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Supporting Information

Pt-Cu Hierarchical Quasi Great Dodecahedrons with Abundant Twinning Defects for Hydrogen Evolution†

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Experiment section

Materials

Hexachloplatinic (IV) acid hexahydrate ($H_2PtCl_6·6H_2O$), Cupric chloride dehydrate ($CuCl_2·2H_2O$), poly(vinylpyrrolidone) (PVP, Mw≈30,000), potassium iodide (KI), ethylene glycol (EG) were purchased from Sinopharm Chemical Reagent Co. Ltd. All chemical reagents were used as received without further purification. Ultrapure Millipore water (18.2 MΩ·cm) was used in the synthesis. All the vials were made of borosilicate glass, with a white phenolic molded screw cap and polyvinyl-faced pulp liner.

Synthesis of Pt-Cu HQGDs.

In a typical synthesis of Pt-Cu HQGDs, an aqueous solution of KI (5 M, 40 μL), H_2PtCl_6 (40 mM, 1 mL), $CuCl_2$ (50 mM, 1 mL), and PVP (160 mg), were mixed together in EG (10 mL) in a 20-mL vial. After the vial had been capped, the mixture was stirred for around 3 min. The resulting homogeneous mixture was transferred into an oil bath and heated at 115 ºC for 10 h before it was cooled to room temperature. The products were collected by centrifugation at 10,000 rpm for 10 min, and then washed with ethanol-acetone mixture twice.

Preparation of working electrodes.

The catalysts dispersed onto a glassy carbon rotating disk electrode (RDE, PINE, PA, USA) were used as a working electrode for HER activity measurement and cycling stability test. The RDE has a diameter of 5 mm and a geometric area of 0.196 cm^2. The electrode was firstly polished with emery paper of decreasing grades and then with Al_2O_3 powders with a size down to 0.05 μm. Prior to the deposition of catalysts, the electrode was thoroughly rinsed with Ultrapure Millipore water three times and then immersed in ethanol to remove contaminants. For the commercial Pt/C (JM, 20 wt% Pt) and the Pt-Cu HQGDs/C (20 wt% Pt), aqueous dispersions were prepared and sonicated for 30 min. 5 μL of the dispersion was then transferred onto the RDE (all the qualities of the Pt were 1.0 mg mL^{-1}). In this case, the loading amounts of Pt were kept as 25.5 μg cm^{-2} for all the samples. Before electrocatalytic measurements, the working electrode was cleaned with plasma (Plasma Cleaner PDC-002, USA) at a power level of 10.5 W for 3 min to remove residue organics, followed by the addition of 10 μL of 0.05 wt% Nafion (diluted from 5 wt% Nafion, Sigma-Aldrich) to cover on the surface of the catalysts. Then the working electrode was dried in air.

The catalysts dispersed onto a 1*1cm^2 square carbon paper were used as a working electrode for HER chronopotentiometry. In this case, the loading amounts of noble metals were kept as 500 μg cm^{-2} for all the samples.

Electrochemical measurements.

Electrochemical measurements were carried out with a three-electrode system on an IM6 electrochemical workstation (Zahner, Germany). Pt wires and Ag/AgCl were used as the counter and reference electrodes, respectively. Hundreds of potential cycles were conducted in a 0.5 M H_2SO_4 solution with continuous Ar gas in the potential region from 0.05 to 1.20 V at a sweep rate of 50 mV s^{-1} till the cyclic voltammetry curves (CVs) stayed unchanged, in order to release residue organics and ions. Before the HER measurement, the electrolyte (0.5 M H_2SO_4) was degassed by bubbling pure hydrogen for at least 30 min to ensure the H_2O/H_2 equilibrium at 0 V. The polarization curves were obtained by sweeping the potential from -0.3 to 0.1 V at room temperature and 1,600 rpm to remove the in situ-formed H_2 bubbles on the RDE, with a sweep rate of 5 mV s^{-1}. The CV was conducted between -0.3 and 0.1 V at 50 mV s^{-1} for 5,000 times to investigate the cycling stability. All potentials were converted to values with reference to a reversible hydrogen electrode (RHE).

RHE calibration.

In all measurements, we used Ag/AgCl as the reference electrode. It was calibrated with respect to RHE. The calibration was performed in the high-purity hydrogen-saturated electrolyte with a Pt foil as the working electrode. The CV was conducted at a scan rate of 1 mV s^{-1}. The average of two potentials at which the current crossed 0 was taken to be the thermodynamic potential for the HER measurement. In a 0.5 M H_2SO_4 solution, $E_{\mathrm{RHE}} = E_{\mathrm{Ag/AgCl}} + 0.20$ V.

Instrumentations.

Scanning electron microscope (SEM) images were obtained with a scanning electron microscope (SEM, JSM-6700F) operated at 5 kV. Transmission electron microscopy (TEM) images were taken using a Hitachi H-7650 transmission electron microscope at an acceleration voltage of 100 kV. High-resolution TEM (HRTEM), high-angle annular dark-field scanning TEM (HAADF-STEM), and energy dispersive X-ray (EDX) analysis were collected on a JEOL ARM-200F field-emission transmission electron microscope operating at 200 kV accelerating voltage. Power X-ray diffraction (PXRD) characterization was performed using a Philips X'Pert Pro X-ray diffractometer with a monochromatized Cu K_α radiation source and a wavelength of 0.1542 nm. ICP-AES (Atomscan Advantage, Thermo Jarrell Ash, USA) was used to determine the concentration of Pt and Cu.

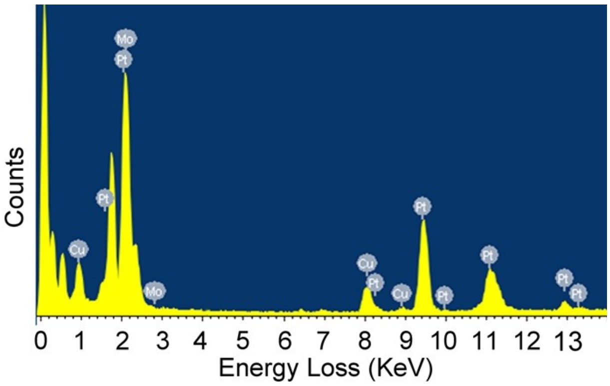

Figure S1. The corresponding EDX spectrum of an individual Pt-Cu HQGD shown in Figure 2A.

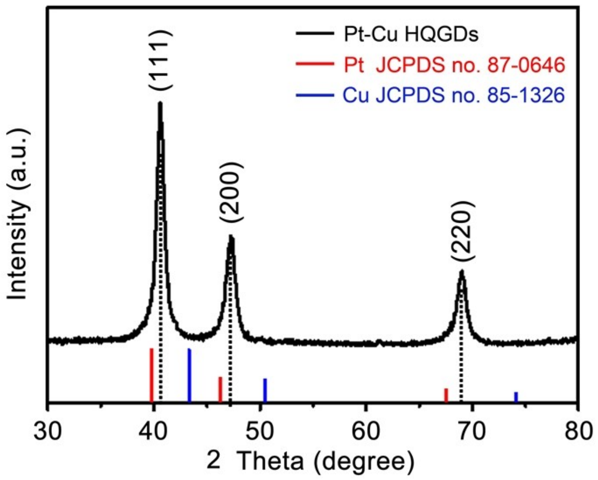

Figure S2. Powder X-ray diffraction (PXRD) pattern of as-prepared Pt-Cu HQGDs. The standard diffraction peaks for Pt and Cu elements are also shown for comparison.

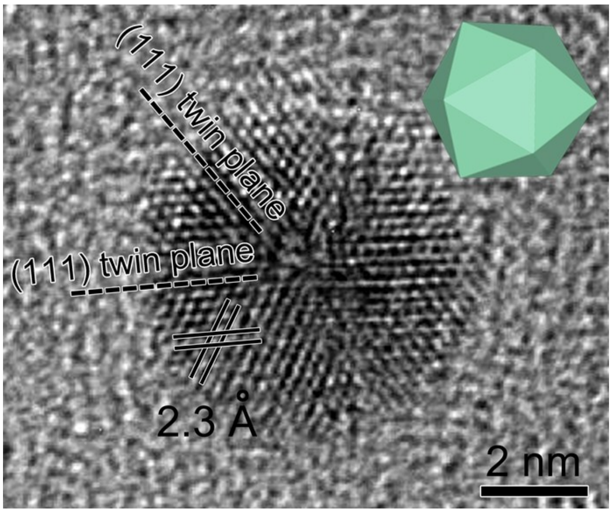

Figure S3. HRTEM image of an individual nanocrystal obtained at 1 h. The inset shows the corresponding geometrical model of the nanocrystal. The fringe spacing of 2.3 Å corresponds to the {111} planes. The (111) twin planes are indicated by dash lines.

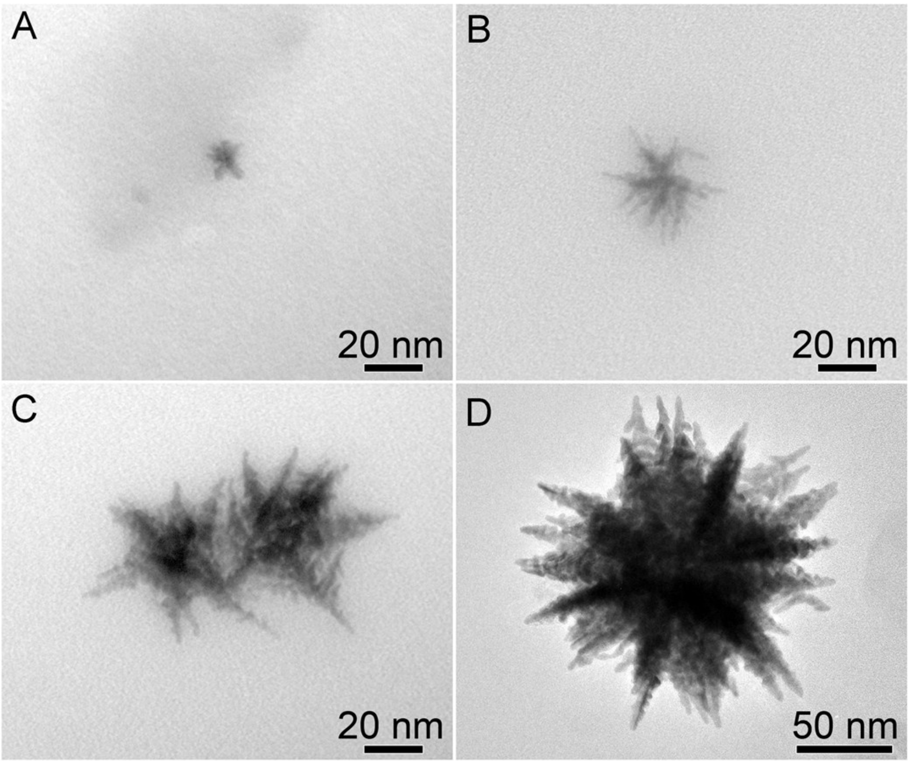

Figure S4. TEM images of Pt-Cu nanocrystals at different reaction stages: (A) t=1.5 h, (B) t=2 h, (C) t=3 h, and (D) t=10 h.

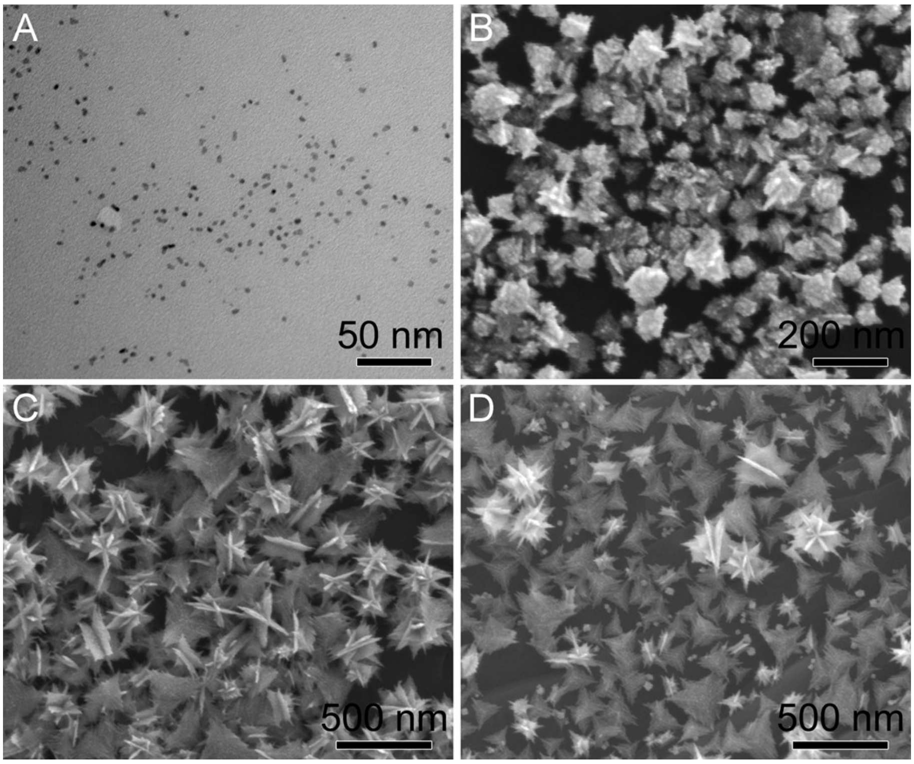

Figure S5. TEM and SEM images of nanocrystals obtained with the addition of different amounts of KI aqueous solution in the synthesis without changes of the other conditions: (A) 0 μL, (B) 20 μL, (C) 80 μL, and (D) 160 μL.

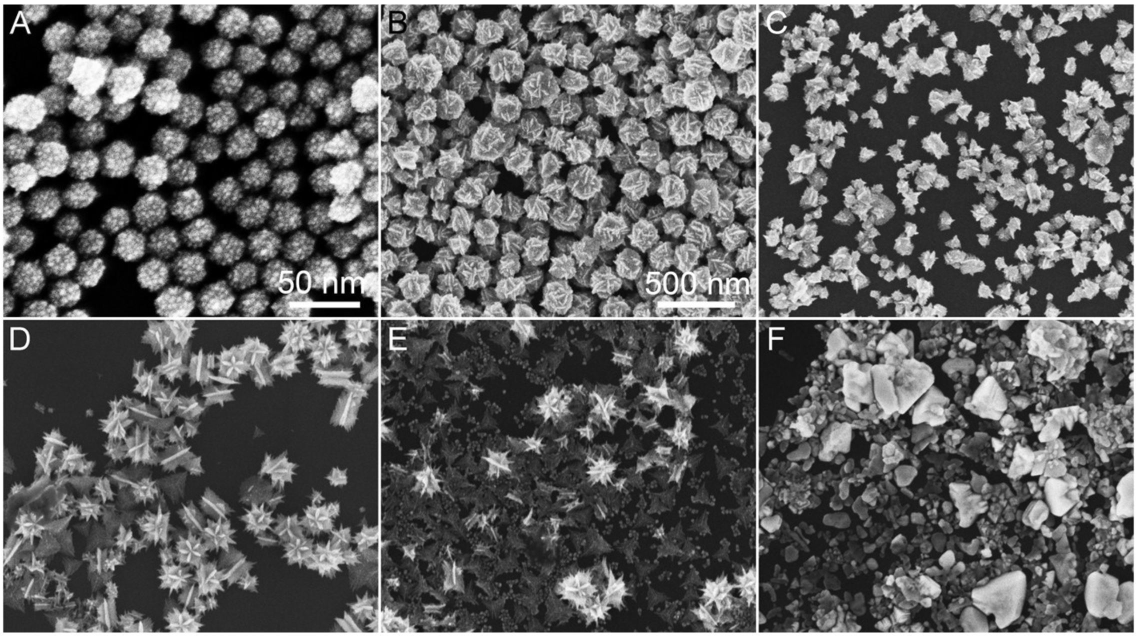

Figure S6. SEM images of nanocrystals obtained with the addition of precursors with different ratios of Pt/Cu without changes of the other conditions: (A) Pt only, (B) 7:1, (C) 4:1, (D) 1:2, (E) 1:4, and (F) Cu only. The scale bar in B also applies to C-F.

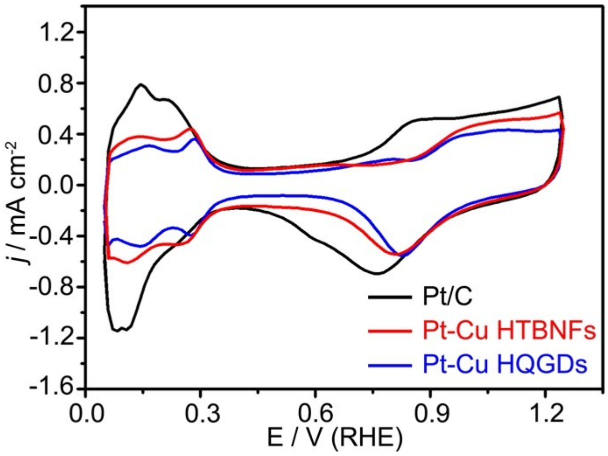

Figure S7. CVs of Pt-Cu HQGDs, Pt-Cu HTBNFs and Pt/C were recorded in Ar-purged 0.5 M H_2SO_4 solution at room temperature with a sweep rate of 50 $mV \cdot s^{-1}$. The ECSA of Pt-Cu HQGDs, Pt-Cu HTBNFs and Pt/C were 24.2, 30.6 and 54.7 m^2 g^{-1} by measuring the charge associated with the hydrogen adsorption/desorption region from CVs.

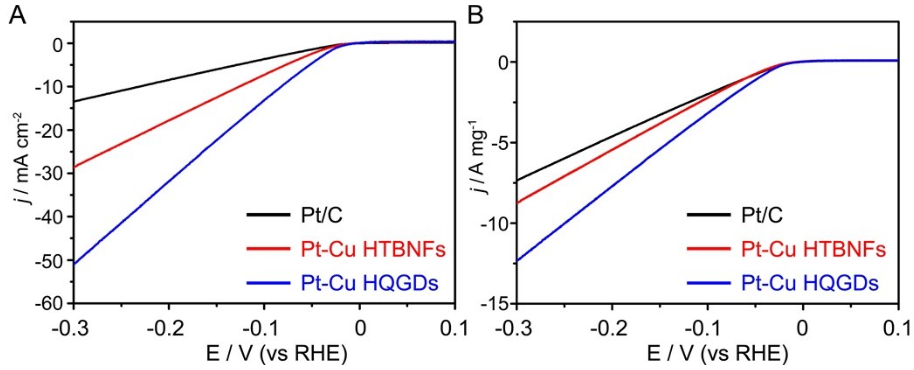

Figure S8. (A) Specific activities and (B) mass activities of Pt-Cu HQGDs, Pt-Cu HTBNFs and Pt/C.

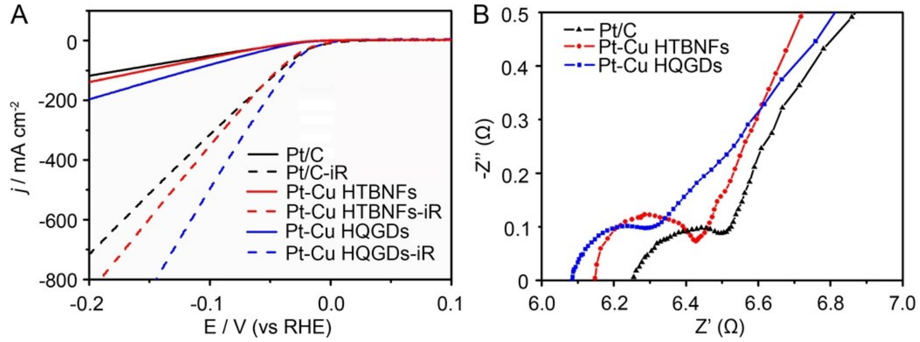

Figure S9. (a) Polarization curves towards HER for commercial Pt/C, Pt-Cu HTBNFs and Pt-Cu HQGDs. Short dash lines show corresponding iR-corrected data. (b) Nyquist plots of commercial Pt/C, Pt-Cu HTBNFs and Pt-Cu HQGDs.

Table S1. Parameters obtained by iR correction according to the resistance of solution.

Catalyst	R_s (ohm)	j (mA cm^{-2})@-0.1 V (witou iR correction)	j (mA cm^{-2})@-0.1 V (with iR correttion)
Pt/C	6.25	51	317
Pt-Cu HTBNFs	6.15	57	354
Pt-Cu HQGDs	6.08	82	494

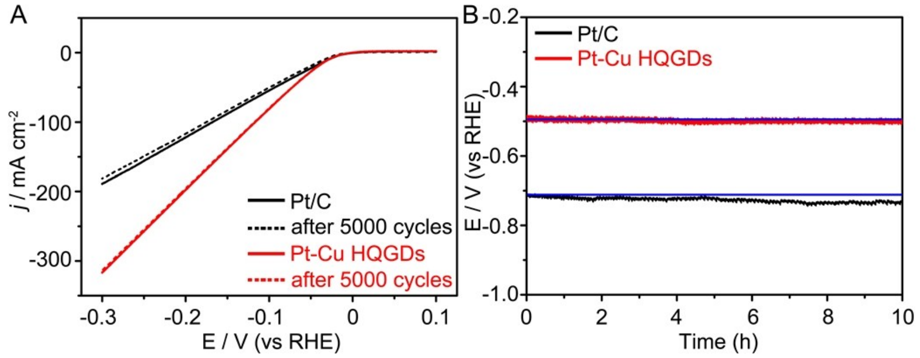

Figure S10. (A) Polarization curves for HER of commercial Pt/C (black) and Pt-Cu HQGDs (red) before (solid lines) and after (dash lines) the durability tests. The durability tests were carried out in a H_2-purged 0.5 M H_2SO_4 solution from -0.3 V to 0.1 V for 5000 cycles at a scan rate of 50 mV s^{-1}. (B) HER chronopotentiometry of polarization curves for HER of commercial Pt/C and Pt-Cu HQGDs under a constant current density of 500 mA cm^{-2} in 0.5 M H_2SO_4 solution.

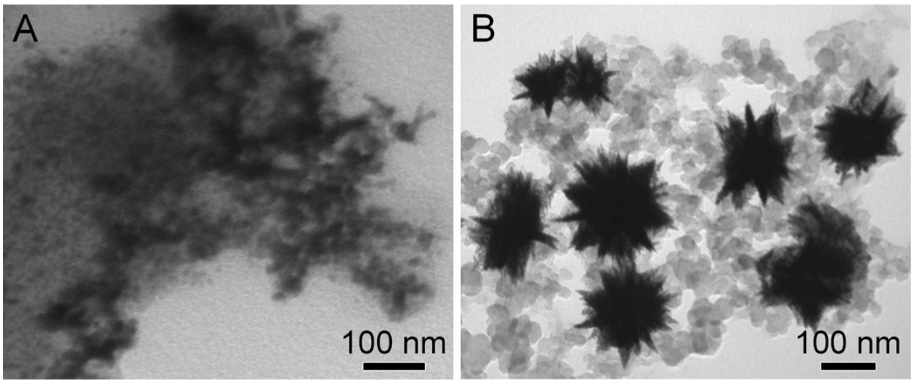

Figure S11. TEM images of (A) commercial Pt/C and (B) Pt-Cu HQGDs after the CV measurements. The tests were conducted in a H_2-purged 0.5 M H_2SO_4 solution from -0.3 V to 0.1 V for 5000 cycles at a scan rate of 50 mV s^{-1}.

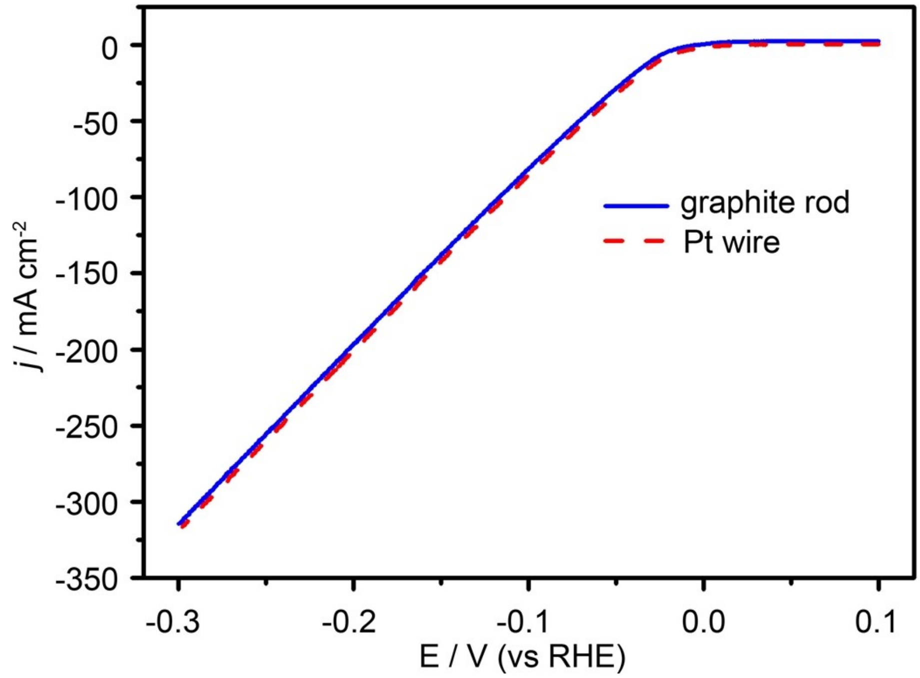

Figure S12. Polarization curves towards HER for Pt-Cu HQGDs with Pt wires (red dashed line) and graphite rod (blue solid line) as counter electrode after the durability tests. The durability tests were carried out in a H_2-purged 0.5 M H_2SO_4 solution from -0.3 V to 0.1 V for 5000 cycles at a scan rate of 50 mV s^{-1}.