Observation of Discrete Au Nanoparticle Collisions by Electrocatalytic Amplification Using Pt Ultramicroelectrode Surface Modification

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Supporting Information

Experimental procedures

The Pt UME was prepared following the general procedure developed in our laboratory.[1] Briefly, a 10 μm platinum wire was sealed in glass after rinsing with ethanol 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. All the electrochemical experiments were performed using a CHI model 660 potentiostat, with the three-electrode cell placed in a Faraday cage. A 0.5 mm diameter tantalum wire was used as counter electrode, and the reference electrode was Ag/AgCl in saturated KCl solution (the reference electrode was further protected from the solution by a KNO_3 salt bridge). All potentials are quoted vs Ag/AgCl. We selected no filters for potential, current, and current converter in the CHI software. The sampling time was 10 ms.

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 thereafter appeared ruby in color.

Before every experiment, the 0.1 M NaOH solution was deaerated with Ar and the Pt UME was subjected to a few potential cycles between 1 and -1 V. A multi-potential step technique was applied and the Pt UME was held at 0 V immediately after first being oxidized at 0.9 V for 10 s. After a stable background was obtained at 0 V, the desired amount of Au NP stock solution was injected and the solution was stirred by bubbling Ar for about 5 to 10 s to uniformly disperse the NPs in the solution. After stirring, the Ar gas tube was lifted far above the solution surface and the current-time curve was recorded.

Additional experimental data

1) Injection of Pt NPs into 10 mM $NaBH_4$, 0.1 M NaOH solution. (Electrode, 10 μm Au UME)

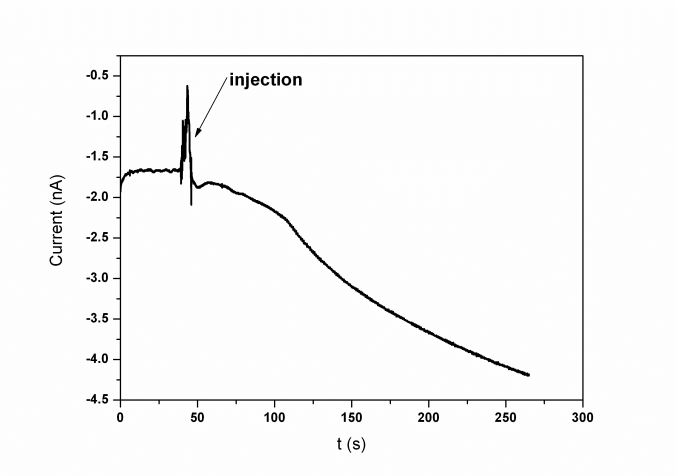

Figure S1. *i-t* curve recorded before and after injecting 50 pM Pt NPs into a 10 mM $NaBH_4$, 0.1 M NaOH solution. The Pt particle concentration was about 50 pM and the electrode potential was -0.7 V vs Ag/AgCl.

2) Control experiment for the effect of citrate in the $NaBH_4$ solution

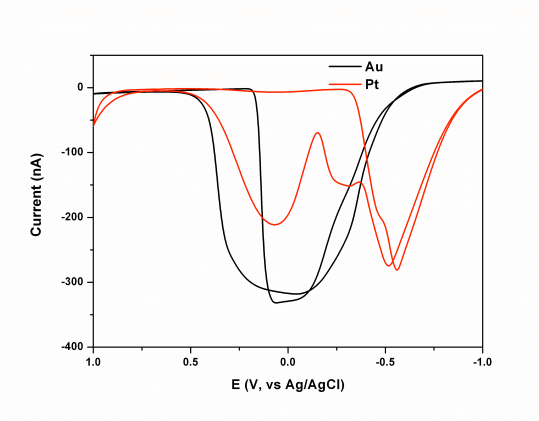

Figure S2. Cyclic voltammograms of Au and Pt UMEs in 10 mM $NaBH_4$, 0.1 M NaOH, 5 μM sodium citrate solution. (Diameter of both UMEs, 10 μm; sweep rate, 100 mV/s).

3) Citrate reduced Au NPs

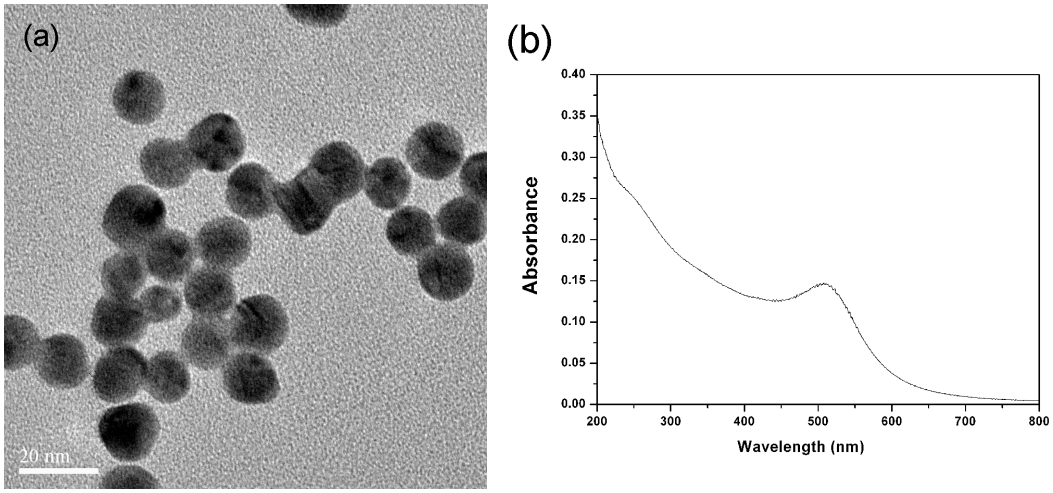

Figure S3. (a) TEM image and (b) UV-vis spectrum of citrate reduced Au NPs.

4) Effect of oxide layer grown on Pt UME

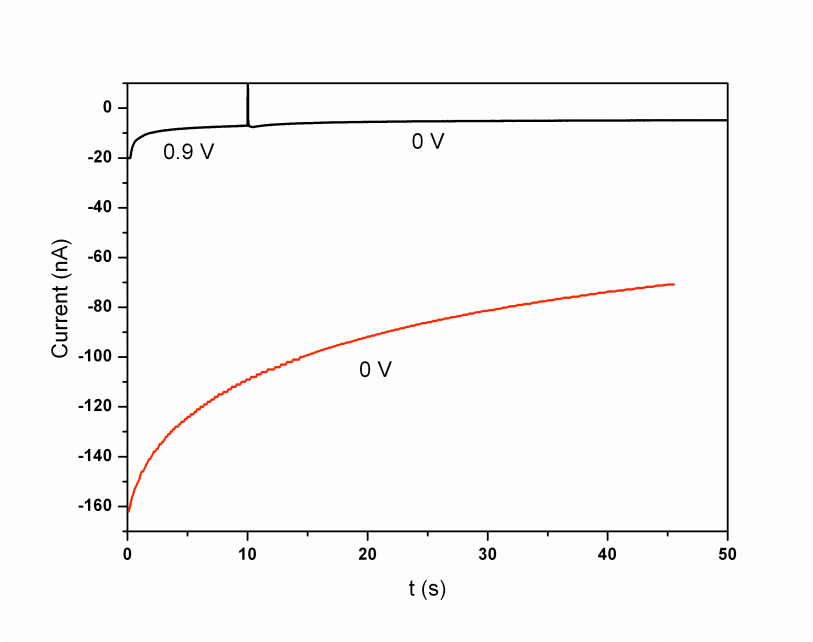

Figure S4. Measurements on Pt UME held at 0 V with (upper, black, multipotential step) and without (bottom, red, *i-t* curve) pre-oxidizing step (at 0.9 V) in 10 mM $NaBH_4$, 0.1 M NaOH solution.

5) Effects of potential and time on Q_O/Q_H.

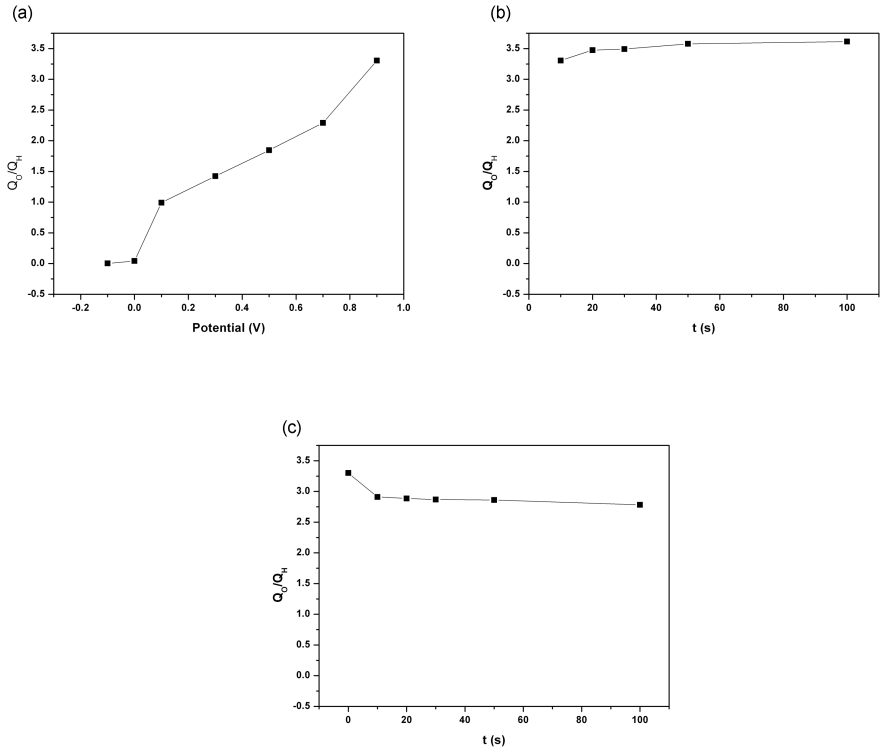

Figure S5. Q_O/Q_H measured on Pt UME (10 μm) after (a) being oxidized at different potentials for 10 s, (b) oxidized at 0.9 V for different times, and (c) oxidized at 0.9 V for 10 s and then held at 0 V for different times.

6) Comparison of the behavior of Pt NPs and Au NPs.

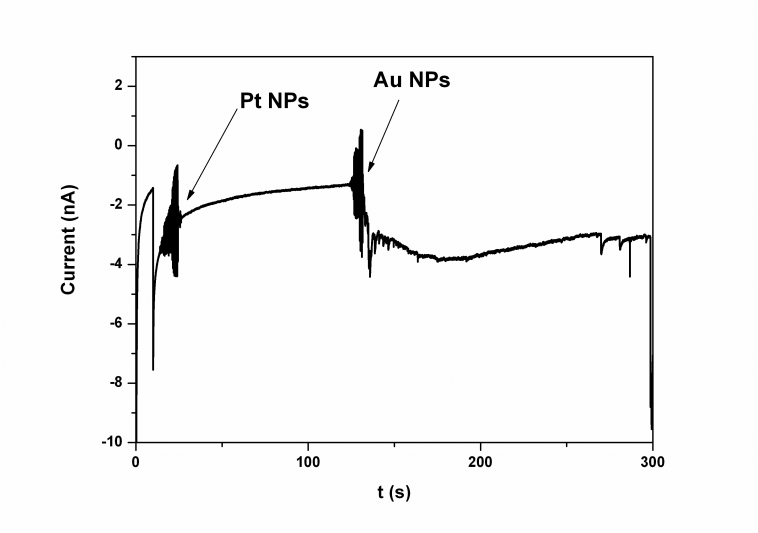

Figure S6. *i-t* curve recorded on a pre-oxidized Pt UME (10 μm) at 0 V after injection of 50 pM Pt NPs and 20 pM Au NPs separately. Electrolyte, 10 mM $NaBH_4$, 0.1 M NaOH.

7) Effect of potential on oxidation current at Au UME

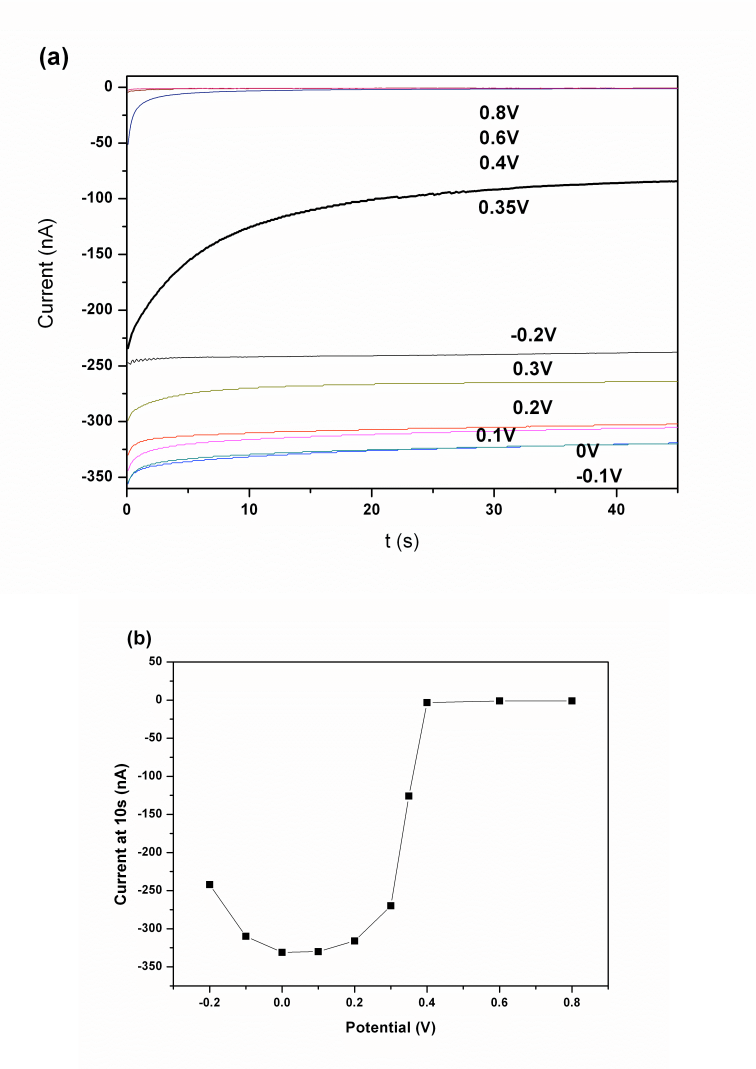

Figure S7. (a) *i-t* curve recorded on a Au UME (10 μm) in 10 mM $NaBH_4$, 0.1 M NaOH at different potentials. (b) Effect of potential on current (current taken at 10 s from each potential step result in panel a).

8) Effect of holding potential on collision peaks

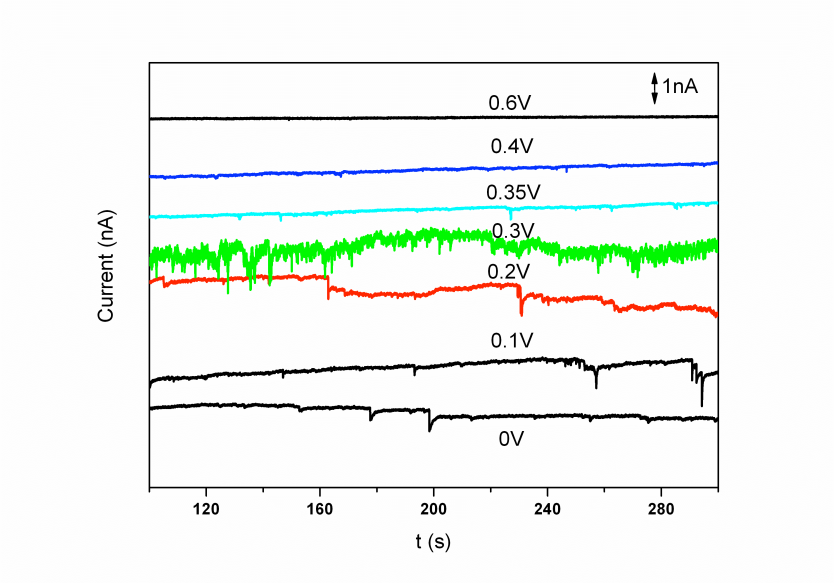

Figure S8. *i-t* curves recorded on a pre-oxidized Pt UME (10 μm) hold at different potentials in the presence of 12 pM Au NPs. Electrolyte, 10 mM $NaBH_4$, 0.1 M NaOH.

[1] Zoski, C. G. *Handbook of Electrochemistry*; 1st ed.; Elsevier: Oxford, 2007.