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Supporting Information

One-pot Synthesis of Lotus-shaped Pd-Cu Hierarchical Superstructure Crystals for Formic Acid Oxidation

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Experimental

Chemicals: Palladium chloride (99.9%), Sodium chloride (99.99%), Polyvinyl Pyrrolidone (PVP-8000) and Glycine were purchased from Sigma-Aldrich. Cupric chloride ($CuCl_2$), Perchloric acid (G.R.) and absolute ethanol were purchased from the China Medicine Shanghai Chemical Reagent Corp. Chemicals were used as received without further purification. Super pure water (18 MΩ cm) was used as the solvent. 0.1 M of Na_2PdCl_4 aqueous solution was prepared by adding 0.235g (4.0 mmol) of NaCl and 0.354g (2.0 mmol) of $PdCl_2$ into 20 mL of water and stirring for 40 minutes. Then, the solution was stored without stirring for one day before use in this experiment.

Synthesis of Pd-Cu hierarchical superstructure crystals

Similar to a typical synthesis, 0.5 mL of 0.1 M Na_2PdCl_4 and 0.5 mL of a 0.1 M $CuCl_2$ aqueous solution were added to 5.0 mL of anaqueous solution containing 0.075 g Polyvinyl Pyrrolidone (PVP-8000) and 0.050 g glycine, and stirred for several minutes. Then, the resulting clear solution was transferred to a 10 mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 210°C for 2 hours before it was cooled to room temperature. The products were separated three times by centrifugation and washing cycles at 10,000 rpm for 20 minutes with ethanol. The collected product was redispersed in water.

Characterizations

The SEM images of the samples were examined with a JEOL7500F (10 kV), a highangle annular dark field scanning TEM (HAADF-STEM) and an energy-dispersive X-ray spectroscopy (EDX) element mapping analysis obtained with a FEI Titan 12 (120 kV). TEM images of the samples were examined with a JEM-2100(UHR) (200 kV). The Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis of samples was performed on an IRIS Intrepid II XSP (ThermoFisher). X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.5418 Å) using a graphite monochromator (40 kV, 40 mA). X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI Quantum 2000 Scanning ESCA Microprobe (Physical Electronics, USA), using Al_{Ka} X-ray radiation (1486.6 eV) for excitation.

Characterization of electrocatalytic activity

Electrochemical experiments were conducted in a standard three-electrode cell at room temperature controlled by a PAR 263A potentiostat/galvanostat (EG&G). The super pure water (18 MΩ cm) purified through a Milli-Q Lab system (Nihon Millipore Ltd.) was used as the solvent. The working electrode was a glassy carbon (GC, Φ=5mm) electrode embedded into a Teflon holder. Prior to the electrochemical test, the GC electrode was mechanically polished using successive amounts of alumina powder of 1.5, 1, and 0.5 μm, and then cleaned in an ultrasonic bath. A certain amount of Pd-Cunanoparticles or Pd black powder were dispersed with super pure water under an ultrasonic bath. The suspension of the Pd-Cu nanoparticles or Pd black was spread on the GC electrode. As soon as the electrode was dried under infrared lamp, 10 μL Nafion diluents in a 0.5 wt.% Nafion® solution were coated onto the electrode surface. An Ag/AgCl electrode and a platinum foil were used as the reference and counter electrode.

The cyclic voltammograms (CVs) were obtained in the nitrogen-saturated 0.1 M $HClO_4$ solution, and the potential was scanned from –0.25 to 0.9 V (Ag/AgCl) at a scan rate 50 mV/s. Voltammogram measurements for formic acid oxidation were determined in the 0.5 M HCOOH + 0.1 M $HClO_4$ solution, and the potential was scanned from −0.25 to 0.9 V (Ag/AgCl) at a scan rate 50 mV/s. The scan was repeated several times to ensure that a stable cyclic voltammetry (CV) was obtained.

Fig. S1 SEM images of the as-synthesized $Pd_{53}Cu_{47}$ hierarchical superstructure crystals.

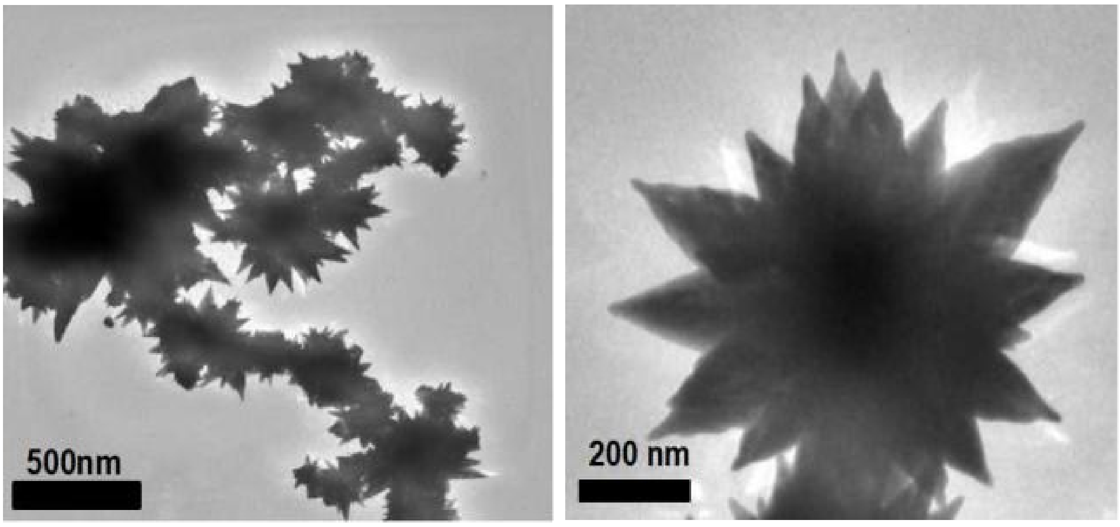

Fig. S2 TEM images of the as-synthesized $Pd_{53}Cu_{47}$ hierarchical superstructure crystals.

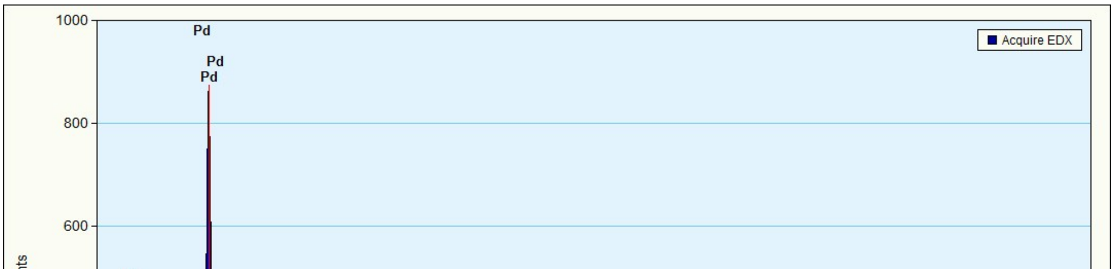

Fig. S3 EDX spectra of the as-synthesized $Pd_{53}Cu_{47}$ hierarchical superstructure crystals. (The signals of Mo came from Mo grid.)

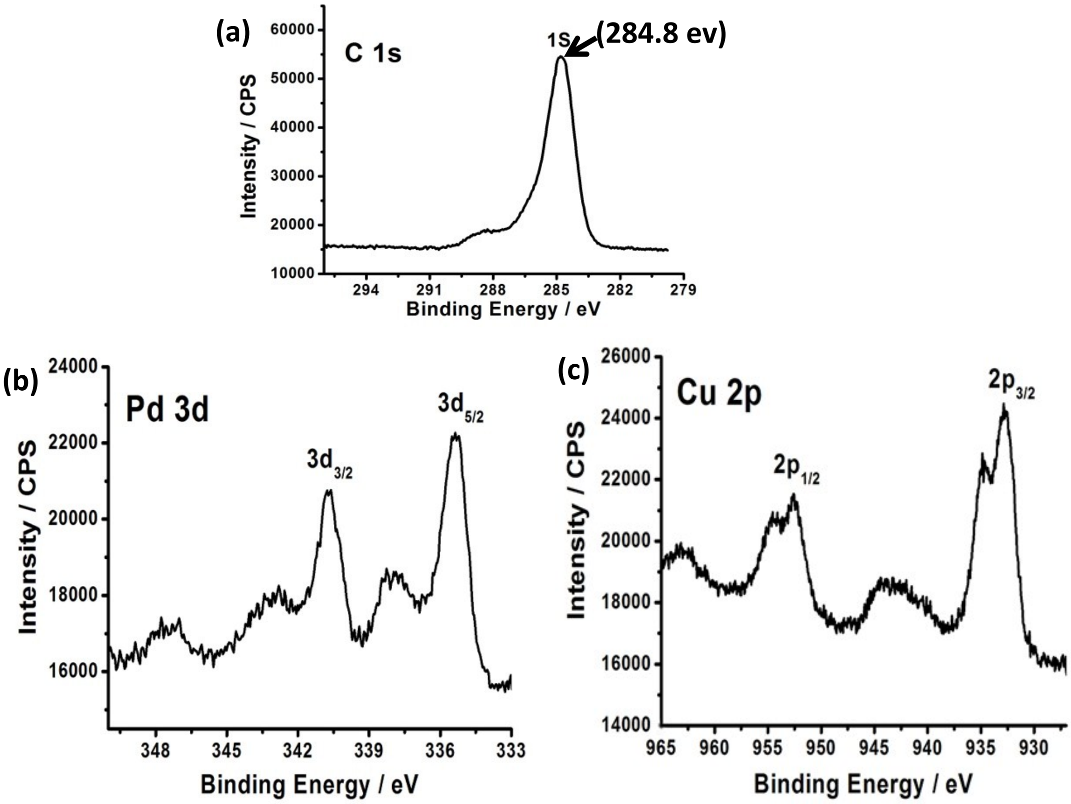

Fig. S4 XPS of the as-synthesized PdCu superstructure nanoalloys. (a) C 1s region; (b) Pd 3d region and (c) Cu 3p region. (The $3d_{5/2}$ and $3d_{3/2}$ peaks at about 335.4 and 340.7 eV are attributed to metallic Pd (b); the $2p_{3/2}$ and $2p_{1/2}$ peaks at about 932.7 and 952.5 eV are attributed to metallic Cu.)

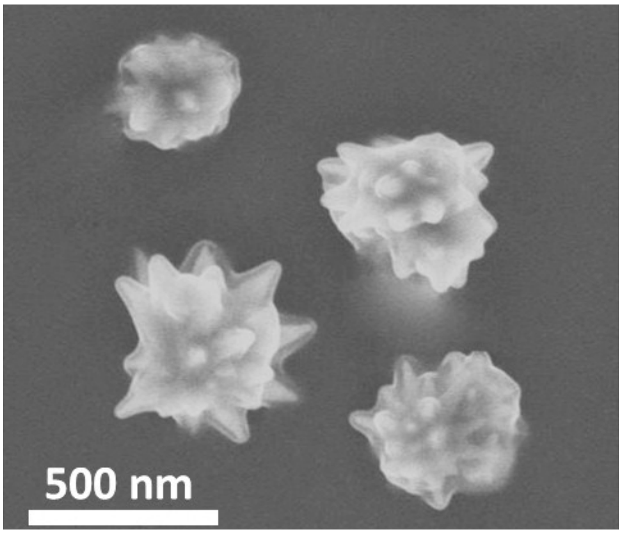

Fig. S5 SEM image of the PdCu superstructure nanoalloys after current-time test.