

## Supporting Information

# Strong Metal-Support Interaction over PtPdCu/Al<sub>2</sub>O<sub>3</sub> towards Hydrogenation of Nitrobenzene

*Fagui Lu<sup>a</sup>, Song Zhou<sup>c, d</sup>, Siqian Li<sup>a</sup>, Haoyu Jiang<sup>a</sup>, Bowen He<sup>a</sup>, Jizhen Qi<sup>e</sup>, Yixiao Zhang<sup>a</sup>, Xi Liu<sup>a</sup>,  
Jian Xu<sup>c</sup>, Yongwang Li<sup>c</sup>, Xi Liu<sup>a\*</sup>, Liwei Chen<sup>a, b, e\*</sup>*

<sup>a</sup> School of Chemistry and Chemical Engineering, In-situ Center for Physical Sciences, Shanghai Jiao Tong University, Shanghai 200240, P.R. China

<sup>b</sup> School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, Shanghai 200240, P.R. China

<sup>c</sup> SynCat@Beijing Synfuels China Technology Co. Ltd., Beijing 101407, P.R. China

<sup>d</sup> School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, P.R. China

<sup>e</sup> i-Lab, CAS Center for Excellence in Nanoscience Suzhou Institute of Nano-Tech and Nano-Bionics (SINANO), Chinese Academy of Sciences, Suzhou 215123, P.R. China

\* Corresponding authors (E-mails: liuxi@sjtu.edu.cn (Xi Liu); lwchen2018@sjtu.edu.cn (Liwei Chen))

## Chemicals

Pt(acetylacetonate)<sub>2</sub> (98%) was got from J&K Chemical Ltd. Anhydrous alcohol (AR), poly(ethylene glycol) (AR), and cyclohexane (AR) were all purchased from General-Reagent. Toluene (AR), AlCl<sub>3</sub> (AR), and tween-60 (CP) were all bought from Sinopharm Chemical Reagent Co., Ltd. Oleylamine (RG) and poly(vinyl pyrrolidone) (PVP, average MW = 40000) were procured from Adamas-Beta. Cu(acetylacetonate)<sub>2</sub> (97%), nitrobenzene (AR), and N, N-dimethylformamide (DMF, GC) were all purchased from Aladdin Industrial Co., Ltd. Pd(acetylacetonate)<sub>2</sub> (Pd, 34.9%) and benzoic acid (99%) were supplied by Macklin. NH<sub>4</sub>HCO<sub>3</sub> (99%) was obtained from Energy-Chemical. All the chemicals were used as obtained without further purification.

## Synthesis of PtPdCu-PVP Nanoparticles

To prepare the PtPdCu nanoparticles, 6.7 mg Pt(acetylacetonate)<sub>2</sub>, 5.1 mg Pd(acetylacetonate)<sub>2</sub>, 4.5 mg Cu(acetylacetonate)<sub>2</sub>, 80 mg benzoic acid, and 100 mg PVP were dissolved in 10 mL DMF with constant stirring and sonication until the mixture became transparent. The resulting homogeneous solution was transferred to a Teflon-lined stainless-steel autoclave and then heated at 160 °C in the oven. After 12 h, the reaction solution was cooled to room temperature. The black precipitates were obtained by high-speed centrifugation and washed three times with anhydrous ethanol. The resulting precipitates were dispersed in 10 mL ethanol for further experiments. The as-synthesized nanoparticles were denoted as PtPdCu-PVP. For the syntheses of Pt, Pd, Cu, PtPd,

PtPdCu<sub>2</sub>, and PtPdCu<sub>5</sub> nanoparticles, all the conditions were similar to those of PtPdCu-PVP, except for changing the amounts of Pt(acetylacetonate)<sub>2</sub>, Pd(acetylacetonate)<sub>2</sub>, and Cu(acetylacetonate)<sub>2</sub>. The total metal precursors were kept to 0.05 mmol.

### **Synthesis of PtPdCu-OAm Nanoparticles**

The PtPdCu-PVP ethanol suspension was transferred into a 50 mL round bottom flask and then 10 mL ethanol, 5 mL oleylamine, and 8 mL toluene were added into it. The mixture was sonicated for 15 min before it was refluxed at 70 °C for 8 h. The oleylamine-capped PtPdCu nanoparticles were obtained by centrifugation at 12000 rpm for 15 min and subsequently purified by the ethanol-cyclohexane (1:1) mixture for 3 times. The oleylamine-capped PtPdCu nanoparticles were denoted as PtPdCu-OAm. The obtained PtPdCu-OAm nanoparticles were dispersed in 10 mL cyclohexane for further experiments.

### **Synthesis of PtPdCu/Al<sub>2</sub>O<sub>3</sub> catalysts**

Firstly, the support of Al<sub>2</sub>O<sub>3</sub> was synthesized by precipitation method. 5 mL poly(ethylene glycol) was added into 0.5 M AlCl<sub>3</sub> aqueous solution and then stirred for 30 min. The NH<sub>4</sub>HCO<sub>3</sub> aqueous solution (0.5 M) was slowly added into the AlCl<sub>3</sub> solution under vigorous stirring until the pH of the mixture reached 8. The suspension was stirred again for 2 h, then centrifuged and washed with water and ethanol. 5 mL tween-60 and 30 mL anhydrous alcohol were added into the precipitate and further homodispersed by sonication. The sample was dried at 80 °C for 12 h and then calcined at 500 °C for 4 h.

8.20 mL PtPdCu-OAm cyclohexane suspension and 20 mL cyclohexane were added into a 50 mL round bottom flask. In order to obtain homodispersed nanoparticles, PtPdCu-OAm cyclohexane solution was sonicated for 15 min. Then 0.5 g Al<sub>2</sub>O<sub>3</sub> was added to the PtPdCu-OAm cyclohexane suspension under magnetically stirring. After continuous stirring for 12 h, the solvent

was completely removed by evaporation at 70 °C under vacuum using a rotary pump. The sample was again dried in air at 80 °C for 12 h. The calculated metal loading was fixed 1.0 wt%. The samples of PtPdCu-OAm supported on Al<sub>2</sub>O<sub>3</sub> (PtPdCu-RT) were first heated at 185 °C for 5 h (PtPdCu-185) or 300 °C for 1 h (PtPdCu-300) in the air for removing the organic shell and then treated under H<sub>2</sub> atmosphere at 150 °C for 1 h. The Pt-185, Pd-185, Cu-185, PtPd-185, PtPdCu<sub>2</sub>-185, and PtPdCu<sub>5</sub>-185 catalysts were prepared through a similar process.

### **Materials Characterization**

X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance diffractometer using Cu K $\alpha$  radiation with a scan rate of 5 °/min. Transmission electron microscopy (TEM) images were obtained using JEOL JEM 2100 at 200 kV with a thermionic LaB<sub>6</sub> source. The scan TEM high-angle annular dark-field (STEM-HAADF) and energy-dispersive X-ray spectroscopy (EDS) mapping were acquired with Hitachi HF5000 microscope at 200 kV using a cold field emission gun. The patterns of X-ray photoelectron spectroscopy (XPS) for the samples were all performed on a Kratos Axis Ultra DLD using Mg K $\alpha$  as the excitation source. The X-ray absorption near-edge structure (XANES) were collected using the Sigray QuantumLeap X210. Energy calibration was undertaken by using Pt foil. *In-situ* diffuse reflectance infrared Fourier transform (DRIFT) spectra of CO adsorption were collected on a Spectrum 100 infrared spectrometer with a MCT detector. Before measurement, each catalyst was pretreated at 150 °C under a flowing Ar atmosphere (30 mL/min) for 1 h and then cooled to room temperature in Ar. After the background spectrum was recorded, the gas flow was switched to 5%CO/Ar gas flow (30 mL/min) for the collection of CO adsorption *in-situ* DRIFT spectra.

### **Catalytic reaction**

The liquid-phase hydrogenation of nitrobenzene was carried out in a 50 mL well-stirred autoclave at 100 °C or 50 °C. 50 mg of the prepared catalysts, 30 mL cyclohexane solvent, 2.04 mL (20 mmol) nitrobenzene, and 2.94 mL (13 mmol) dodecane (as internal standard) were transferred into the autoclave, which was flushed with H<sub>2</sub> several times in order to purge any trace of oxygen. The temperature was raised to 100 °C or 50 °C and then the vessel was pressurized to 3 MPa by pumping in H<sub>2</sub>. High stirring speed (600 rpm) was used in order to reduce the mass transfer limitations from the gas to the liquid phase, to increase the rate of reactant transfer from the liquid to the catalyst surface, and to minimize the external diffusion resistance. After the reaction, the resultant mixture was analyzed using gas chromatography (Agilent 7890 B).

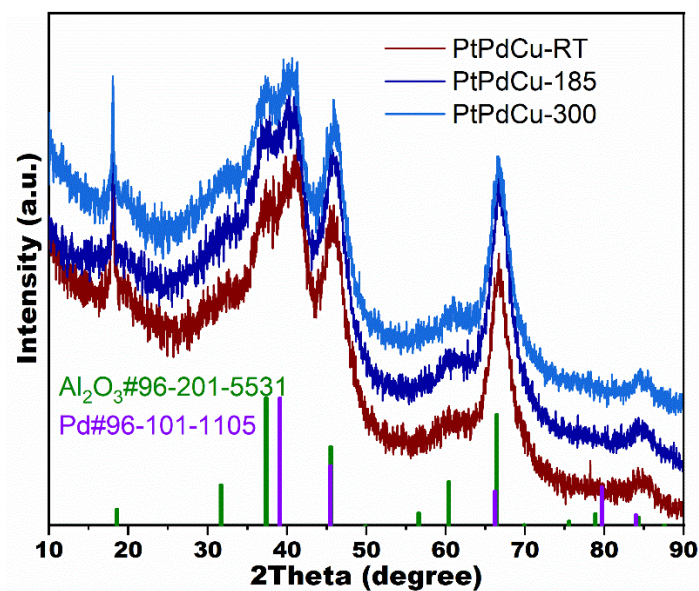
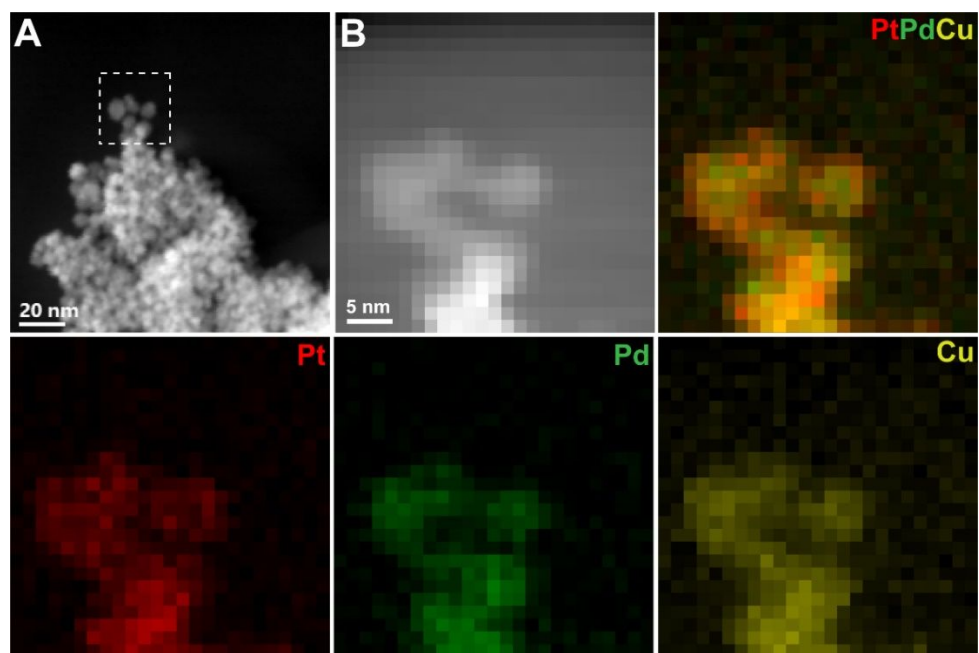
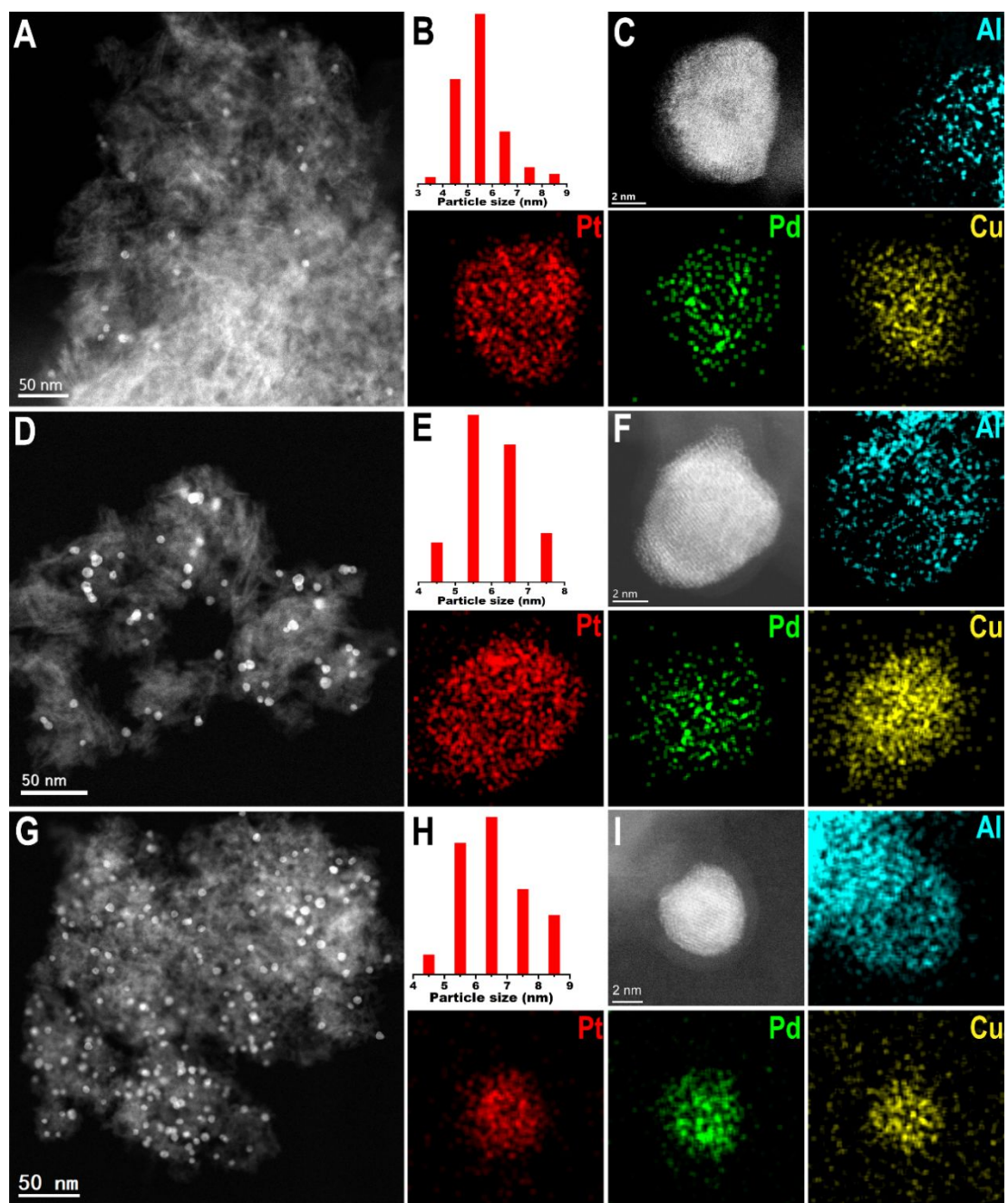


Figure S1. XRD patterns of PtPdCu/Al<sub>2</sub>O<sub>3</sub> catalysts.

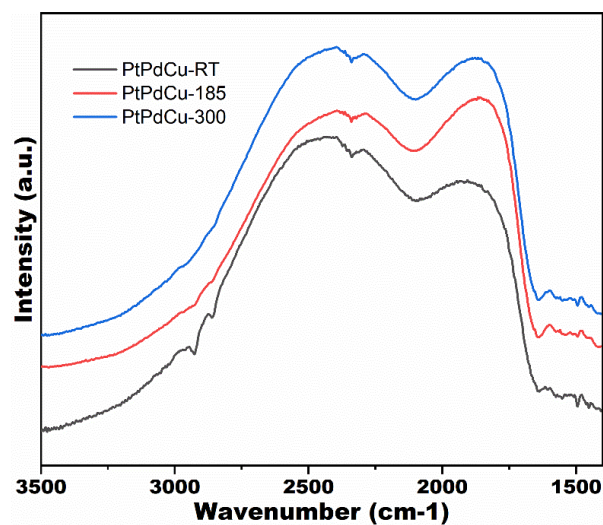


**Figure S2.** STEM-HAADF image (A), STEM-HAADF image and corresponding element map (B) of PtPdCu-PVP.

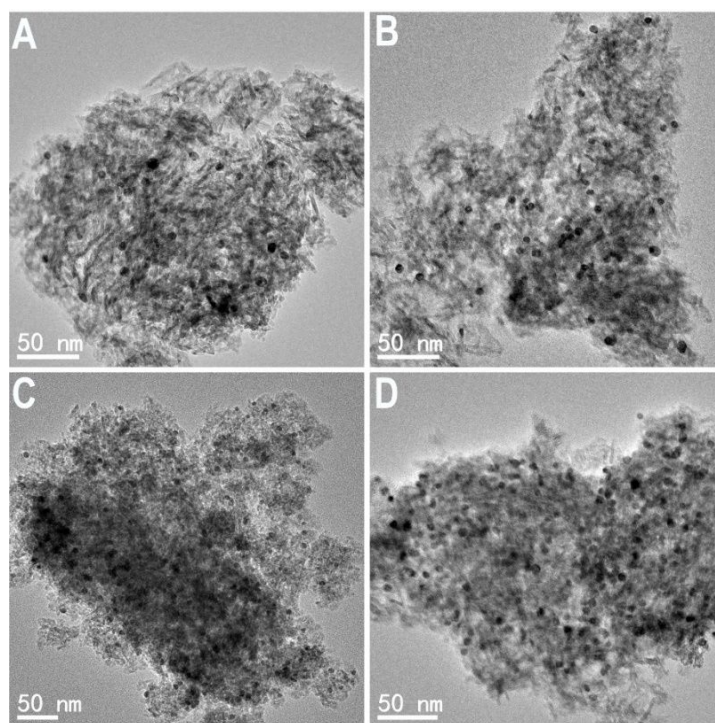


**Figure S3.** STEM-HAADF image (A), particle size distribution (B), STEM-HAADF image and corresponding element map (C) of PtPdCu-RT; STEM-HAADF image (D), particle size distribution (E), STEM-HAADF image and corresponding element map (F) of PtPdCu-185; STEM-HAADF image (G), particle size distribution (H), STEM-HAADF image and corresponding element map (I) of PtPdCu-300.





**Figure S4.** FT-IR spectra of PtPdCu/ $\text{Al}_2\text{O}_3$  before and after thermal treatment. The C-H stretching bands (2800-3000  $\text{cm}^{-1}$ ) are disappeared in the FTIR spectrum for PtPdCu-185 and PtPdCu-300.



**Figure S5.** TEM images of (A) 0.1%, (B) 0.5%, (C) 1.0%, and (D) 2.0% loading PtPdCu-185. The TEM images of PtPdCu-185 with different metal loading show the uniform dispersion of nanoparticles on support, where the distribution density of the PtPdCu nanoparticles is proportional to metal loading.



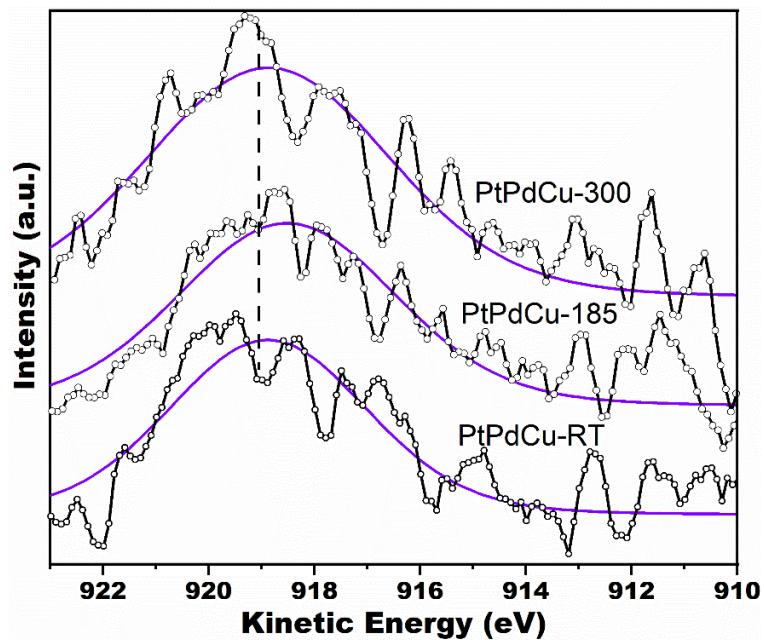


Figure S6. Cu LMM Auger spectra of PtPdCu/Al<sub>2</sub>O<sub>3</sub> catalysts.

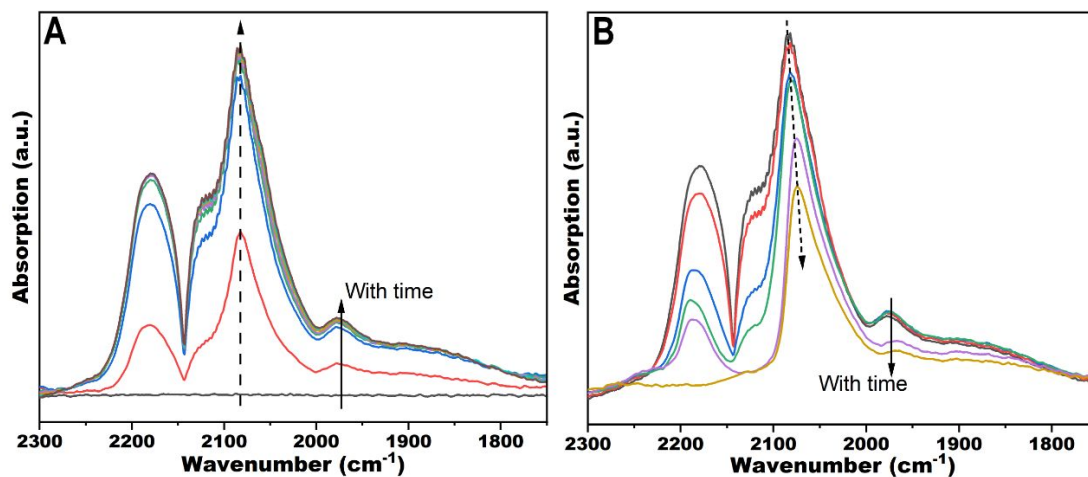
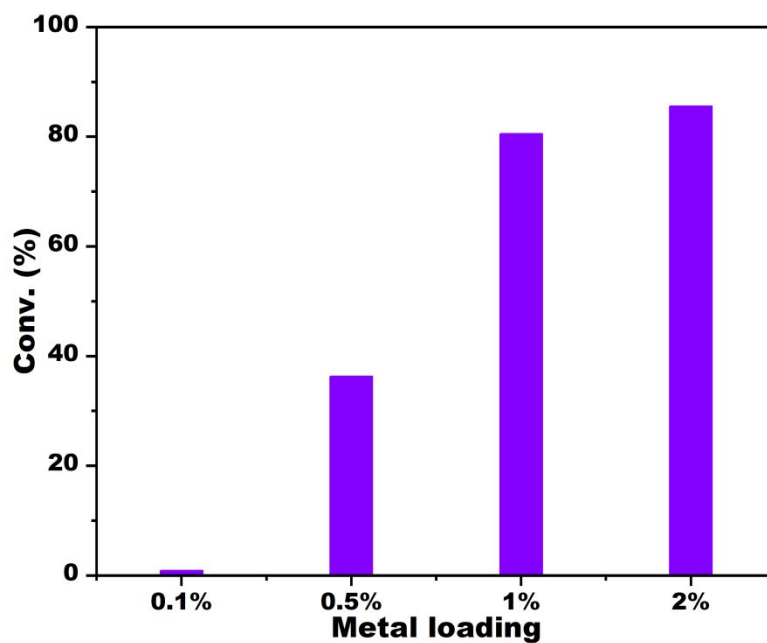
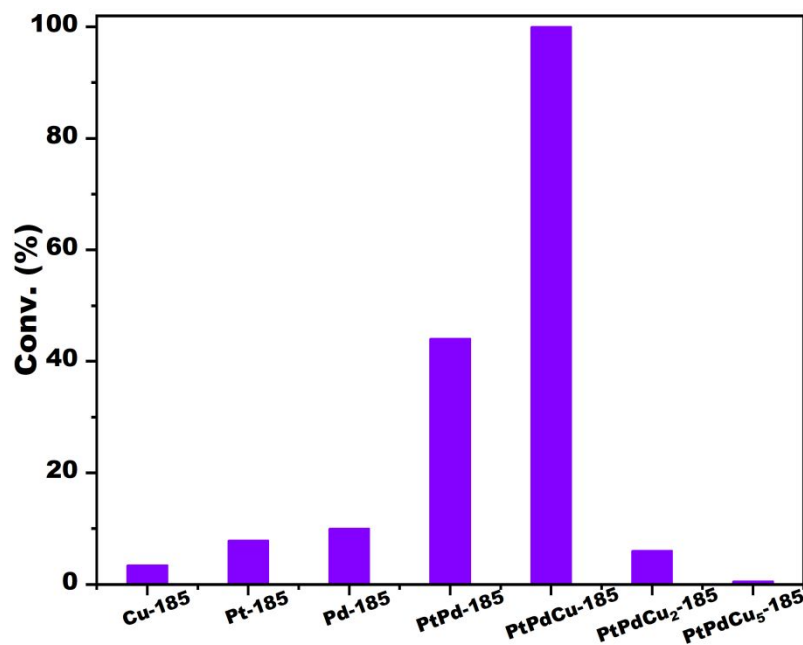


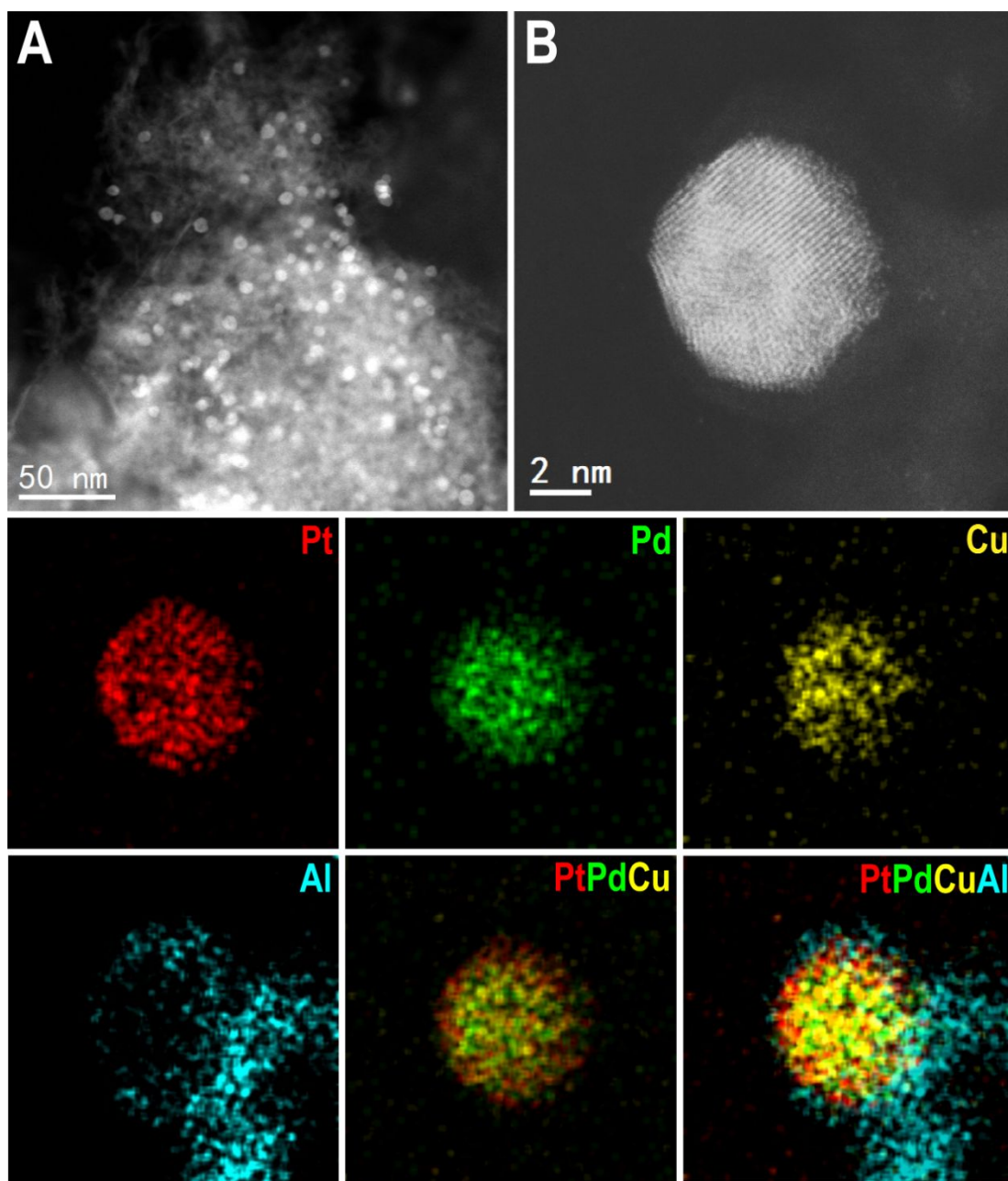
Figure S7. *In-situ* DRIFT spectra of CO adsorption (A) and desorption during an Ar flush (B) on PtPdCu-185.



**Figure S8.** The nitrobenzene conversion over different loading PtPdCu-185. Reaction condition: 50 mg catalyst, 600 rpm, 3 MPa H<sub>2</sub>, 100 °C, 1 h, 30 ml cyclohexane, 20 mmol nitrobenzene.



**Figure S9.** The nitrobenzene conversion over Cu-185, Pt-185, Pd-185, PtPd-185 and PtPdCu<sub>x</sub>-185 (atomic ratio Pt: Pd: Cu = 1:1:1, 1:1:2, 1:1:5) catalysts. Reaction condition: 50 mg catalyst, 600 rpm, 3 MPa H<sub>2</sub>, 100 °C, 2 h, 30 mL cyclohexane, 20 mmol nitrobenzene.



**Figure S10.** STEM-HAADF image (A), STEM-HAADF image and corresponding element map (B) of used PtPdCu-185.