

Supporting Information

Atomic Scale Deposition of Pt around Au Nanoparticles to Achieve Much Enhanced Electrocatalysis of Pt

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➤ Experimental section

Chemicals and Materials

Hydrogen tetrachloroaurate (III) hydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was purchased from Strem Chemicals. Oleylamine (>70%), 1,2,3,4-tetrahydronaphthalene (tetralin), borane *t*-butylamine complex (TBAB) and Nafion solution (5% in a mixture of lower aliphatic alcohols and water) were purchased from Sigma Aldrich. Hexane (98.5%), ethanol (99%), 2-propanol (99%), perchloric acid (70%), formic acid (88%) and sulfuric acid (98%) were from Fisher Scientific. The commercial C-Pt catalyst (20% mass loading, Pt particle size 2-3 nm in diameter) was obtained from Fuel Cell Store. Deionized water was from a Millipore Autopure system. All reagents were of analytical grade and used without further purification.

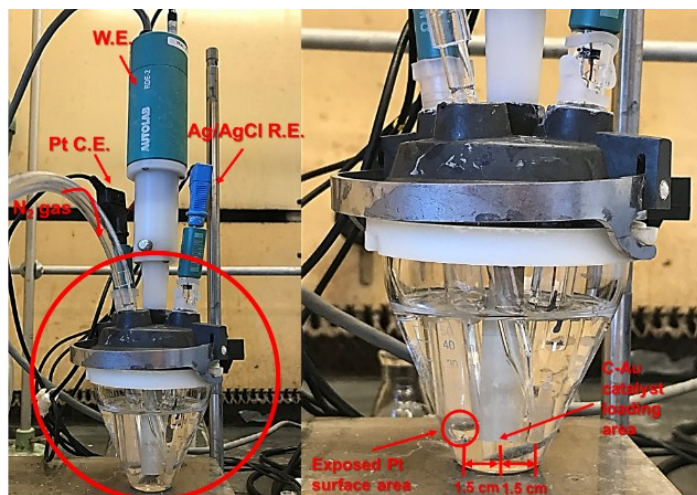
Synthesis and Characterizations

Synthesis of 5 nm Au NPs. These NPs were prepared according to the method published previously¹. Briefly, 0.2 g HAuCl_4 was dissolved in 10 ml of tetralin and 10 ml of OAm at 4 °C under N_2 flow and vigorous magnetic stirring. 0.5 mmol TBAB was dissolved in 1 ml of tetralin and 1 ml of OAm *via* sonication. The solution was then injected into the HAuCl_4 solution when the temperature is below 4 °C. The mixed solution was then stirred for 2 h at 4 °C before 40 ml of acetone was added to collect Au NPs *via* centrifugation (8500 rpm, 8 min). The product was dispersed in 20 ml hexane, precipitated out by adding 40 ml of ethanol and centrifugation, and re-dispersed in hexane.

Catalyst Preparation. 10 mg Au NPs were drop-wise deposited onto 10 mg KetjenBlack EC-300-J carbon by sonicating the mixture of Au NP dispersion in hexane and C, giving C-Au. The C-Au was annealed overnight in air at 150 °C to remove the surfactant. After cooling down to room temperature, the C-Au was suspended in a mixture of deionized water, isopropanol and Nafion (V/V/V=4/1/0.05) to form a catalyst ink (2 mg/mL). For each test, 20 μ L of the catalyst ink was deposited on a newly polished glassy carbon rotating disk electrode (GC-RDE) (0.196 cm²) and dried in ambient conditions. For each sample, the Au catalyst mass loading was kept at 0.1 mg_{Au}/cm².

Characterizations. Transmission electron microscopy (TEM) images were acquired from a Philips CM20 (200 kV). X-ray diffraction (XRD) patterns were collected on a Bruker AXS D8-Advanced diffractometer (Cu K α λ =1.5418 Å). The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was measured by a JY2000 Ultrace ICP atomic emission spectrometer equipped with a JYAS 421 autosampler and 2400 g/mm holographic grating. Scanning transmission electron microscopy (STEM) analyses were carried out on a Hitachi HD2700C (200 kV) with a probe aberration corrector, at the Center for Functional Nanomaterials, Brookhaven National Lab. The electron energy loss spectroscopy (EELS) line-scan was obtained by a high-resolution Gatan-Enfina ER with a probe size of 1.3 Å. A power law function was used for EELS background subtraction.

Electrochemical Measurements. Electrochemical measurements were carried out on an Autolab 302 potentiostat (Eco Chemie B.V, Holland) with GC-RDE (catalyst loading area: 0.196 cm²) as a working electrode (W.E.), Ag/AgCl (4 M KCl) as a reference electrode (R.E.), and a Pt wire (commercial source, separate Pt-wire electrode, 0.8 x 6 mm, exposed Pt wire surface area: 15.57 mm²) as a counter electrode (C.E.). The distances between C.E., W.E. and R.E. are kept same as 1.5 cm (see the set-up photo below). The reference electrode was calibrated to reversible hydrogen electrode (RHE) before the measurements and all potentials were converted to the RHE scale ($V_{\text{Ag/AgCl}} + 0.26 \text{ V} = V_{\text{RHE}}$ in 0.1 M HClO₄ solution, $V_{\text{Ag/AgCl}} + 0.223 \text{ V} = V_{\text{RHE}}$ in 0.5 M H₂SO₄ solution). The atomic scale Pt deposition was carried out for the C-Au NPs under cyclic voltammetry potential cycling from different voltage ranges and different cycling numbers in 50 mL N₂-saturated 0.5 M H₂SO₄ electrolyte solution with a constant scan rate of 100 mV/s. After the Pt deposition, the electrolyte solution was changed according to different electrochemical catalysis. The FAOR CVs were obtained from 0 to 1.2 V in 50 mL N₂-saturated 0.1 M HClO₄ + 0.1 M HCOOH with a scan rate of 50 mV/s. The HER LSVs were obtained in 50 mL N₂-saturated 0.5 M H₂SO₄ with a scan rate of 2 mV/s and rotation speed at 1600 rpm. 10 h Chronoamperometry i-t test for the stability test was carried out at the constant potential of 0.4 V in 50 mL 0.1 M HClO₄ + 0.1 M HCOOH (FAOR) with the electrode rotation speed at 1000 rpm. In the CO stripping test, the catalyst was first immersed in the 50 mL CO-saturated 0.1 M HClO₄ at 0.1 V for 20 min to form a CO adsorption layer on Pt surface. Then N₂ was purged into solution for 20 min to get rid of remaining CO in solution. CO stripping CV was performed from 0 - 1.2 V with a scan rate of 20 mV/s. The ECSA was calculated by a conversion factor of 420 μ C/cm².²



References

1. Zhu, W.; Michalsky, R.; Metin, O.; Lv, H.; Guo, S.; Wright, C. J.; Sun, X.; Peterson, A. A.; Sun, S. *J. Am. Chem. Soc.* **2013**, *135*, 16833-16836.
2. Wang, G.; Huang, B.; Xiao, L.; Ren, Z.; Chen, H.; Wang, D.; Abruna, H. D.; Lu, J.; Zhuang, L. *J. Am. Chem. Soc.* **2014**, *136*, 9643-8649.

➤ Figures

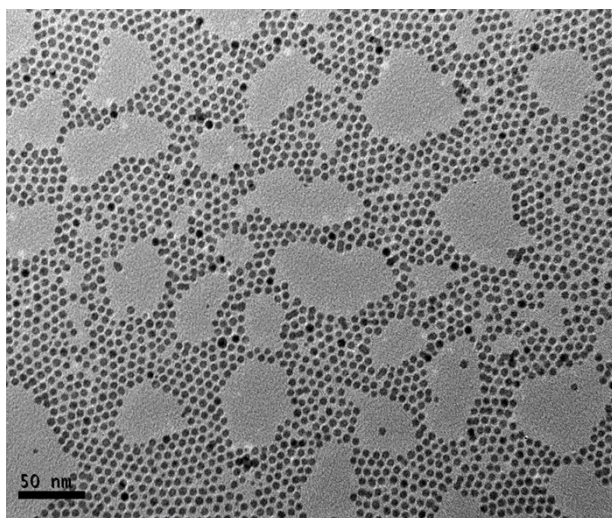


Figure S1. TEM image of the as-synthesized 5 nm Au NPs.

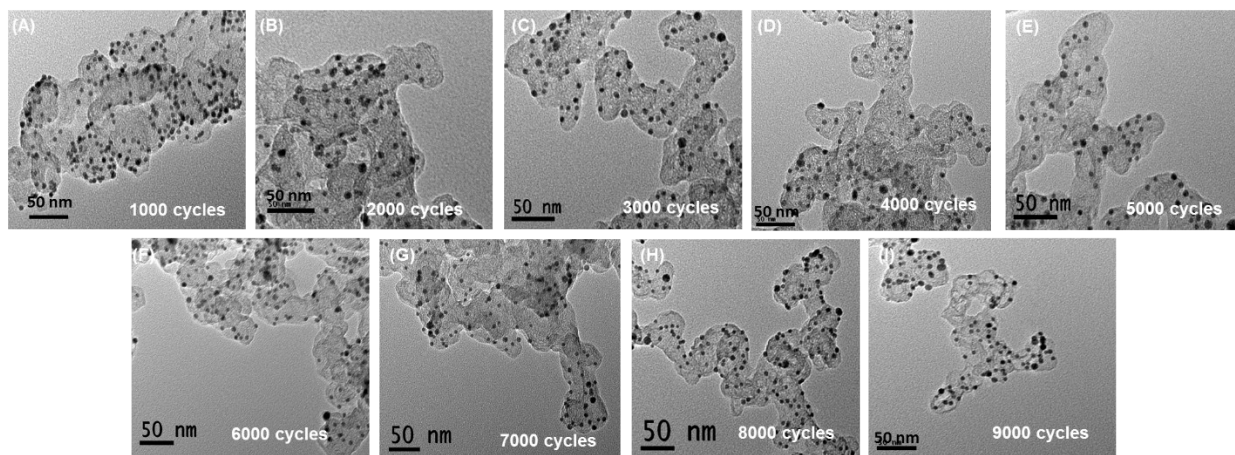


Figure S2. TEM images of the Au NPs after different numbers of CV cycling from 0.6 V to 1.0 V (vs. RHE): (A) 1000, (B) 2000, (C) 3000, (D) 4000, (E) 5000, (F) 6000, (G) 7000, (H) 8000, and (I) 9000.

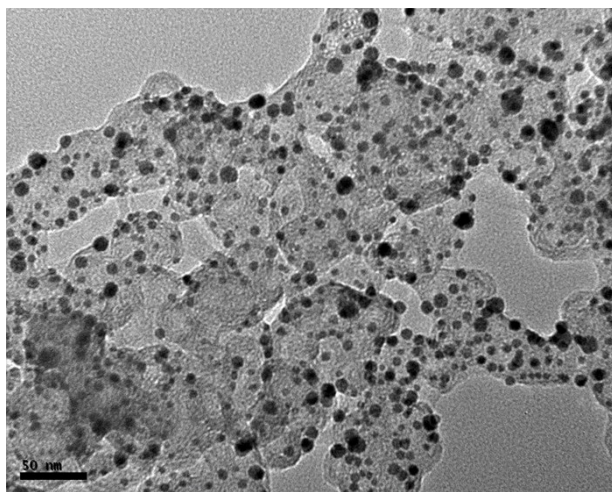


Figure S3. TEM image of the Au NPs after 11000 CV cycling between 0.6 V to 1.0 V (vs. RHE).

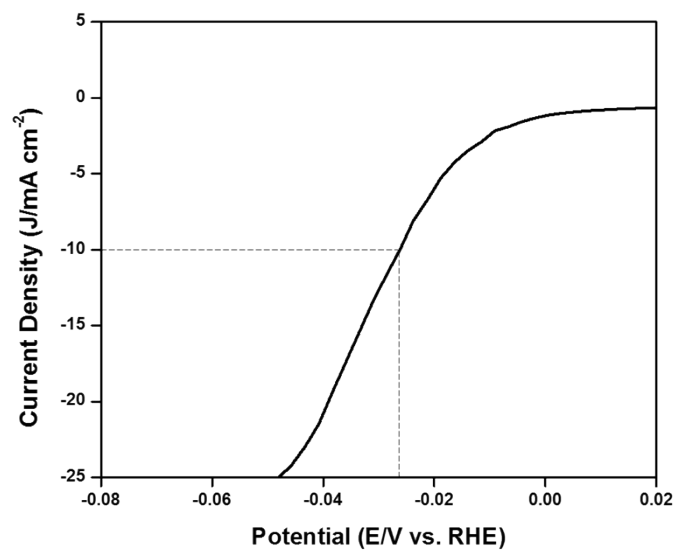


Figure S4. HER polarization curve of the commercial C-Pt (20 wt%). Scan rate: 2 mV/s.

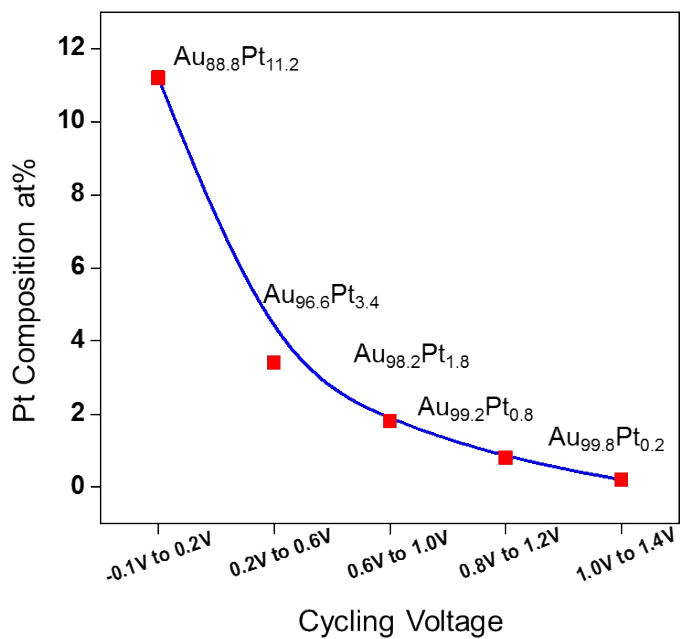


Figure S5. Pt composition change after 10000 potential cycling from different potential ranges. Scan rate 100 mV/s.

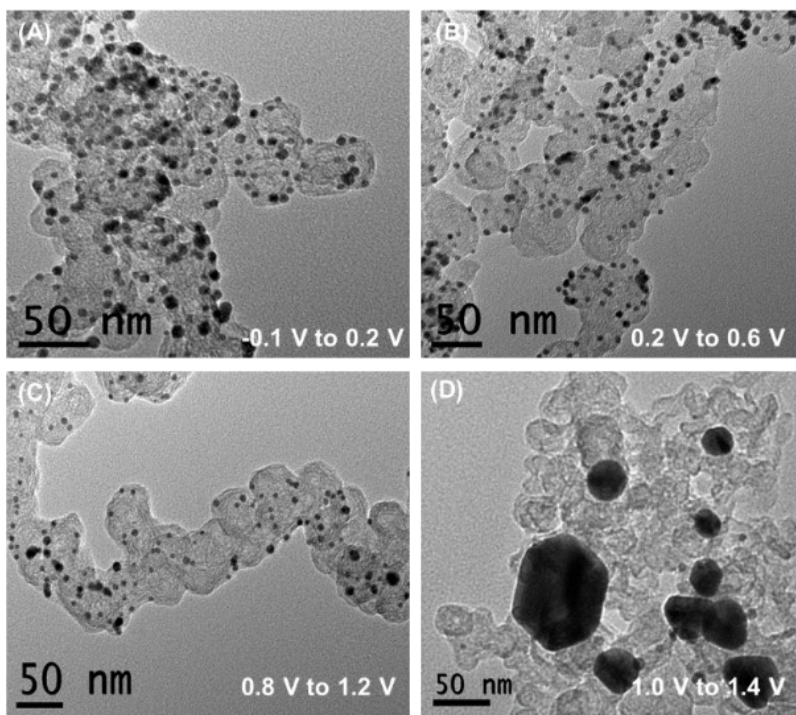


Figure S6. TEM images of Au NPs after cycling 10000 times from (A) -0.1 V to 0.2 V, (B) 0.2 V to 0.6 V, (C) 0.8 V to 1.2 V, (D) 1.0 V to 1.4 V. Scan rate 100 mV/s.

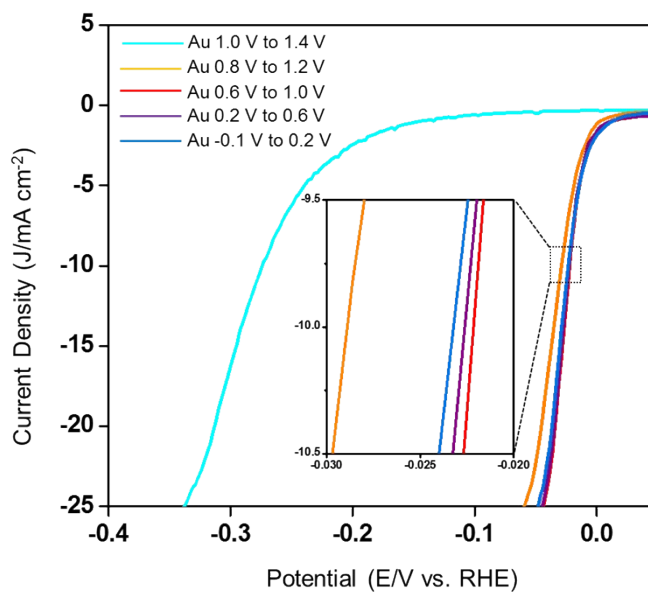


Figure S7. HER polarization curves of the Au NPs after 10000 potential cycling from different potential ranges (no iR correction). Scan rate: 2 mV/s.

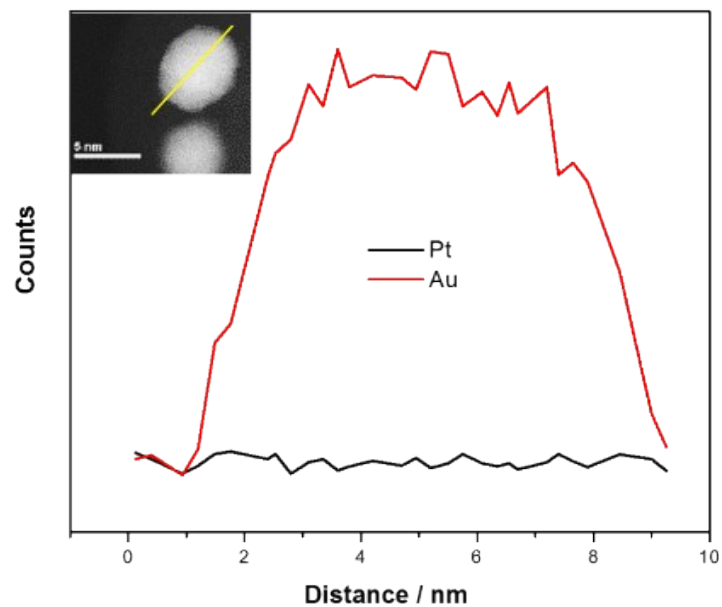


Figure S8. EELS-line scan of a single C-Au_{98.2}Pt_{1.8} NP.

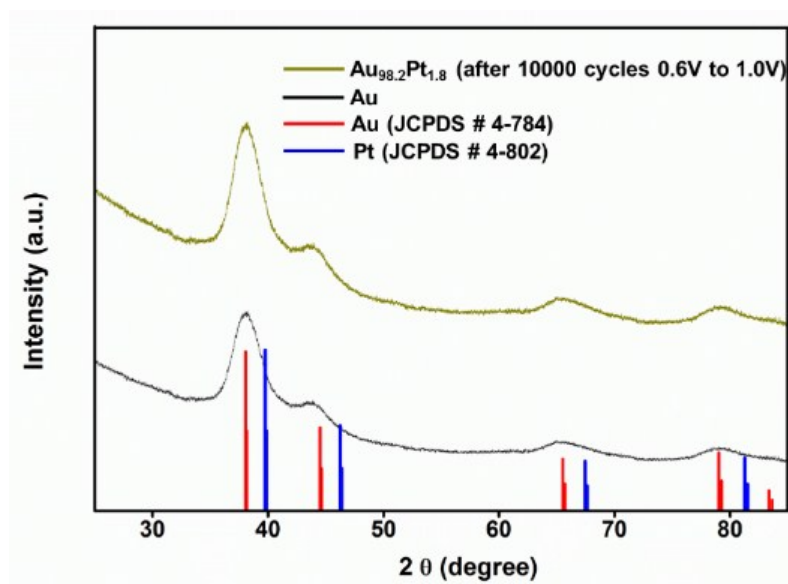


Figure S9. XRD of the Au NPs before and after 10000 CV cycles from 0.6 V to 1.0 V. Standard Peaks for Au (JCPDS # 4-784) and Pt (JCPDS # 4-802) are also shown.

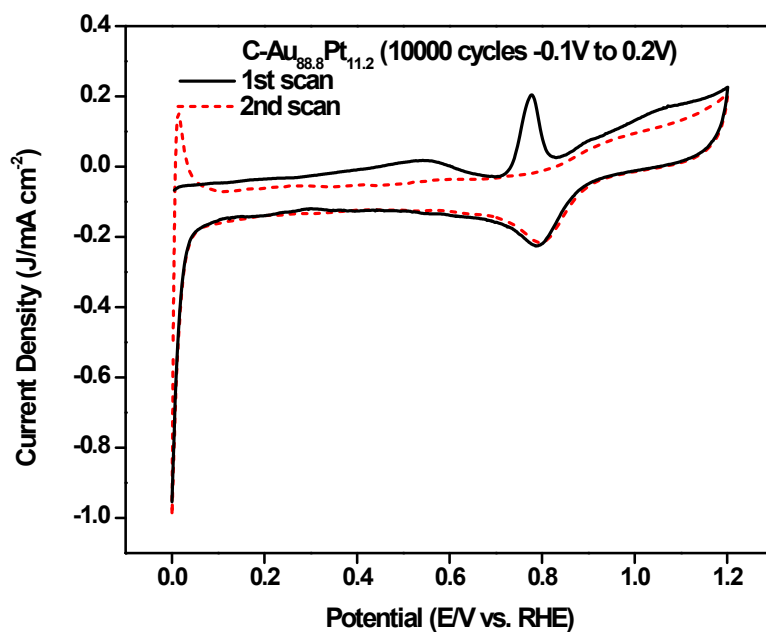


Figure S10. CO stripping for C-Au_{88.8}Pt_{11.2} obtained after 10000 cycles from -0.1 V to 0.2 V. Scan rate of 20 mV/s.

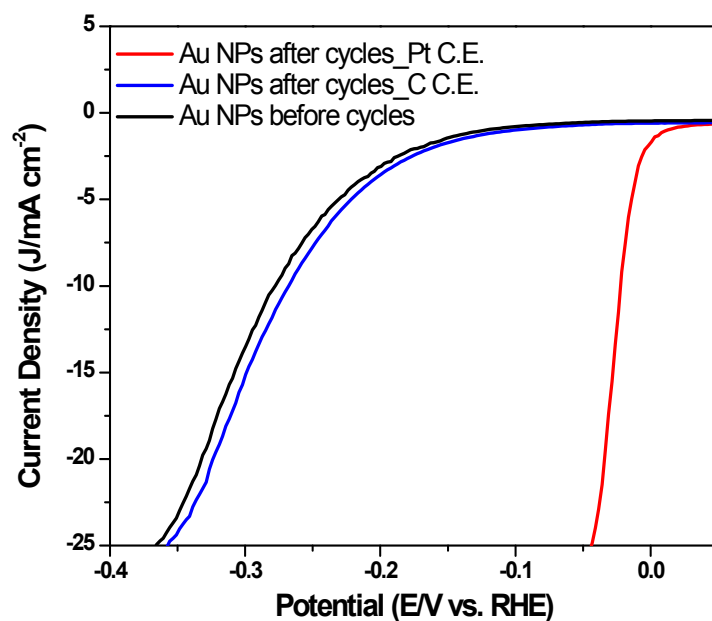


Figure S11. HER LSVs (in 0.5 M H₂SO₄, no iR correction) of the Au NPs before and after 10000 CV cycles from 0.6 V to 1.0 V by using Pt CE and graphite CE, respectively.

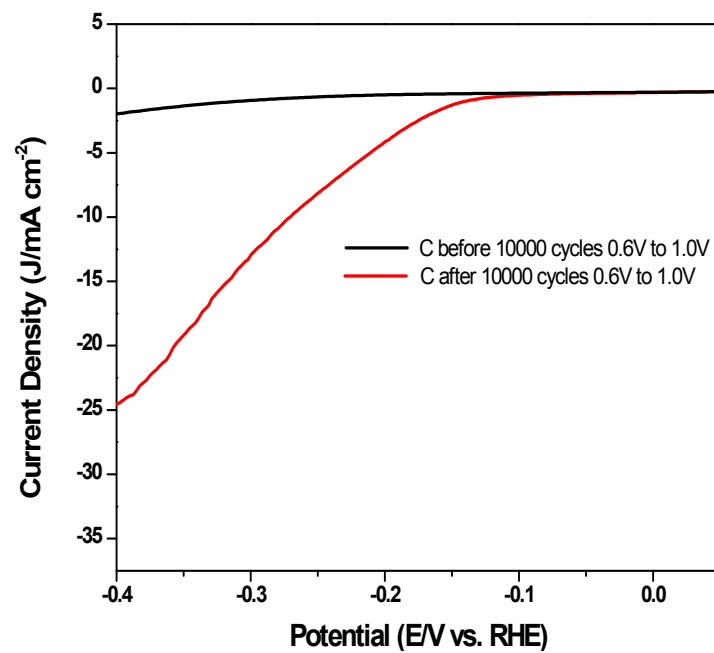


Figure S12. HER LSVs (in 0.5 M H₂SO₄, no iR correction) for pure carbon support before and after 10000 CV cycles from 0.6 V to 1.0 V by using Pt CE.