Synthesis and Characterization of porous Pt-Cu alloy for Catalysts with Enhanced Activity toward hydrogen evolution reaction

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Methods

Materials. Commercial platinum/carbon (Pt/C) (Pt loading: 20 wt%, Pt on carbon black) was purchased from Alfa Aesar. Cuprous chloride (CuCl, powder, 97.0%), Potassium hexachloroplatinate (IV) (K_2PtCl_6), potassium chloride (KCl, 99.5%), potassium hydroxide (KOH, 85.0%), nafion perfluorinated resin solution, methanol (CH3OH, 99.5%) were purchased from Tianjin Chemical Reagent (Tianjin, China).

Synthesis of CuCl NCs. To obtain uniform CuCl NCs, CuCl micropowder was first dissolved in saturated KCl, giving a $HCuCl_2$ solution according to Eq. 1. Then the solution was added lots of pure water. As a result, the reverse reaction (i. e. CuCl precipitation) could proceed at very high rates, leading to uniform CuCl NCs formed via quick and homogenous nucleation and growth, which is refered to the literature[1].

Synthesis of porous Pt-Cu NPs. Porous Pt-Cu NPs were typically synthesized by using 10 mL of 1 mM K_2PtCl_6, and 10 mL of as-prepared uniform CuCl NCs was quickly added, and then the mixture was stirred at room temperature until the solution color changed from milk white to black, indicating the Pt-Cu NPs was Synthesized. Following the CuCl cores being dissolved in saturated KCl solution, porous Pt-Cu NPs inherited from the CuCl templates are obtained. The synthesized Pt-Cu NPs was immersed into concentrated nitric acid (HNO_3) solution for 30 h. Following the Cu was removed after this dealloying treatment.The final product was collected by centrifugation at 12000 rpm for 20 min, followed by three consecutive washing/centrifugation cycles with water, and then stored for further characterization. To avoid particle aggregation, the alloyed Pt-Cu nanoparticles were supported on carbon nano tube (CNT) /carbon black (acid treated CB). The final product with 20 wt% Pt loading was denoted.

Characterization. The particle size and morphology were investigated using an FEI Technai G^2 F20 transmission electron microscope equipped with a field-emission gun and an EDS unit. Absorption spectra were recorded in a Hitachi U-3010 spectrometer. X-ray diffraction (XRD) was recorded on a Bruker D^8 ADVANCE diffractometer equipped with Cu Kαradiation. X-ray photoelectron spectroscopy (XPS) analyses were performed using a PHI Quantum 2000 scanning ESCA Microprobe spectrometer. The inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was conducted using a Thermo Scientific iCAP6300 (Thermo Fisher Scientific, US).

Electrochemical investigations. Electrochemical measurements were performed using a standard three-electrode glass cell (CHI 660D). The electrolyte cell was composed of three electrodes: a glassy carbon with an area of 0.07 cm^2 as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and graphite plate was used as the counter electrode. The measurements were conducted in solution.

One milligram of Pt-Cu NPs were resuspended in a mixture containing 0.5 mL of isopropanol, 0.5 mL of deionized water and 10 μL of Nafion (0.5 wt %) ultrasonicating for approximately 0.5 h to form a 1 mg mL−1 catalyst ink. The catalyst ink (3 μL) was deposited on the glassy carbon working electrode (diameter = 3 mm) that was polished prior to catalyst deposition by 0.3 and 0.05 mm alumina powder. Then the working electrode was dried in air. The HER experiments with chronoamperometric (CV) and LSV measurements of Pt-Cu/CNT、Pt/C catalysts were conducted in N_2-saturated 0.5 M H_2SO_4.

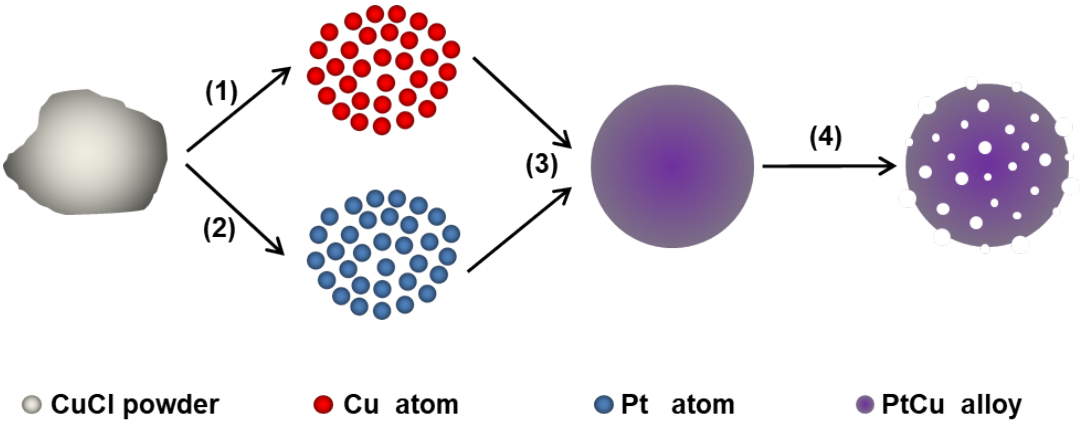

Figure S1 Schematic illustration of the formation of porous Pt-Cu NPs.

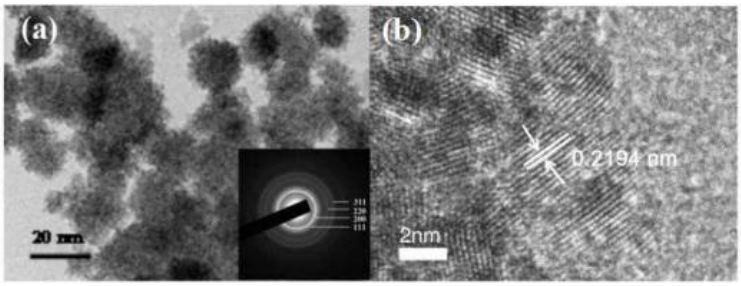

Figure S2 Characterization of the as prepared Pt-Cu alloy, (a) TEM image, (b) HRTEM image

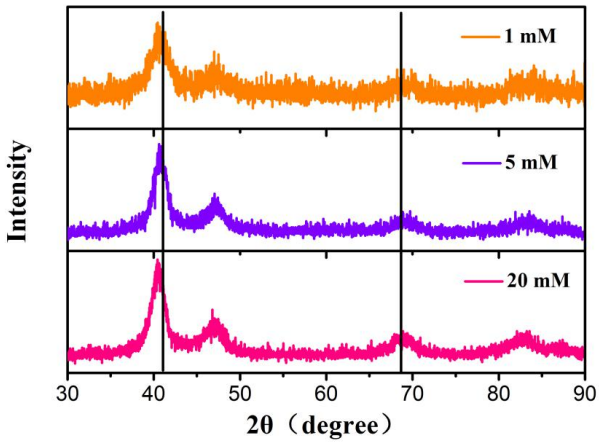

Figure S3 XRD spectra of Pt-Cu nanostructures under different Pt precursor concentration.

Table S1 Metal Contents of PtCu nanoparticles derived from ICP-MS before and after acid treatment.

	Analysed from ICP-MS		
	Pt (wt%)	Cu (wt%)	Pt/Cu atomic ratio
Before acid treatment	37.192	11.354	1:1
after acid treatment	192.868	15.976	4:1

1. Liu, H.; Zhou, Y.; Kulinich, S. A.; Li, J.-J.; Han, L.-L.; Qiao, S.-Z.; Du, X.-W., Scalable synthesis of hollow Cu2O nanocubes with unique optical properties via a simple hydrolysis-based approach. Journal of Materials Chemistry A 2013, 1 (2), 302-307.