Supporting Information for

Electrodeposition of Isolated Platinum Atoms and Clusters on Bismuth – Characterization and Electrocatalysis

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Chemicals and Materials

Chloroplatinic acid solution (8% H_2PtCl_6**),** Perchloric acid ($HClO_4$, 70%), sodium perchlorate ($NaClO_4$, 98%), methyl viologen dichloride ($MVCl_2$, 98%), potassium chloride (KCl, 97%), and bismuth powder (100 mesh, 99%) were all purchased from Sigma Aldrich. Graphite powder (crystalline, 325 mesh, 99%) was received from Alfa Aesar. Glass tubing (o.d./i.d. 2/1.16 mm) was received from Sutter Instruments. Water used during the experiments was Milli-Q (18.3 M/cm, EDM Millipore, MA, TOC <3 ppb). The solutions prepared from ultrapure water that contained very few organic contaminations were very critical for Pt deposition and detection experiments. These solutions were finally filtered with a 0.1 µm diameter pore (Millex-Syringe, PVDF-0.1 µm, Merck Milliipore Ltd.) before electrochemical measurements.

Preparation of Femtomolar H_2PtCl_6 Solution

Preparation of fM solutions of accurate concentration is difficult because of adsorption and errors during dilution. Four initial volumetric flasks were prepared with 1 mM of the analyte of interest. These flasks were allowed to sit at room temperature in a dark environment for 3 h. After 3 h, flasks were poured out, and another 1 mM solution of the analyte of interest was placed in the flask and allowed to equilibrate for another 3 h. After this saturation process, the flasks were emptied and filled with ultrapure water 6 times. For the final solutions, serial dilutions were made by pipetting 10 µL of the initial solution into 10 mL of the solvent inside an equilibrated flask until concentrations of picomolar were achieved. Four flasks were necessary because the beginning solution generally had mM amounts of analyte (mM to µM to nM to pM). From this stock solution of picomolar amounts of analyte, samples were diluted into fM level for the electrochemical analysis, which were completed in vials that were equilibrated as previously discussed. [1, 2]

Fabrication of Bi UME

The preparation of a Bi UME is depicted in Figure S1. In detail, the glass capillaries were cleaned by sonication in 10% nitric acid and subsequently washed with copious amounts of ultrapure water. Then, the capillaries were dried in an oven at 120 °C overnight. After cooling, the end of one capillary was inserted into the methane-oxygen flame. The flame temperature was adjusted to a suitable point that can melt Bi metal but not borosilicate glass. By a fine control of the heating, an open glass channel with a cone shape (half-cone angle $\leq 5^{o}$) could be readily prepared before its complete sealing. We optimized the heating process to fabricate a very narrow channel (i.e., almost cylindrical shape) as a template for Bi UME preparation. We filled the bismuth powder in the capillaries, and taped them on the bottom. To prevent the Bi metal from air oxidation during thermal fabrication, we covered the bismuth powder with crystalline graphite powder. We used a straight tungsten rod (comparable to the inner size of capillary tubing) to press tightly the filled both powder layers. Then, we placed the materials filled portion of the capillaries into the flame. The flame temperature has to be adjusted before borosilicate glass softening. Simultaneously, we vigorously pushed the rigid metal rod, and extruded a small amount of Bi metal through the open channel. Subsequently, we mechanically polished the capillary end and exposed a disk of Bi.

Polishing of the Bi UME on 5000 grit sandpaper was a good way to renew the surface. This fine polishing produces a smooth electrode surface. Since the prepared template channels were almost cylindrical, a limited time of polishing led to only small change in the electrode size, as confirmed by electrochemical measurements. For Pt plating experiments, the surface of Bi UME was activated by voltammetric polarization in 100 mM $HClO_4$ (potential range between -0.2 V and -1.8 V vs Ag/AgCl; scan rate, 0.1 V/s; segments: 10). This procedure is a critical step for successful Pt plating. The underlying mechanism may be due to surface contaminants stripped off by both strong reducibility of the generated hydrogen and local convection of the formed hydrogen gas nanobubbles.

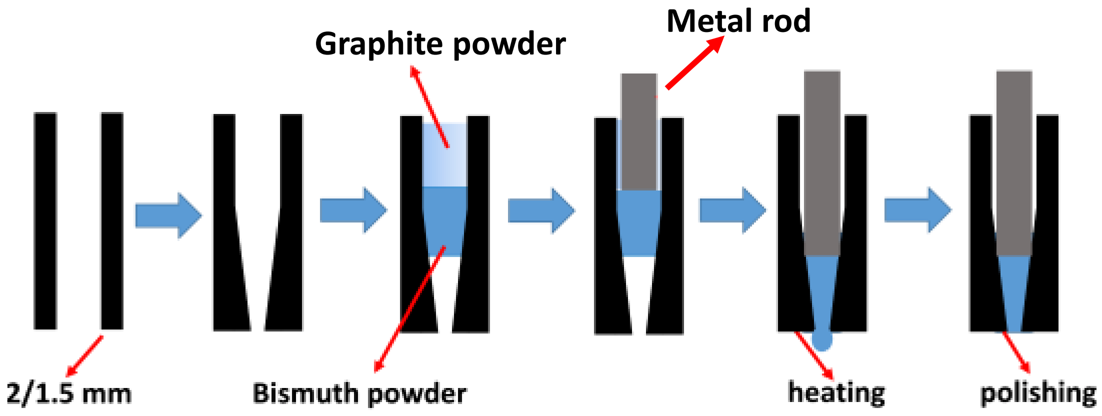

Figure S1. Schematic representation of fabrication of Bi UME.

Electrochemical Measurements

All the experiments were carried out on a CHI 900C potentiostat. The working electrode was the prepared Bi UME with a typical radius of *ca.* 250 nm. The reference electrode was Ag/AgCl/1.0 M KCl, which was 0.235 V versus normal hydrogen electrode (NHE). The counter electrode was a large graphite rod. The cell-on function in potentiostat was switched on during electrochemical measurements, which were useful to protect Bi UME and its deposit. [3] In addition, the electrostatics damage protection (i.e., connecting the operator and the samples with the real ground) was always used to protect the Bi UME and its deposit. Each experiment was carried out in a completely deaerated solution with an Ar blanket. All related sensitive electrochemical measurements were conducted in a well-grounded Faraday cage. The electrochemical cell was a homemade Teflon container with a cap coverage that has a maximum volume of 5 mL. The Teflon material showed very weak adsorption of the samples.

Data for Table 1

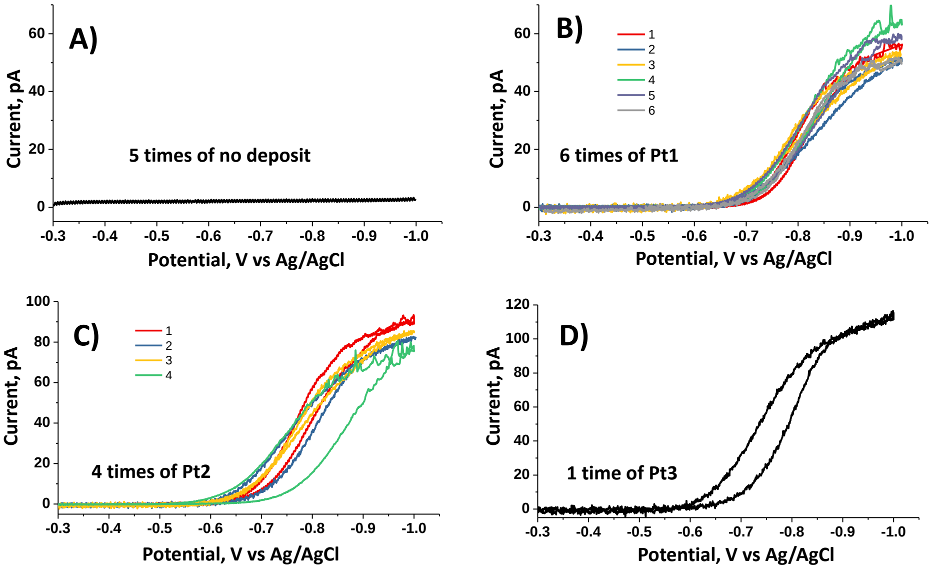

Figure S2. (A-D) Voltammograms showing HER detection on Pt deposits after 10 s plating, grouped by a common range of the limiting current and the half-wave potential. The experimental details can be seen in the main text. The total trial number was 16, which consisted of 5, 6, 4, and 1 times of no deposit, Pt1, Pt2, Pt3, correspondingly.

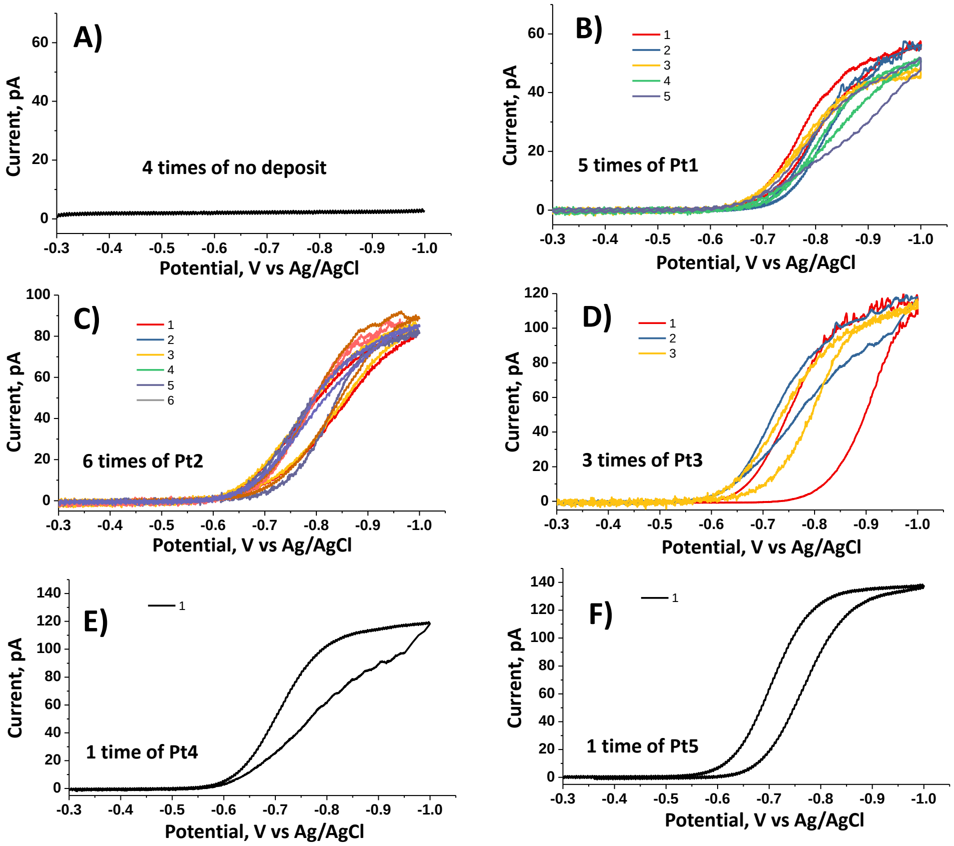

Figure S3. (A-E) Voltammograms showing HER detection on Pt deposits after 20 s plating, grouped by a common range of the limiting current and the half-wave potential. The experimental details can be seen in the main text. The total trial number was 20, which consisted of 4, 5, 6, 3, 1, and 1 times of no deposit, Pt1, Pt2, Pt3, Pt4, and Pt5, correspondingly.

Nucleation and Growth of Clusters

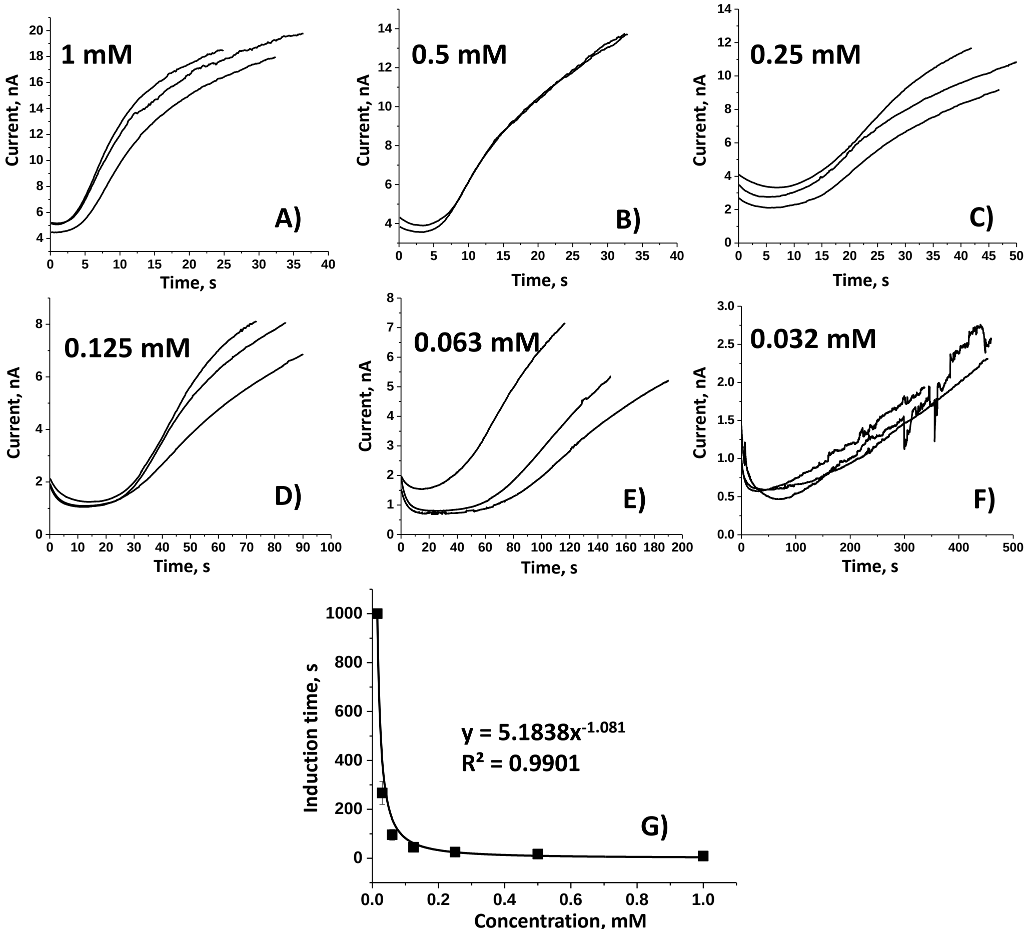

Figure S4. Amperometric traces (A-F) showing the induction time as a function of the concentration of $PtCl_6^{2-}$. A carbon fiber UME was biased at -0.1 V vs Ag/AgCl to drive the nucleation and growth of Pt deposits. Experiments were performed in 20 mM $HClO_4$ deaerated solutions. (G) The experimental data (symbol) and fitted curve (solid line) between the induction time and the concentration of $PtCl_6^{2-}$.

Reference

[1] Dick, J. E.; Bard, A. J., *J. Am. Chem. Soc.* **2015**, *137*, 13752.
[2] Dick, J. E.; Bard, A. J., *J. Am. Chem. Soc.* **2016**, *138*, 8446.
[3] Kim, J.; Renault, C.; Nioradze, N.; Arroyo-Currás, N.; Leonard, K. C.; Bard, A. J., *J. Am. Chem. Soc.* **2016**, *138*, 8560.