

Supporting Information

Open Circuit (Mixed) Potential Changes Allow the Observation of Single Metal Nanoparticle Collisions with an Ultramicroelectrode

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Experimental Details

Reagents

Platinum hexachloric acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and hydrogen tetrachloroaurate (HAuCl_4) were obtained from Alfa Aesar (Ward Hill, MA). Sodium phosphate monobasic anhydrous (Na_2HPO_4) and sodium phosphate monobasic monohydrate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) were obtained from Fisher Scientific (Pittsburgh, PA). All other chemicals were obtained from Sigma or Aldrich, unless otherwise stated. All chemicals were used as received. Millipore water ($>18 \text{ M}\Omega$) was used in all experiments. Platinum (99.99%) and Gold (99.99%) wires, 10 μm diameter, from Goodfellow (Devon, PA) were used to fabricate the UMEs.

Preparation of Ultramicroelectrodes (UME)

Pt and Au UMEs were prepared following the general procedure developed in our lab. Briefly, a 10, 25, or 100 micron metal fiber was sealed in glass after rinsing with ethanol and water. The electrode was then polished with alumina powder water suspension to a mirror finish. The surface area was checked with standard redox electrochemistry of ferrocene methanol.

Instrumentation

The electrochemical experiments were performed using a CHI model 660 and model 630 potentiostat (CH Instruments, Austin, TX) with the three-electrode cell placed in a Faraday cage. A 0.5 mm diameter tantalum wire and 3 mm diameter carbon rod were 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 KClO_4 salt bridge). The potential is quoted vs. Ag/AgCl in saturated KCl solution but the potential change is only relative. No filters were selected for potential, current, and current converter in the CHI software. TEM images were obtained using a FEI Tecnai transmission electron microscope and JEOL 20100F transmission electron microscope. Galaxy 16D (VWR, Westchester, PA) is used for particle purification.

Preparation of metal nanoparticles (NPs)

The platinum nanoparticle (diameter 4 nm) solution was prepared by dissolving 1 mM H_2PtCl_6 and 1.2 mM sodium citrate in 40 mL water. Then 2.7 mL of 60 mM freshly-made NaBH_4 solution was added drop wise under vigorous stirring. The reaction was stopped after 30 min.

The platinum nanoparticle (diameter 32 ± 3 nm) solution was prepared according to the procedure reported elsewhere.¹ Seed-mediated growth procedure is used to prepare stable citrate-capped large Pt NPs. Seed particles were prepared as follows. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (3.8 mM, 7 mL) was added to boiling ultrapure water (90 mL) with stirring. After 1 min, 2.2 mL of solution containing 1% sodium citrate and 0.05% citric acid was added, followed by quick addition of freshly prepared NaBH_4 (0.08%, 1.1 mL). After 10 min, the solution was cooled to room temperature. For the 32 nm particle, 1 mL of Pt seed solution was added to 29 mL of water with stirring. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.4 M, 0.045 mL) was added, followed by addition of 0.5 mL solution containing 1% sodium citrate and 1.25% ascorbic acid. The temperature was slowly increased to the boiling point (~ 5 °C/min). The reaction time was 1 h. Nanoparticles were washed two times by precipitation in a centrifuge.

The gold NP solution was prepared by first boiling 50 mL of a 0.01% (by weight) aqueous HAuCl_4 solution. One mL of 1% sodium citrate solution was then injected under stirring. The solution was kept boiling for another 15-30 min. The solution obtained appeared ruby colored.

Pretreatment

Before every experiment, the solution was deaerated with Ar and all electrodes were polished prior to use with alumina (0.05 μm) paste on microcloth pads (Buehler, Lake Bluff, IL). The Au UME was subjected to a few potential cycles between 0.4 and -0.8 V. An open circuit potential (OCP) – time technique was applied. After a stable background OCP was obtained, the desired amount of diluted Pt NP stock solution ($\sim \mu\text{L}$) was injected and the solution was stirred by bubbling Ar for about 5-10 s in order to uniformly disperse the NPs in the solution. After stirring, the Ar gas tube was lifted far above the solution and the OCP-time curve was recorded under an Ar atmosphere under quiet conditions.

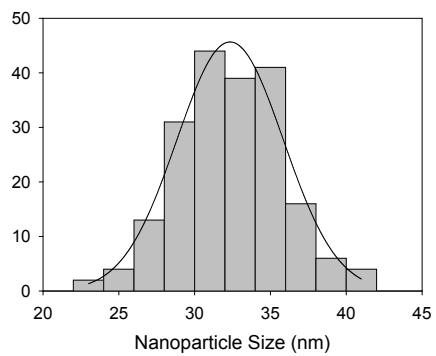
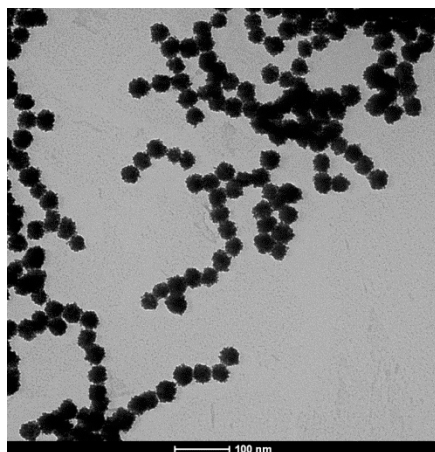


Figure S1. TEM image of Pt nanoparticles and the size distribution. The average nanoparticle diameter is about 32 ± 3 nm.

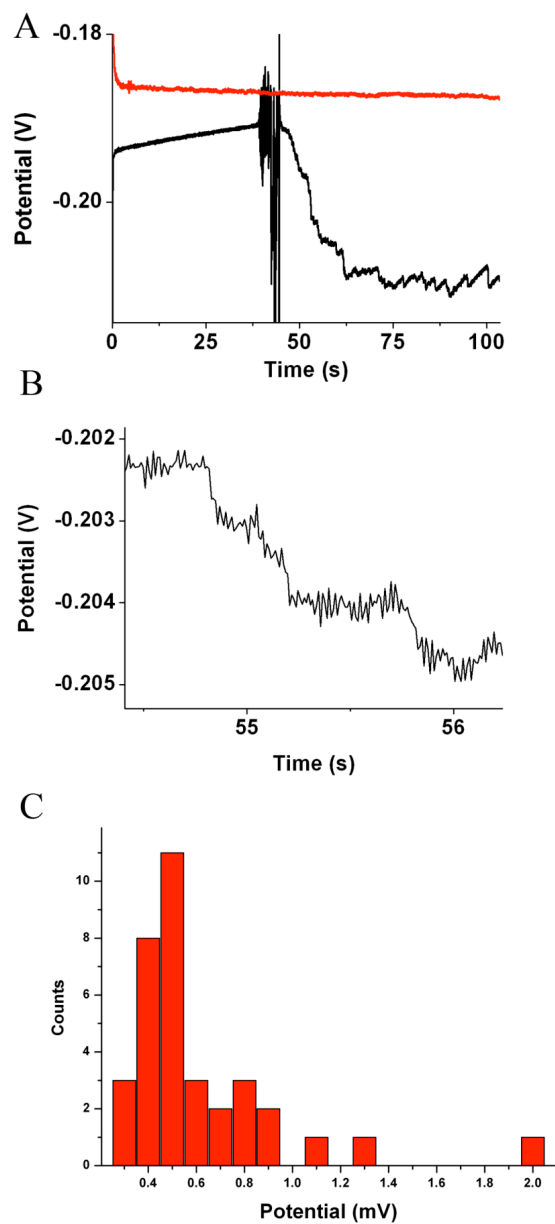


Figure S2. (A) The OCP vs. time curves without (red upper curve) and with injected 2 nm radius Pt NPs (black bottom curve, the large noisy OCP spikes pointing upward and downward in the curve is caused by opening the Faraday cage when the Pt NPs are injected) at the Au UME (radius, 5 μm); NP concentration, 100 pM; solution, 50 mM phosphate buffer (pH 7.0) and 15 mM hydrazine, under Ar. (B) Zoom-in of the marked region in panel (A); (C) Statistical distribution of the number of all recognizable potential steps of different amplitudes over a 50 s period.

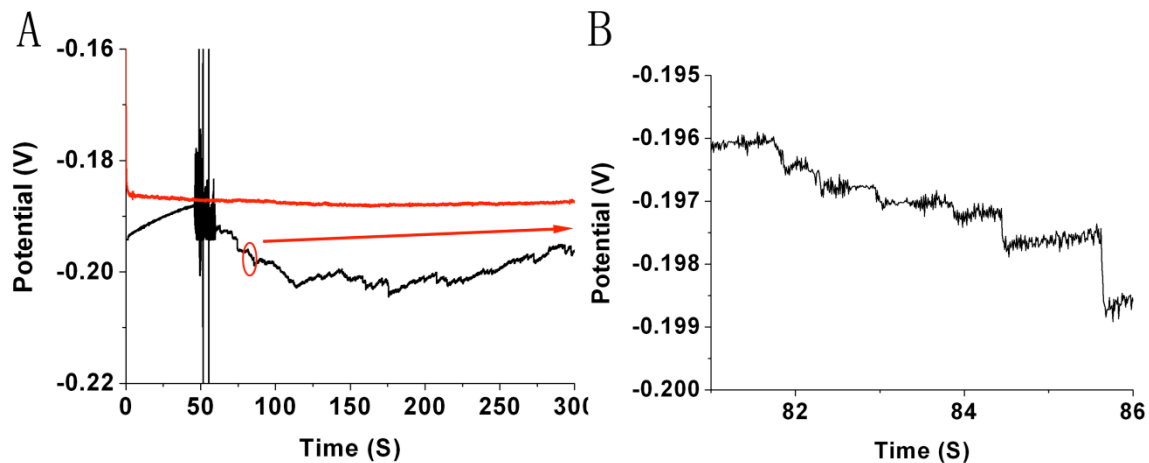


Figure S3. Another example of a typical collision curve. OCP vs. time curve on a Au UME (radius, 5 μm) in a solution containing 50 mM phosphate buffer (pH 7.0) and 15 mM hydrazine, under Ar. In the left panel, the upper (red) curve is the OCP of the Au electrode without injection of Pt NPs. The bottom (black) curve is the OCP of the Au electrode with injection of 500 pM Pt NPs (2 nm radius). The right panel shows a zoom-in of the black curve in the left panel as indicated by the red arrow.

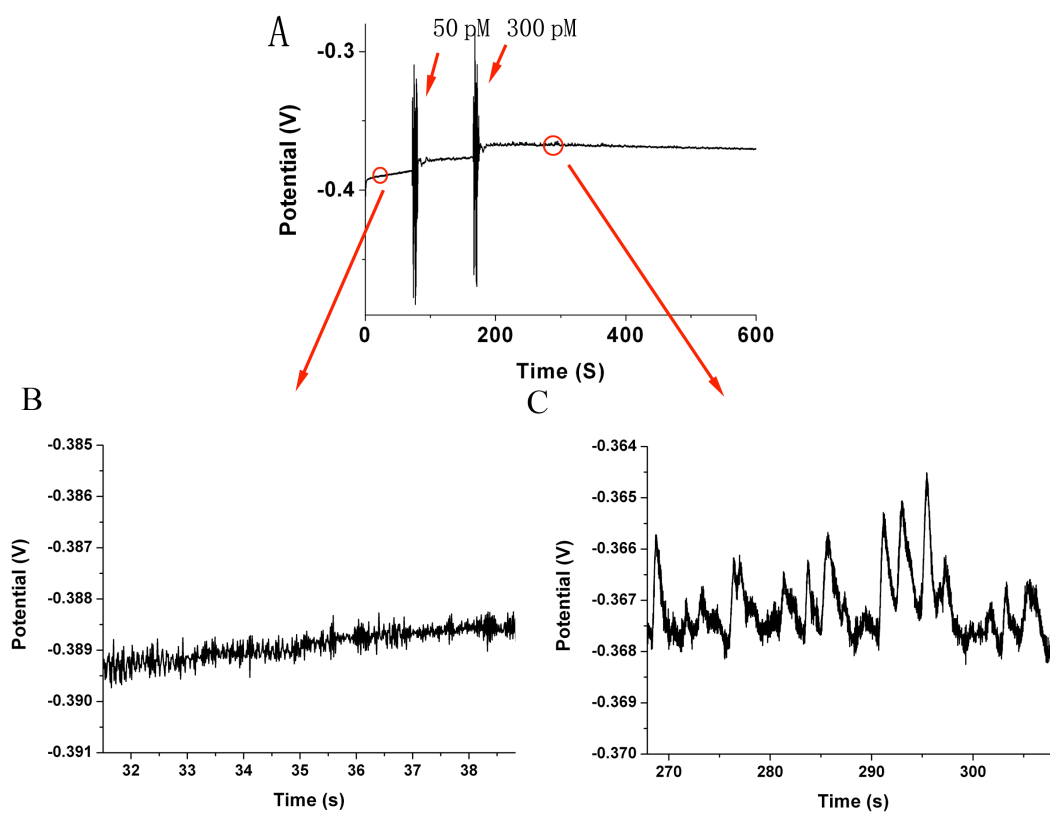


Figure S4. (A) OCP vs. time curve after injection of 50 pM and 300 pM Au NP (radius, 9 nm) on a Pt UME (radius, 5 μ m). (B) and (C) Zoom-in of the marked region in panel (A). Solution: 50 mM phosphate buffer (pH 7.0) and 15 mM hydrazine, under Ar.

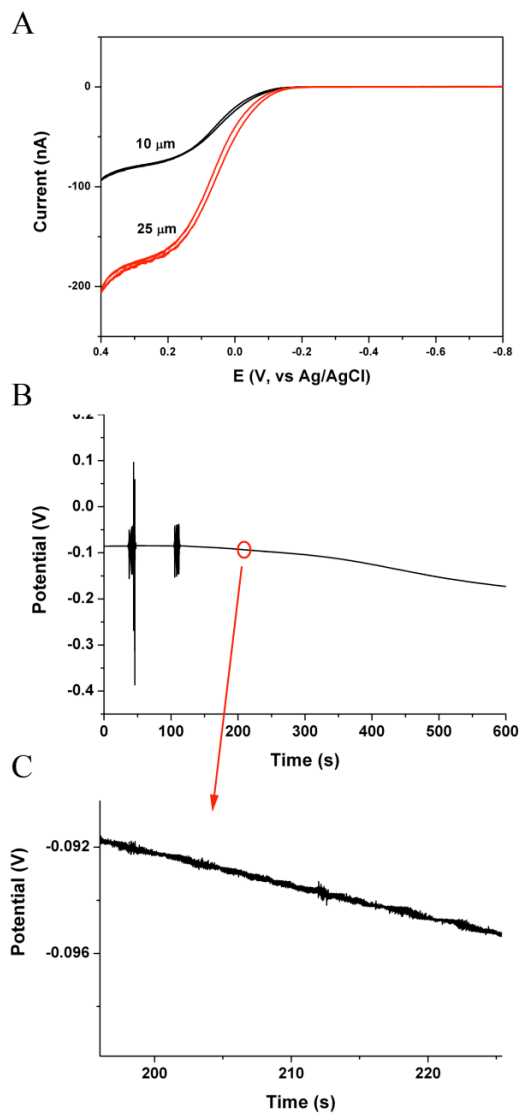


Figure S5. (A) Cyclic voltammograms at 5 μm and 12.5 μm radius Au UMEs in a solution containing 50 mM phosphate buffer (pH 7.0) and 15 mM hydrazine, under Ar. (B) OCP vs. time curve after injection of 50 pM and 300 pM 2 nm radius Pt NP solutions with 12.5 μm radius Au UME. (C) Zoom-in of the marked region of panel (B).

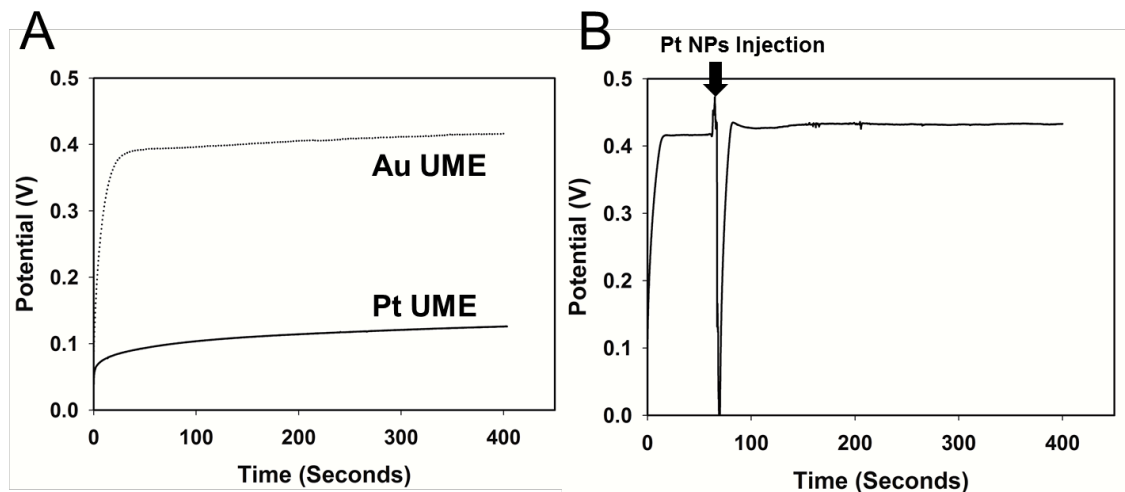


Figure S6. (A) OCP vs. time curves of Au and Pt UMEs in a solution of 50 mM phosphate buffer (pH 7.4), Ar. (B) OCP vs. time curve with injected 7.5 pM of Pt NPs (radius, 16 nm) at a Au UME in 50 mM phosphate buffer (pH 7.4) under Ar. Radius of Pt and Au UMEs are 5 μm .

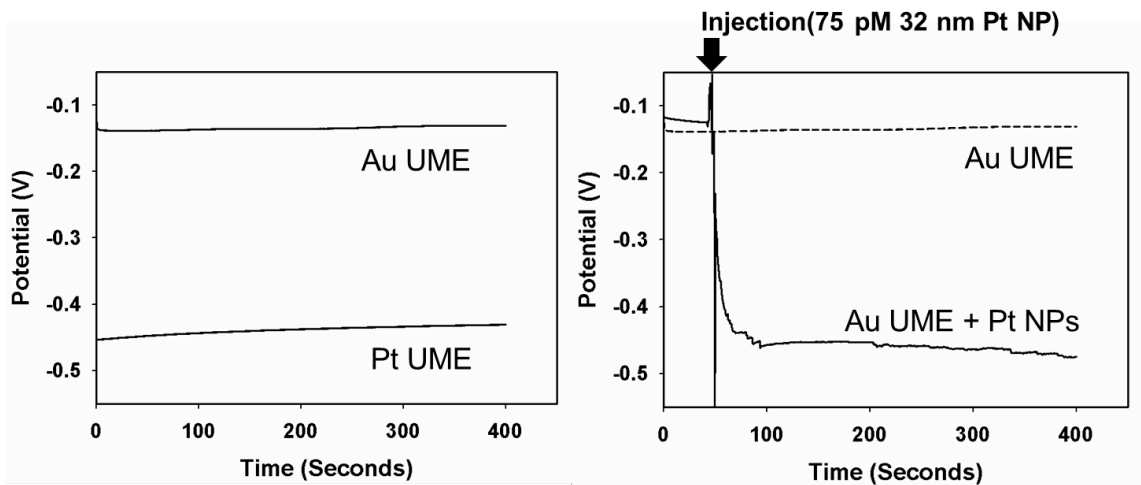


Figure S7. (A) OCP vs. time curves of Au and Pt UMEs in a solution of 5 mM phosphate buffer (pH 7.0) and 15 mM hydrazine. (B) OCP vs. time curve with injected 75 pM of Pt NPs (radius, 16 nm) at a Au UME in a solution of 5 mM phosphate buffer (pH 7.0) and 15 mM hydrazine. (Radius of Pt and Au UMEs, 5 μ m).

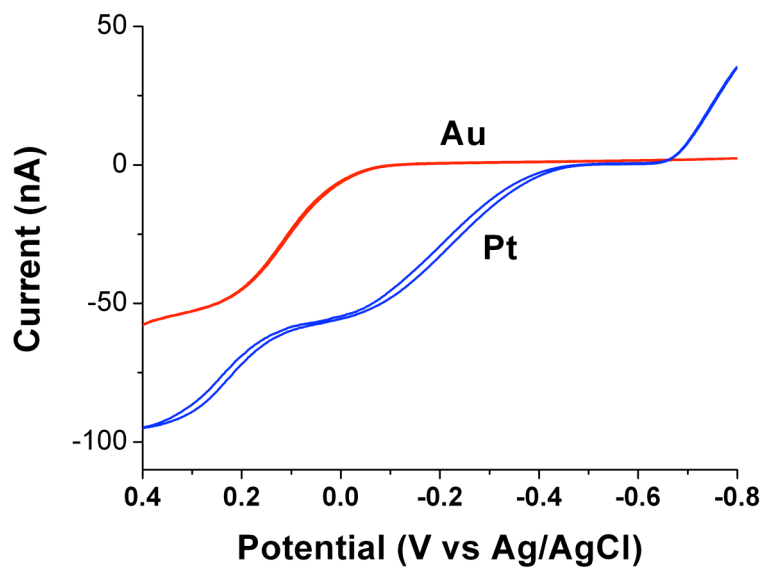


Figure S8. Cyclic voltammograms of Au and Pt UMEs in a solution of 50 mM phosphate buffer (pH 7.0) and 15 mM hydrazine, under Ar (radius of Pt and Au UMEs: 5 μm ; scan rate, 100 mV/s).

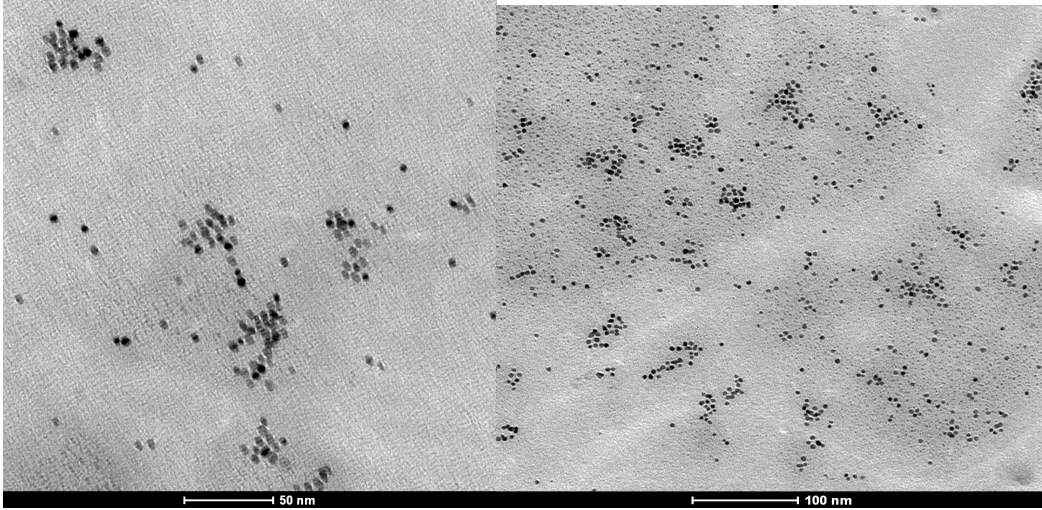


Figure S9. TEM images of Pt NPs (diameter 4 ± 0.8 nm).

[†] These authors contributed equally to this work.

¹ Bigall, N. C.; Härtling, T.; Klose, M.; Simon, P.; Eng, L. M.; Eychmüller, A. *Nano Lett.* **2008**, *8*, 4588-4592.