

Supporting Information for New Journal of Chemistry

**One-Pot Synthesis of Bimetallic PdCu Nanoframes as Efficient Catalyst
for Methanol Oxidation Reaction**

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1. Experimental Section

1.1. Chemicals and Materials

Oleylamine (Acros, 80%-90%), palladium acetylacetonate ($\text{Pd}(\text{C}_5\text{H}_7\text{O}_2)_2$, 98 %), copper acetylacetonate ($\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$, 98%), and hexane (99.5%) were purchased from Tokyo Chemical Industry Co., Ltd, Shanghai. Chloroform ($\geq 99\%$) and ethanol ($\geq 99.5\%$) were purchased from Sinopharm Chemical Reagent Co. Ltd. Commercial Pt/C catalyst E-TEK Pt/C (20 wt % Pt nanoparticles 2-5 nm on Vulcan XC-72R carbon support) was purchased from Alfa Aesar. All the chemicals were of analytical grade and used as received without further purification.

1.2. Synthesis of mesoporous PdCu NFs

PdCu NFs are prepared by a one-pot solvothermal method. In a typical synthesis, 0.08 mmol $\text{Pd}(\text{acac})_2$, 0.12 mmol $\text{Cu}(\text{acac})_2$ and 10 ml oleylamine are mixed under stirring at 100 °C under N_2 for 30 min. After cooling to room temperature, the mixture is transferred into an autoclave, and then charged with NH_3 at 5 bar. The autoclave is heated to 165 °C for 4 h under stirring. The resulting black colloidal product is collected by centrifugation and washed several times with ethanol and chloroform.

1.3. Materials Characterization

The morphology of the PdCu NFs is observed by a transmission electron microscopy (TEM) (TecnaiG220, FEI, American) equipped with a Gatan CCD794 camera operated at 200 kV. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), elemental mapping, high-resolution TEM (HRTEM) and Energy dispersive X-ray (EDX) and EDX line-scan are carried out on a Tecani G2 F20 TEM with an accelerating voltage of 200 KV. Mo TEM grid is used. The powder wide-angle X-ray diffraction pattern (XRD) is recorded on a X`Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu K α X-ray source ($\lambda = 1.540598 \text{ \AA}$).

1.4. Methanol Oxidation Reaction

The electrocatalytic investigations are conducted using a CHI 842D electrochemical analyzer (Chenhua Co., Shanghai, China) using a conventional three-electrode cell including a Ag/AgCl (saturated KCl), Pt wire, and modified glassy carbon (GCE) as a reference, counter, and working electrode, respectively. The working electrodes are coated with the catalysts with the same loading amount of 10 μg , flowed by addition of 3 μL Nafion (0.05 %) and dried under vacuum at 80 $^{\circ}\text{C}$ before the electrochemical measurements.

Prior to the measurements, the working electrodes are cleaned via steady state cyclic voltammograms (CVs) scanned in a N_2 -saturated 0.1 M HClO_4 between -0.2 to 1.2 V. After that, the CVs are performed in a 0.1 M N_2 -saturated HClO_4 at a scan rate of 50 mV s^{-1} without and with 1 M methanol to measure the electroactive surface areas (ECSAs) and MOR, respectively. The ECSAs are calculated by the following equation: $\text{ECSA} = Q_{\text{H}} / m \times 210$, where Q_{H} is the charge for H_{upd} adsorption determined using $Q_{\text{H}} = 0.5 \times Q$ (where Q is the charge in the H_{upd} adsorption–desorption area obtained after the double layer correction region between 0 and 0.37 V), m is the Pt loading amount on the working electrodes, and 210 $\mu\text{C cm}^{-2}$ is the charge required for the monolayer adsorption of hydrogen on the Pt surface.

The specific and mass activities are obtained by normalized the measured current densities in reference to the ECSAs and loading amount of Pt, respectively. The MOR durability tests are tested in a 0.1 M N_2 -saturated HClO_4 at a scan rate of 50 mV s^{-1} containing 1 M methanol at 0.6 V with cycles from 0 to 2,000 at room temperature.

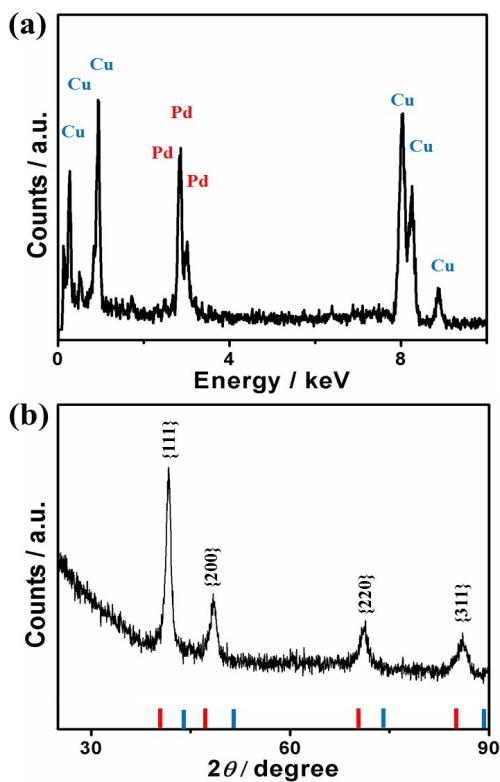


Figure S1. (a) EDX analysis and (b) wide-angle XRD pattern of PdCu NFs. The Pd and Cu peak positions are shown at the bottom.

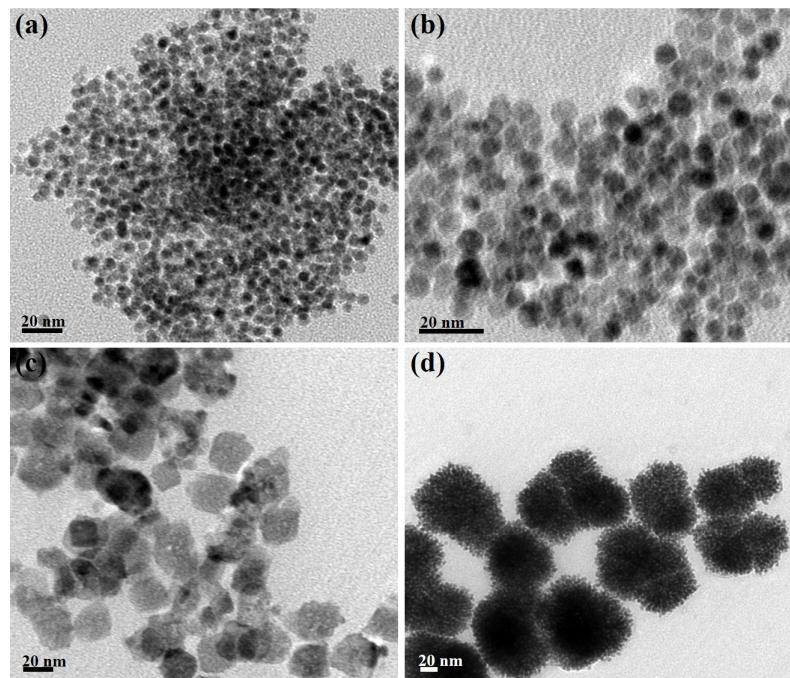


Figure S2. (a) TEM image of PdCu NCs prepared using N_2 instead of NH_3 , (b) PdCu NCs obtained using twice concentration of Pd and Cu precursors, (c) mono Cu NCs and (d) mono Pd NCs synthesized using NH_3 .

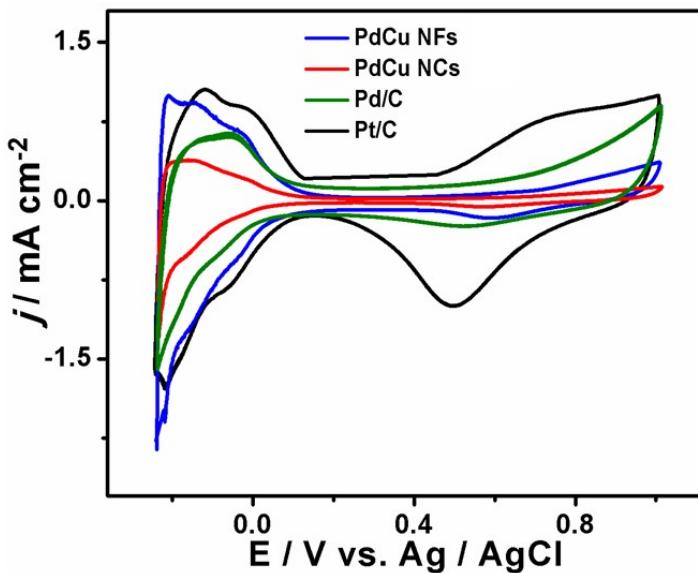


Figure S3. CVs of different catalysts measured in N_2 -saturated 0.1 M HClO_4 at a scan rate of 50 mV s^{-1} .

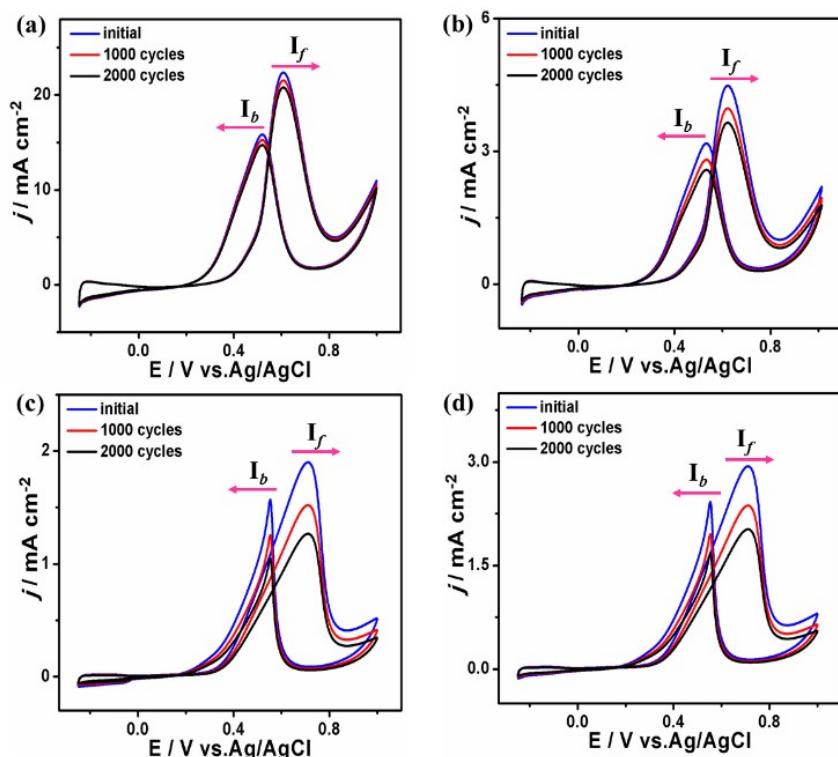


Figure S4. CVs for MOR durability on (a) PdCu NFs, (b) PdCu NCs, (c) Pd/C, and (d) Pt/C, respectively, in 0.1 M HClO_4 with 1 M CH_3OH at a scan rate of 50 mV s^{-1} .

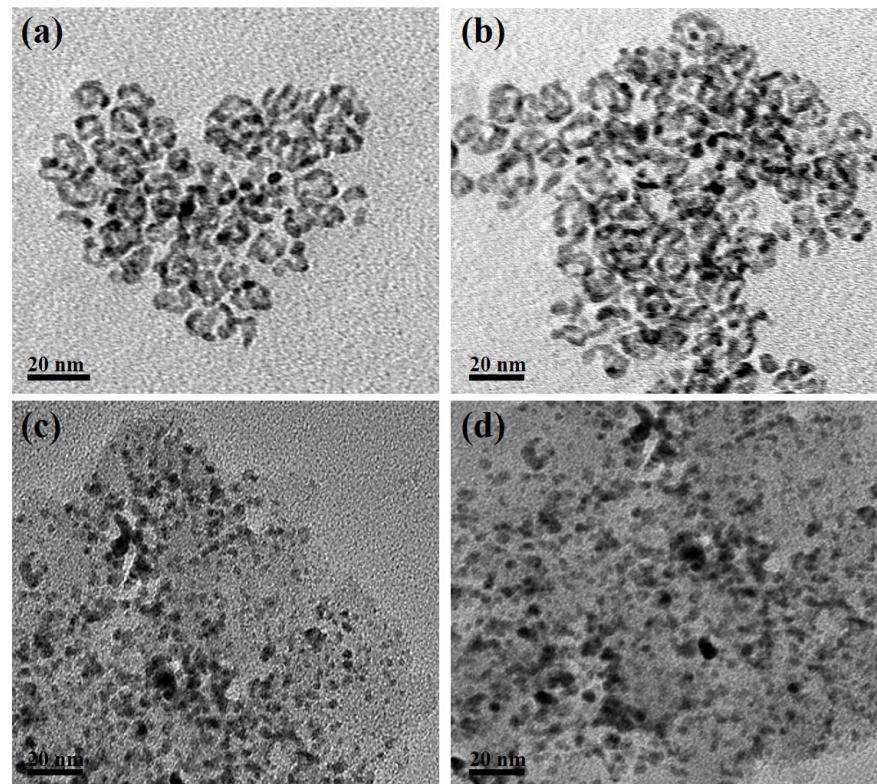


Figure S5. TEM images for (a and b) PdCu NFs and (c and d) commercial Pd/C catalyst before (a and c) and after (b and d) MOR durability test, respectively.