

Supporting Information

Facile Synthesis of Hollow Palladium/Copper Alloyed Nanocubes for Formic Acid Oxidation

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1. The Corresponding EDS Spectrum of the as-prepared Hollow PdCu Alloyed Nanocubes Supported on MWCNTs

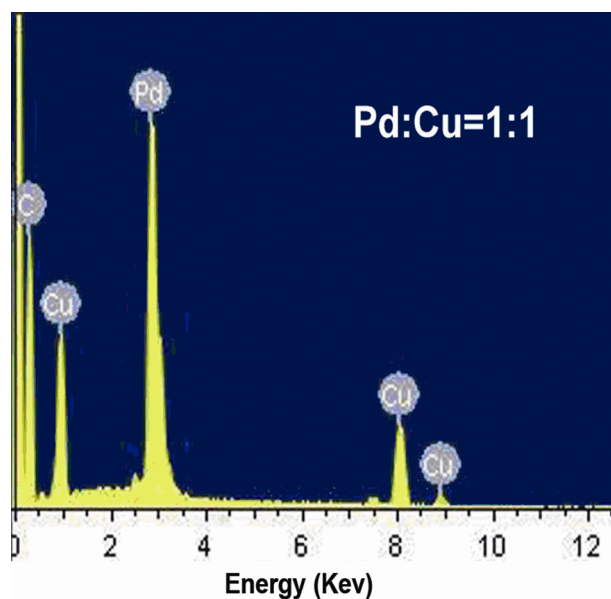


Figure S1. The EDS spectrum of the as prepared H-PdCu/MWCNTs catalyst.

2. HRTEM image on the face of PdCu nanocubes

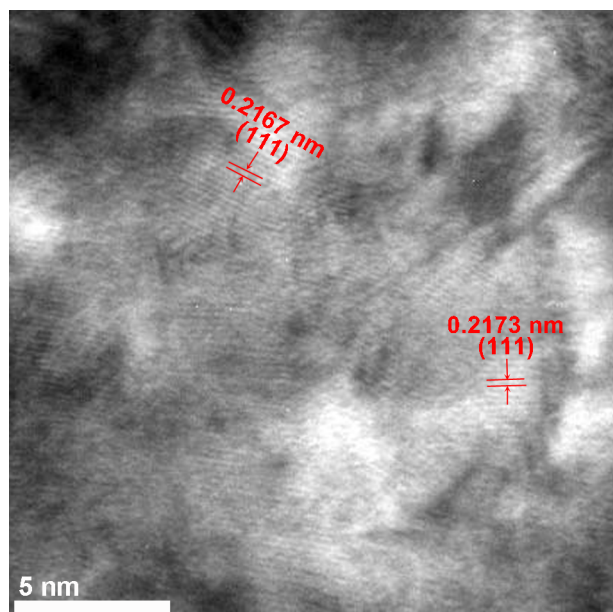


Figure S2. HRTEM image on the face of PdCu nanocubes.

3. The XRD Pattern and the Corresponding Size Distribution Histograms of Individual Nanoparticles of the PdCu Supported on MWCNTs when the Reaction Time is One Hour

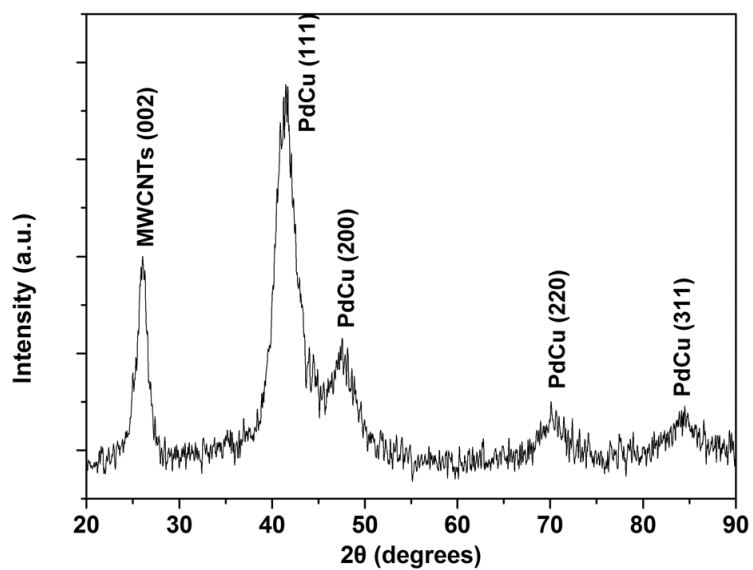


Figure S3. The XRD pattern of the PdCu nanoparticles supported on MWCNTs for one hour.

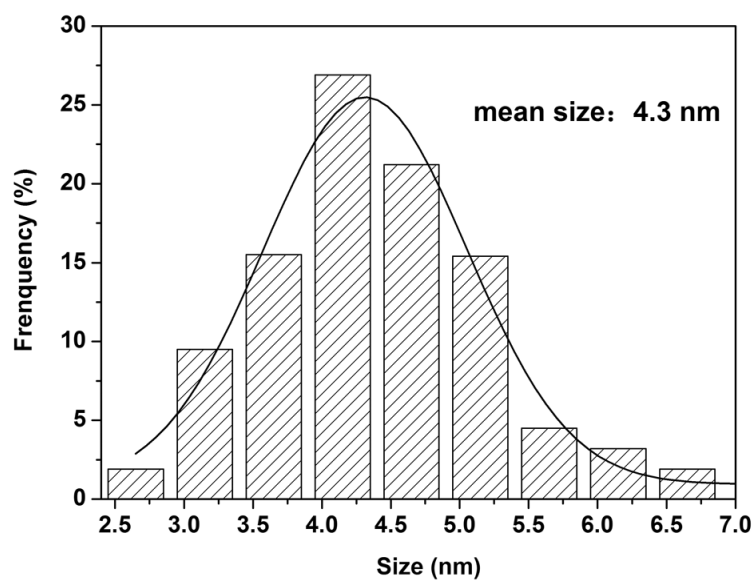


Figure S4. The corresponding size distribution histograms of individual PdCu alloyed nanoparticles supported on MWCNTs for one hour.

4. EDAX mapping analyzed the Pd and Cu.

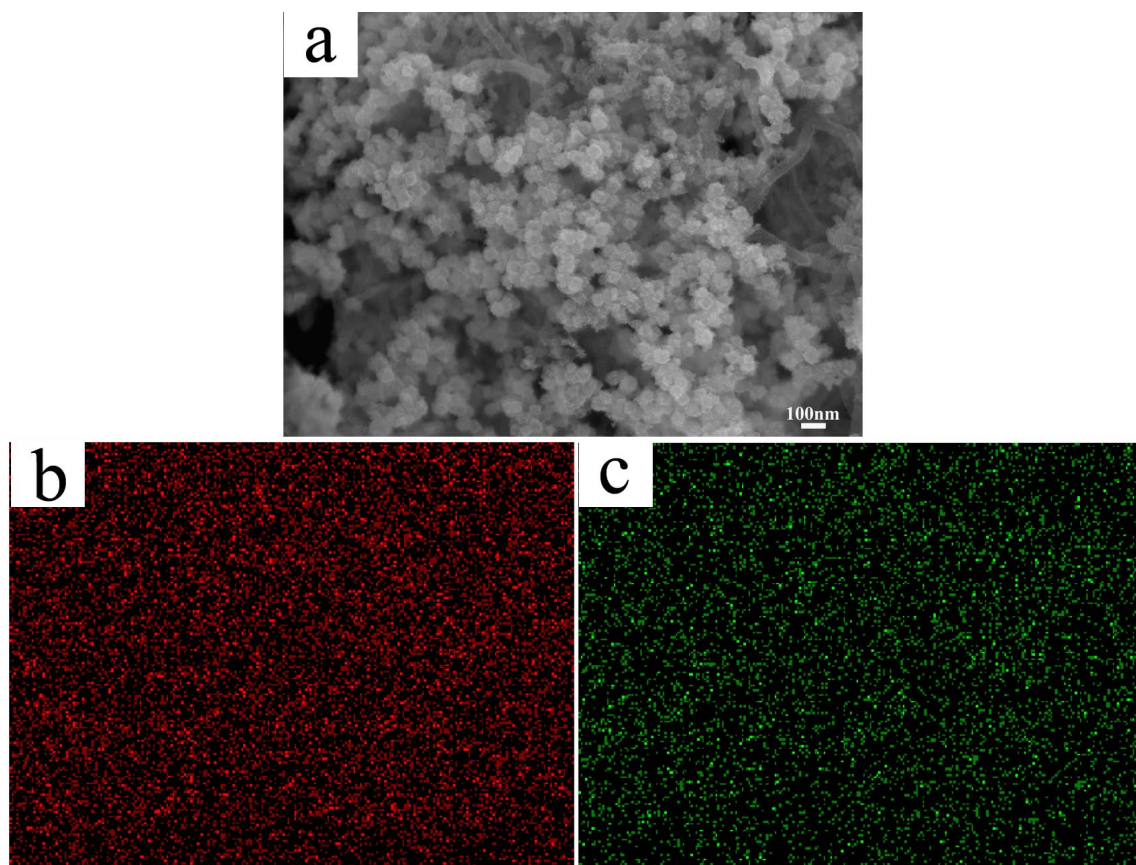


Figure S5 (a) FE-SEM and EDAX mapping analysis of the (b) Pd and (c) Cu in the PdCu nanocubes.

5. The selection of the reaction temperature to the formation of palladium/copper alloy nanostructures.

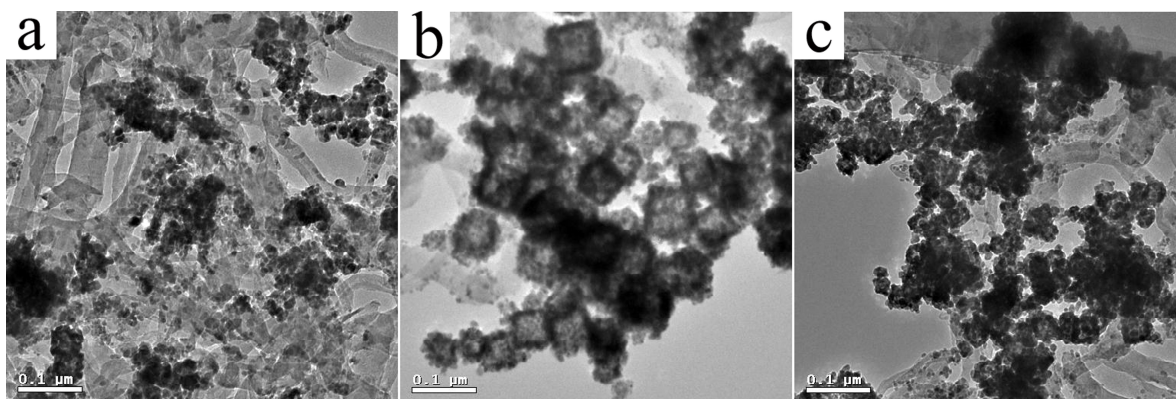


Figure S6. TEM images of the PdCu catalyst supported on MWCNTs prepared at (a) 140, (b) 160 and (c) 180°C.

In this study, the selection of the reaction temperature is important to the formation of palladium/copper alloyed nanostructures, and the self-assembly process. A similar situation happened when the preparations were performed under different temperatures, including 140, 160, and 180°C (Figure S6a-6c). The reaction at 180°C led to some aggregates. However the preparation performed at 160°C could obtain the hollow nanocubes. When a lower temperature (i.e., 140°C) was adopted, very few nanocubes were yielded, which may be due to the low temperature is not conducive to oriented attachment process in the dynamics. Therefore, the preparation of the hollow structure can be optimized at the temperature around 160°C.

6. Theoretical Calculation Method:

The experimental results show the hollow palladium/copper alloyed nanocubes were formed through the combination among nanoparticles. We try to explain the formation mechanism theoretically through surface energy (γ) calculations, which is defined as the

surface excess free energy per unit area of a particular crystal plane and is one of the basic parameters in surface physics.

The surface energy γ is evaluated as

$$\gamma = \frac{1}{2A} [E_{slab} - E_b] \quad (1)$$

where E_{slab} is the slab energy, E_b is the bulk energy with the same number of atoms as that in the slab model, and A is the surface area.¹

7. Electrochemical Investigation

The electrochemical measurements were conducted in a three-electrode cell, using a Solartron 1287 electrochemical test system (Solartron Analytical, England). A glassy carbon disk coated with catalyst was used as the working electrode. An Ag/AgCl electrode and a platinum foil (1 cm²) were used as the reference-electrode and counter-electrode, respectively. The glassy carbon disk was rinsed with DD water and dried at room temperature before the catalyst layer was applied to the disk. The thin film electrode was prepared as follows: 5 mg of catalyst was added into 0.5 mL of ethanol and 50 μ L of 5 wt% perfluorosulfonic acid (PFSA), and dispersed by ultrasonication for approximately 30 min to obtain a homogeneous ink. Next, using a pipette, 15 μ L of the ink was uniformly dispersed onto a freshly polished glassy carbon electrode (3 mm o.d.) and was dried under ambient conditions. The apparent surface area of the glassy carbon electrode was 0.0706 cm²; thus, the metal loading was 386 μ g·cm⁻².

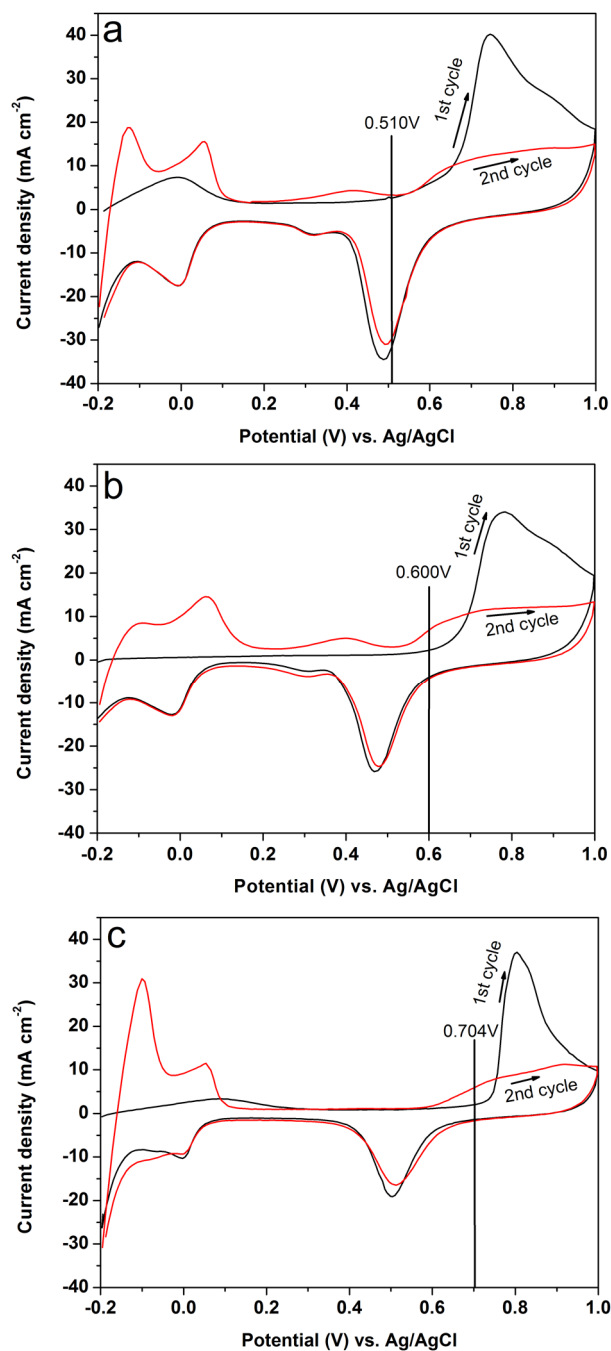


Figure S7. CO-stripping voltammograms of (a) H-PdCu/MWCNTs catalyst, (b) S-PdCu/MWCNTs catalyst, and (c) Pd/MWCNTs catalyst in 0.5 M H₂SO₄ at a scan rate of 20 mV s⁻¹.

To demonstrate the increased surface area resulting from the hollow structure, carbon monoxide (CO) stripping voltammetry studies were performed on H-PdCu/MCNTs, solid PdCu nanoparticles supported on MWCNTs (S-PdCu/MWCNTs), and Pd/MWCNTs,

respectively. The H-PdCu/MCNTs catalyst shows a stripping peak area that is much larger than those of the S-PdCu/MWCNTs catalyst and Pd/MWCNTs catalyst (see Figure S7).

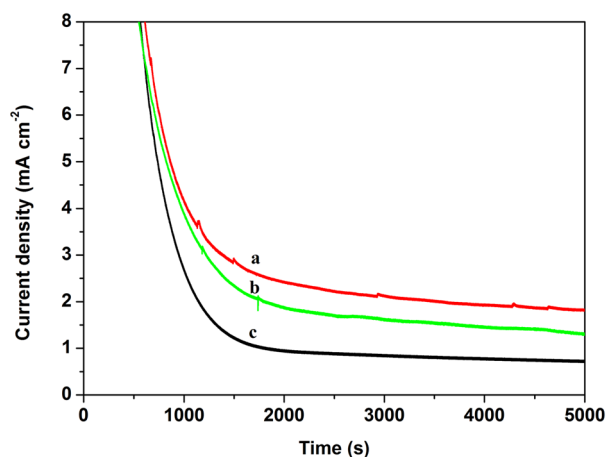


Figure S8. Chronoamperometric curves of the (a) H-PtCu/MWCNTs catalyst, (b) S-PdCu/MWCNTs catalyst, and (c) Pd/MWCNTs catalyst on a glassy carbon electrode. Electrolyte: 0.5 M H₂SO₄ + 0.5 M HCOOH aqueous solution; Potential: 0.1 V; Temperature: 20 ± 1°C.

To further evaluate the activity and stability of these catalysts, chronoamperometry tests were conducted in 0.5 M H₂SO₄ and 0.5 M HCOOH at 0.1 V for 5000 s (see Figure S8). As shown in the Figure, these curves reflect the activities and stabilities of the various catalysts in catalyzing the formic acid oxidation reaction. The much higher anodic current and slower degradation in current for the reaction on H-PdC/MWCNTs catalyst than those on S-PdCu/MWCNTs catalyst and Pd/MWCNTs catalyst indicate its better catalytic activity and the higher stability for formic acid oxidation.

8. Experimental details

Synthesis of PdCu alloy hollow nanocubes supported on MWCNTs: An aqueous solution of PdCl₂ (3.3 mg/mL, 3.8 mL), 20 mg of CuSO₄·5H₂O, and 50 mg of glutamate were mixed together in 40 mL of EG. The pH of the system was adjusted to ca. 11 by the dropwise

addition of the 8 wt% KOH/EG solution under vigorous stirring. During the process, the green solution turned into dark blue. Subsequently, 30 mg of pristine MWCNTs were added, and the solution was ultrasonicated and stirred for 2 hr to obtain a homogeneous suspension. Upon completion, the suspension was transferred into a 50 mL Teflon-lined stainless-steel autoclave. The autoclave was sealed, heated at 160°C for 6 hr, and air-cooled to room temperature. Finally, the product was collected by filtration and washed several times with DD water. The obtained product was dried at 40°C under vacuum for 8 hr. The catalyst thus obtained was denoted as H-PdCu/MWCNTs. PdCu catalysts supported on MWCNTs with Pd:Cu nominal atomic ratios of 1:0, 2:1, 1:1, 1:2, and 1:0 were prepared under similar conditions and denoted as Pd/MWCNTs, Pd₂Cu₁/MWCNTs, Pd₁Cu₁/MWCNTs, Pd₁Cu₂/MWCNTs, and Cu/MWCNTs, respectively.

Synthesis of Pd nanoparticles supported on MWCNTs: A control experiment was conducted in the absence of CuSO₄·5H₂O under nearly identical conditions as the typical experiment.

Synthesis of PdCu nanoparticles on supported MWCNTs: The experiment was conducted at 140°C under nearly identical conditions as the typical experiment.

Electrochemical CO stripping voltammograms were obtained by oxidizing preadsorbed CO (CO_{ad}) in 0.5 M H₂SO₄ at a scan rate of 50 mV s⁻¹. CO gas (99.99%) was purged through 0.5 M H₂SO₄ for 2000 s to allow complete adsorption of CO onto the catalyst. The working electrode was maintained at 0.1 V (vs. Ag/AgCl electrode), and excess CO in the electrolyte was removed by purging with high-purity nitrogen for 30 min. The amount of adsorbed CO was evaluated by integrating the CO_{ad} stripping peak and correcting for the capacitance of the electric double-layer. The activity of the catalysts in the oxidation of formic acid was

evaluated in a solution containing 0.5 M H₂SO₄ and 0.5 M HCOOH, and cyclic voltammetry was performed by applying a linear potential scan at a sweep rate of 50 mV s⁻¹. The cycling was repeated until a reproducible cyclic voltammetry curve was obtained before the measurement curves were recorded. High-purity nitrogen was purged through the solution for 15 min before the tests were performed. All electrochemical experiments were performed at 20 ± 1°C.

References

1. L. Yang, H. Yang, Z. Yang, Y. Cao, X. Ma, Z. Lu and Z. Zheng, *J. Phy. Chem. B*, 2008, **112**, 9795-9801.