

## ***Supporting Information***

# **Tuning synthesis of Platinum-Copper nanoparticles with hollow-core and porous shell for selective hydrogenation of furfural to furfuryl alcohol**

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## **Experimental**

### **Materials**

All chemicals were used as received from Aladdin unless specified. These include platinum acetylacetonate ( $\text{Pt}(\text{acac})_2$ , 97%), copper acetylacetonate ( $\text{Cu}(\text{acac})_2$ , 97%), oleylamine (OAm, 80-90%), oleic acid (OA, 85%), cetyltrimethyl ammonium bromide (CTAB, 99%), furfural (99%), dodecane (99%), chloroform (99%), methanol (99%), and  $\gamma$ -aluminium oxide ( $\gamma\text{-Al}_2\text{O}_3$ , 99%).

### **Preparation of Pt-Cu hollow-core structure:**

In a typical process, under an argon atmosphere, 34.0 mg  $\text{Pt}(\text{acac})_2$  and 65.5 mg  $\text{Cu}(\text{acac})_2$  were dissolved in 40 mL OAm and 10 mL OA in 130°C oil bath for 5 min, then directly dipped into oil bath which was preheated to 225°C and stirred at 225°C for 6 min, then a CO flow was applied into bottle with a flow (~190 mL/min) for specific time (The reaction time for synthesis of L-PNPs, M-PNPs and S-PNPs were 2min, 10min and 45min, respectively). The dispersion was then cooled down to room temperature, washed and separated by dispersing the reaction mixture in 10 mL chloroform and 50 mL ethanol, followed by centrifugation at 5000 rpm for 10 min. This procedure was repeated three times to get rid of the excess reactants and capping agents. The final products were dispersed in chloroform or dried in vacuum at 60°C for further characterization and use.

### **Preparation of Pt-Cu nanoparticles:**

under an argon atmosphere, 34.0 mg  $\text{Pt}(\text{acac})_2$ , 65.5 mg  $\text{Cu}(\text{acac})_2$  and 182.5 mg CTAB were dissolved in 40 mL OAm and 10 mL OA in 130°C oil bath for 5 min, then directly dipped into oil bath which was preheated to 225°C and stirred at 225°C

for 6 min, then a CO flow was applied into bottle with a flow (~190 mL/min) for 45min. The following process was the same as Pt-Cu hollow-core structure.

#### **Preparation of $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Supported Catalysts:**

45 mg  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 5 mg nanocrystals were dispersed in methanol and sonicated for 30 min respectively, then the two dispersions were mixed and sonicated for 30 min. The resultant solids were precipitated out by centrifugation and dried under a stream of argon gas.

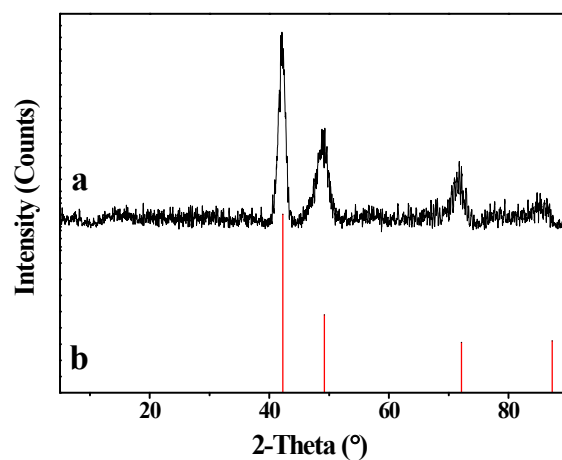
#### **Furfural hydrogenation:**

The liquid-phase hydrogenation was carried out in a well-stirred pressure vessel (100 mL). 50 mg  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported catalysts were dispersed in 30 mL methanol by sonication, and then transferred into a pressure vessel. 166  $\mu$ L furfural and 100  $\mu$ L dodecane was added. H<sub>2</sub> flow was applied into the bottle to blow air away for several minutes in order to remove any trace of oxygen. The temperature was then raised to 150°C and the vessel was pressurized by 2 MPa H<sub>2</sub>. Products were withdrawn at regular intervals, filtered and analyzed by a gas chromatography.

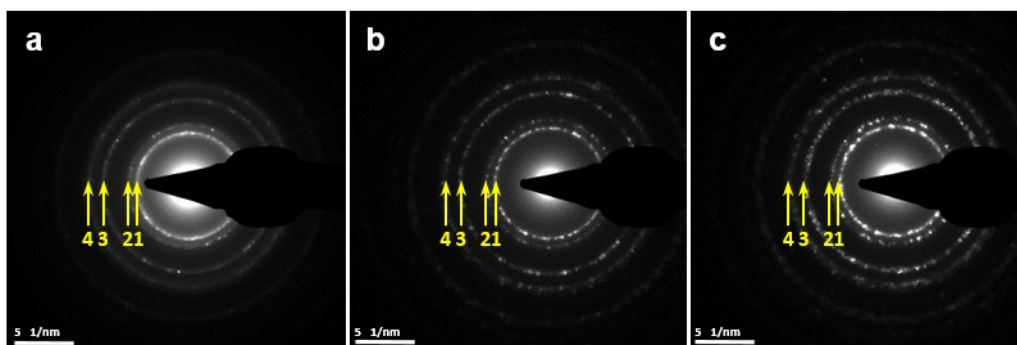
#### **Characterization of catalysts**

The transmission electron microscopy (TEM) including high-resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectrum (EDS) and selected-area electron diffractions (SAED) studies were performed on a FEI TECNAI G2 F20 STWIN transmission electron microscope at an operating voltage of 200 kV, equipped with a Gatan Orius CCD camera. Samples were prepared by dropping chloroform dispersion of samples onto 300-mesh carbon-coated nickel grids and slowly evaporating the solvent. The X-ray photoelectron spectroscopies (XPS) and Auger spectroscopies of the samples were recorded on a Thermo Fisher Scientific K-Alpha X-ray photoelectron spectrometer. The catalytic products were analyzed by a gas chromatograph (Agilent Technologies: GC 7890A/MSD 5975C).

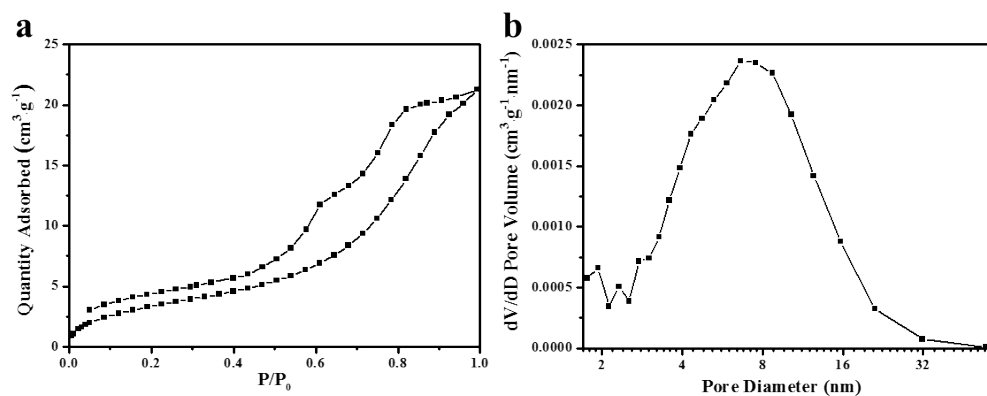
## Supporting Figures



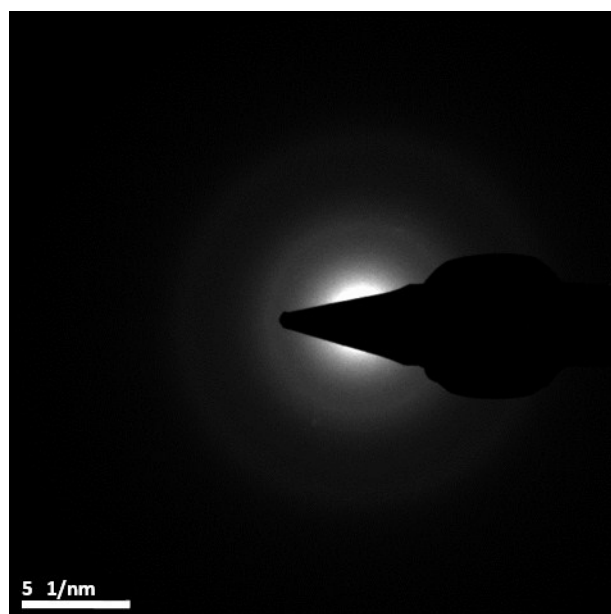
**Fig. S1** (a) XRD pattern of typical Pt-Cu with porous shell and hollow core, (b) Pattern of JCPDS No.35-1358, *fcc* Cu<sub>3</sub>Pt.



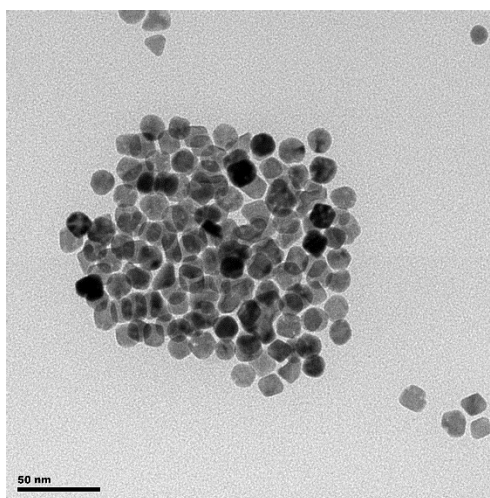
**Fig. S2** Selected-area electron diffractions (SAED) of (a) L-PNPs, (b) M-PNPs and (c) S-PNPs. (1, 2, 3, 4 correspond to electron diffraction pattern of *fcc* Pt-Cu alloy {111} {200} {220} {311} planes, respectively.)



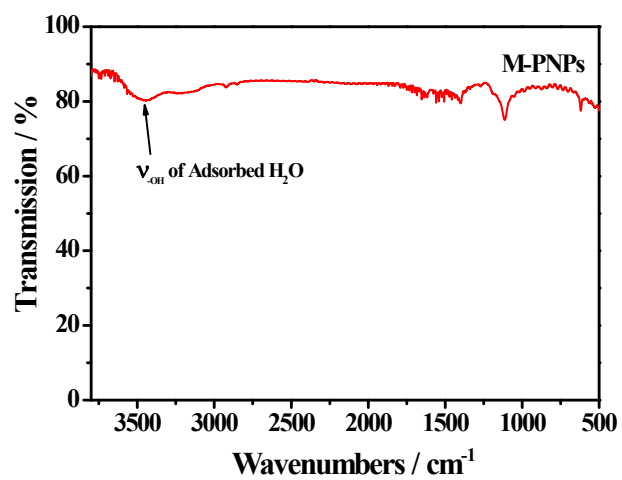
**Fig. S3** (a) BET-Nitrogen adsorption/desorption isotherms of Pt-Cu M-PNPs and (b) BJH adsorption pore distribution of Pt-Cu M-PNPs.



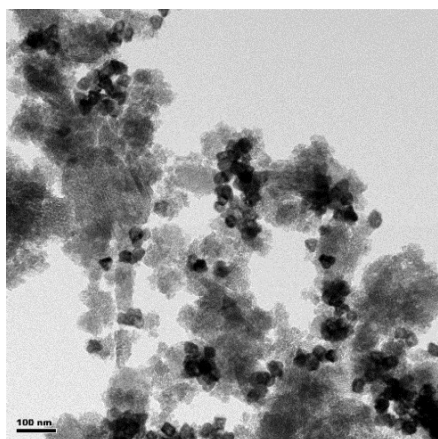
**Fig. S4** Selected-area electron diffractions (SAED) of ultrasmall particles with poor crystallinity produced at initial time during morphologic evolution of Pt-Cu hollow-core structure.



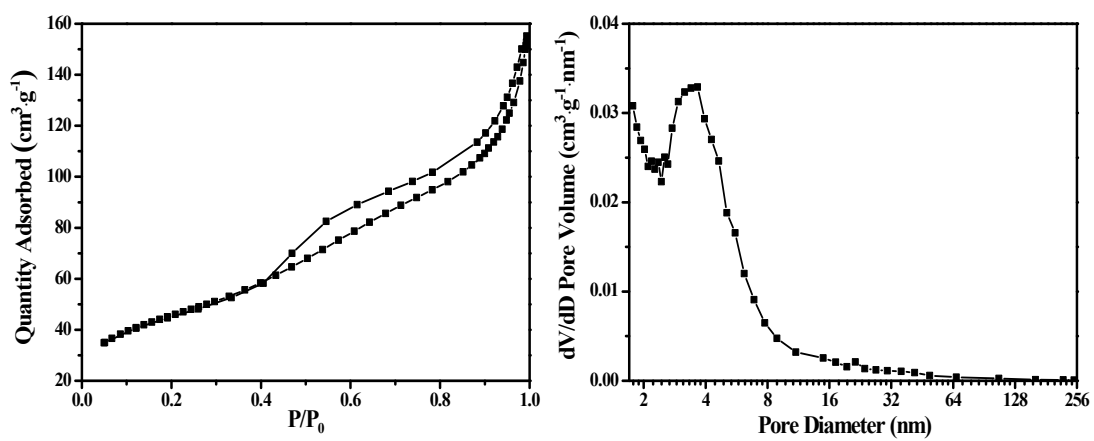
**Fig. S5** TEM image of Pt-Cu nanoparticles without hollow structure.



**Fig. S6** FT-IR spectrum of Pt-Cu M-PNPs.



**Fig. S7** TEM image of Pt-Cu M-PNPs supported on  $\text{Al}_2\text{O}_3$ .



**Fig. S8** (a) BET-Nitrogen adsorption/desorption isotherms of  $\text{Al}_2\text{O}_3$  and (b) BJH adsorption pore distribution of  $\text{Al}_2\text{O}_3$ .