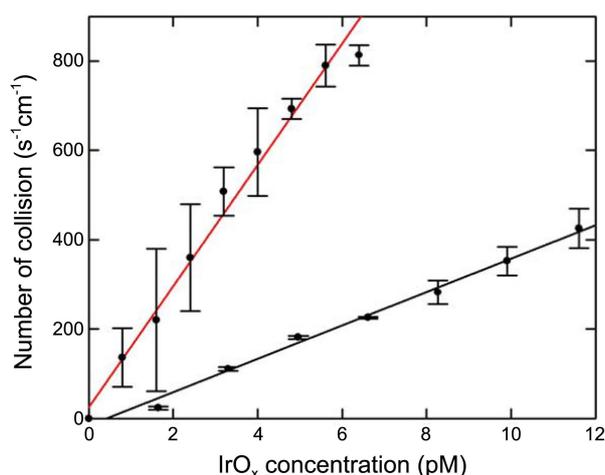


Figure 7. Correlation between the number of collisions and concentration of IrO_x NPs at Pt UME (red) and Cu UME (black) (for 3 replicate measurements).

fore, the observed current transient is due to the water oxidation reaction by IrO_x NP, not the other reactions such as UME or NP direct oxidation, considering the redox potential of each reaction.

The collisional frequency of the current transient increased in proportion to the particle concentration as shown in Figure 6. The relation between collisional frequencies and NP concentrations is obtained as shown in Figure 7. The black line which is obtained in this study with the Cu UME has a lower slope than the red line which was obtained in a previous study with the pre-treated Pt UME.³

The difference in slope is possibly due to the difference of adhesion coefficients between IrO_x NP and the Cu or Pt UME. The collisional frequency is expressed as a function of adhesion coefficient as follows:

$$f_p = -\pi r_d^2 k_{\text{ads}} C_p$$

where k_{ads} (cm s⁻¹) is the rate constant for adsorption, C_p is a concentration of NP, and r_d is the radius of the UME.⁵ The adsorption constant on the Pt UME was about 3.6 times larger than that of the Cu UME. The synthesized IrO_x NP has poor size distribution. The IrO_x NP observed by the single NP collision is ~30 nm in diameter, which is a small aggregation size (~1 nm) for IrO_x NP. Many small IrO_x NP therefore exist in a NP stock solution. If the adsorption constant is sufficiently large, a noisier frequency due to the small IrO_x NP can occur, resulting in poor frequency reproducibility. Therefore, the standard deviation of each point is much smaller in the case of Cu UME than in the case of pre-treated Pt UME. A more reproducible and narrower distribu-

tion in collisional frequency was therefore obtained at Cu UME, indicating that the reproducibility in collisional frequency is superior when using the Cu UME. In addition, the pre-treatment step required for the use of Pt UME was not required for the Cu UME. In conclusion, the Cu UME is more advantageous and effective than the Pt UME for the IrO_x NP collision experiment with good reproducibility and stability.

Conclusion

We observed IrO_x NP collision on Cu UME by electrocatalytic amplification of water oxidation reaction. Cu UME was tested as a new UME material for the electrochemical oxidation of water. Cu UME shows a lower background current than Pt UME. IrO_x NP collision on the Cu UME shows the same “blip” response as that of the IrO_x NP collision on the Pt UME. In terms of NP collision frequency analysis, the collision frequency on both Cu UME and Pt UME is proportional to the concentration of IrO_x NP, but a difference is observed in the slope and error bar. Therefore, the NP collision is affected by the adsorption coefficient between the NP and UME, resulting in a frequency change.

The bare Cu UME shows a lower adsorption coefficient than Pt UME for the IrO_x NP collision, but has better linear relationship with the concentration of IrO_x NP and better reproducibility than Pt UME, which required special pre-treatment by NaBH₄.

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