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Supporting Information

For

Deficient Copper Decorated Platinum Nanoparticles for Selective Hydrogenation of Chloronitrobenzene

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Experimental

S1. Preparation of Cu-PVP

1 gram anhydrous CuCl_2 was dissolved in 80 ml purified water (18 Mohm), then 40 ml NaOH aqueous solution (containing 0.65 g NaOH) was added to form blue precipitation $\text{Cu}(\text{OH})_2$, which was washed by water for three times to remove residue salt; Then the washed precipitation was added into 100 ml $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25%) to form dark-blue solution $(\text{Cu}(\text{NH}_3)_4(\text{OH})_2)$. 3.50 g PVP-K30 was dissolved into $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$ aqueous solution and the mixture was dried at 353 K into a black paste. The black paste was added into 50 ml NaBH_4 aqueous solution (containing 3.00 g NaBH_4) under flowing argon gas; after 1 hour reaction time, acetone was added to form precipitate. The precipitate was treated with water and acetone in turn for three times, and further freeze-dried to obtain PVP-Cu.

S2. Preparation of Pt- PVP

1 g PVP-K30 was dissolved in Pt EG colloid solution (56.25 g, 0.32 wt.%), and then acetone was added to form precipitate; then the precipitate was treated with water and acetone in turn for three times, and further freeze-dried to obtain PVP-Pt.

S3. Preparation of Pt -PVP /Cu-PVP

0.18 g PVP-Cu was dispersed in 20 ml EG solution and above PVP-Pt solution was added to form a mixture. After stirring for 2 hours, 10 ml water was added; after 1 hour stirring, acetone was added to form precipitate. The precipitate was treated with water and acetone in turn for three times, and further freeze-dried to obtain PVP-Pt/PVP-Cu.

S4. Preparation of PtCu-PVP (alloy)

0.4 g anhydrous CuCl_2 was dissolved in 30 ml purified water (18 Mohm), then 20 ml NaOH aqueous solution (containing 0.26 g NaOH) was added to form blue precipitation $\text{Cu}(\text{OH})_2$, which was washed by water for three times to remove residue salt; Then the washed precipitation was added into 40 ml $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25%) to form dark-blue solution $(\text{Cu}(\text{NH}_3)_4(\text{OH})_2)$. After 1 g PVP-K30 was dissolved in the $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$ aqueous solution, the Pt/PVP EG solution (56.25 g, containing 0.18 g Pt) was added under stirring. 50 ml NaBH_4 aqueous solution (containing 3.00 g NaBH_4) was

added in to the mixture under flowing argon gas; after 1 hour reaction time, acetone was added to form precipitate. The precipitate was treated with water and acetone in turn for three times, and further freeze-dried to obtain PtCu-PVP.

S5. The ex-situ treatment of the sample in the XPS apparatus

The samples were loaded on the stub and transferred to the ex-situ treatment chamber in the XPS apparatus (ESCALAB 250Xi). After treated by 1 hour flowing argon gas, the samples were further treated by flowing H₂/Ar (5/95) gas at room temperature for 10 hours, then the gas was evacuated and Ar gas was backfilled to remove original gas; further the gas was evacuated in order that the pressure was lower than 1×10^{-5} Torr. Then the samples were transferred to the measurement chamber to execute XPS measurements. The scan numbers for every samples were 20.

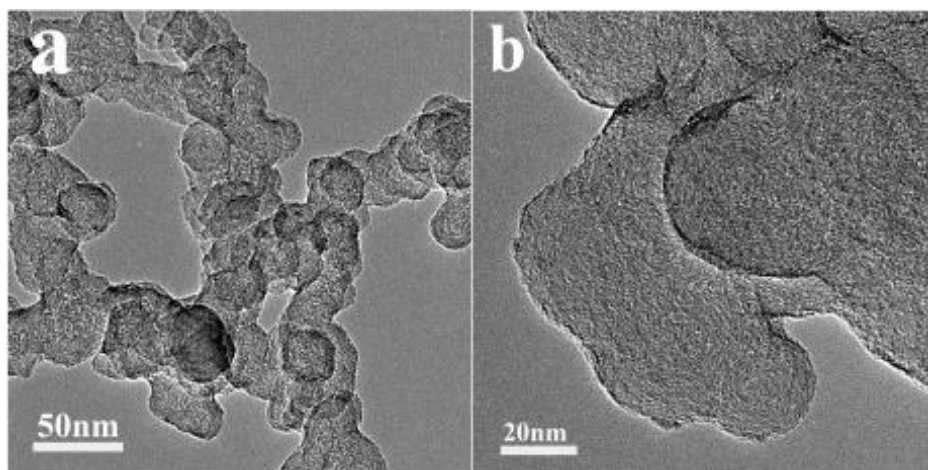


Fig. S1 (a), (b) The TEM images of activated carbon.

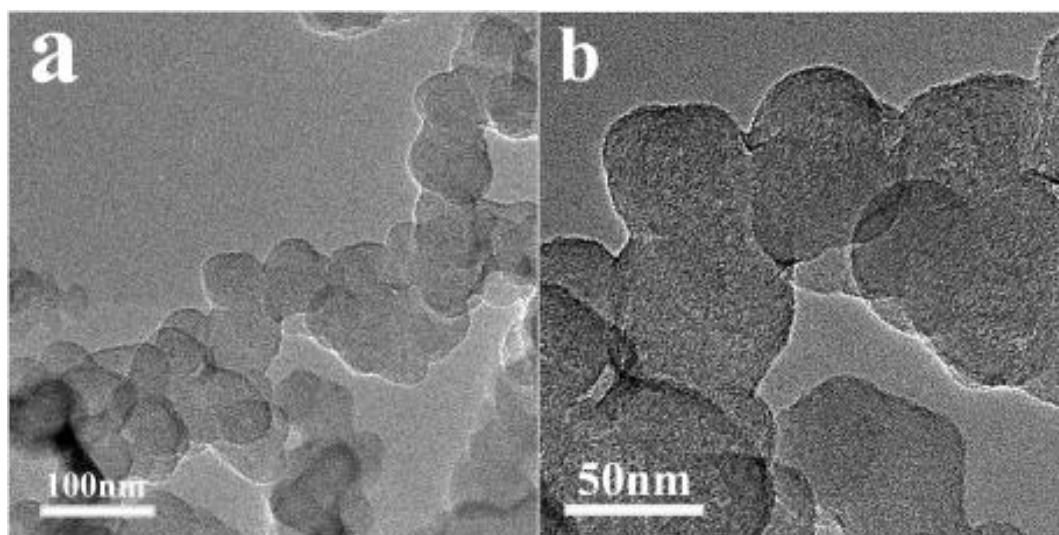


Fig. S2 (a), (b) The TEM images of 5Cu/C.

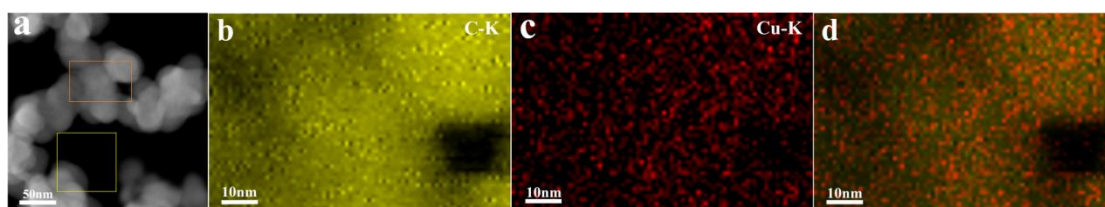


Fig. S3 The STEM images of (a) $\text{Cu}(\text{OH})_2/\text{C}$; the element mapping of (b) carbon, and (c) copper in the orange framework of (a); (d) the combined image of (b) and (c).

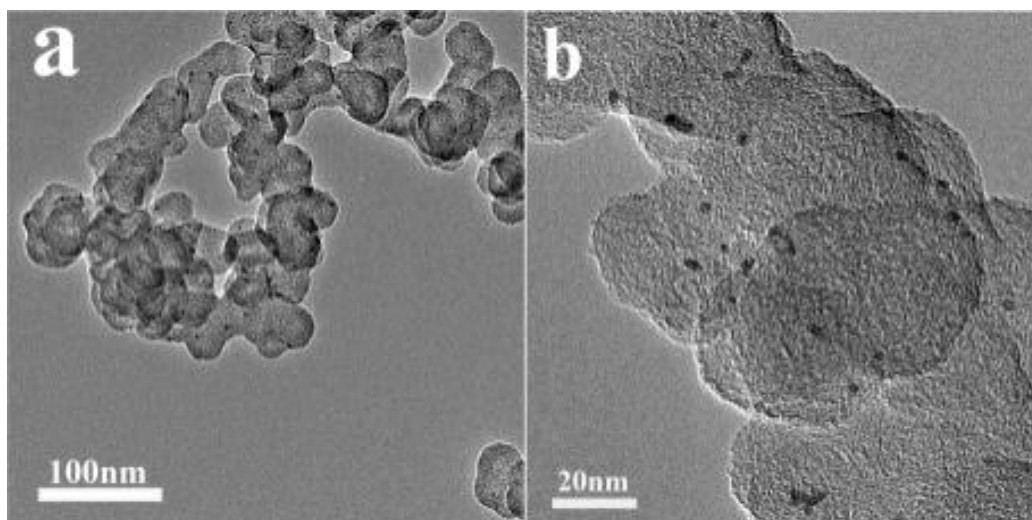


Fig. S4 (a), (b) The TEM images of 2Pt/C.

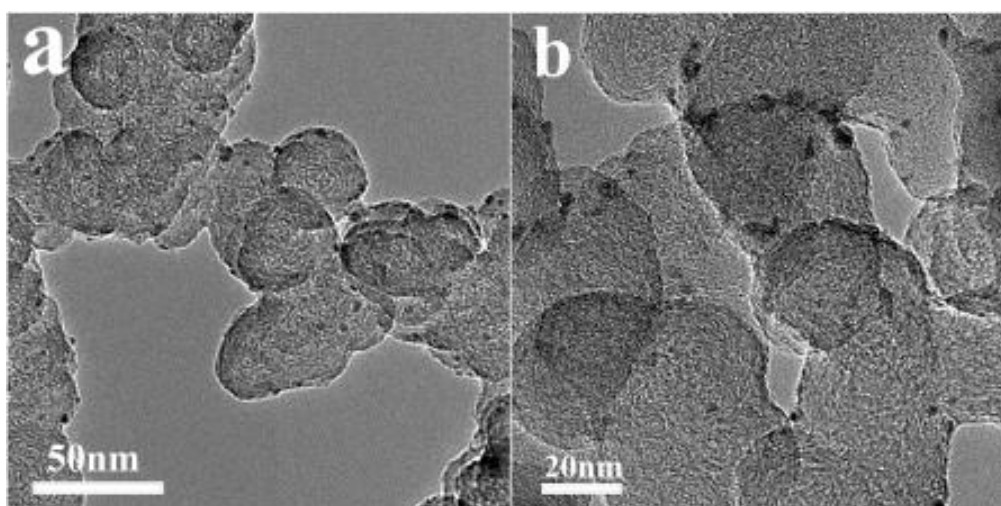


Fig. S5 (a), (b) The TEM images of 5Cu/C-2Pt.

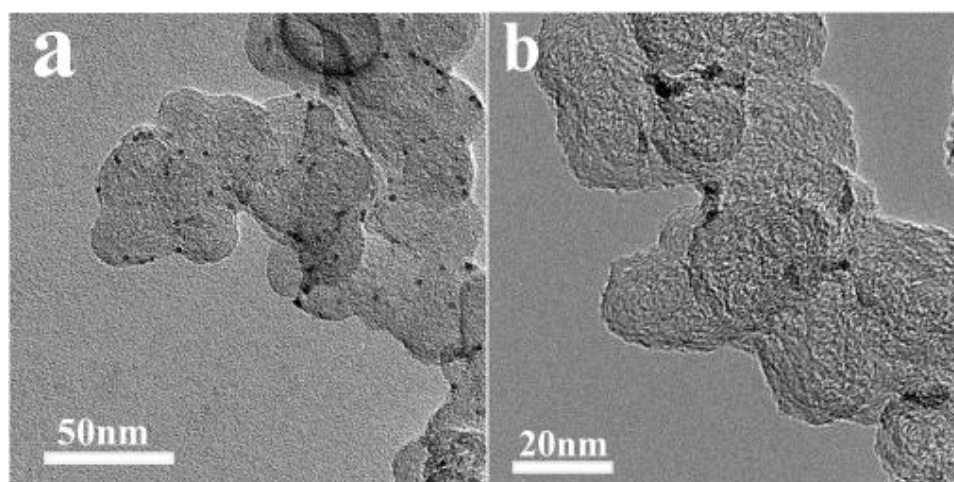


Fig. S6 (a), (b) The TEM images of 2Pt/C-5Cu.

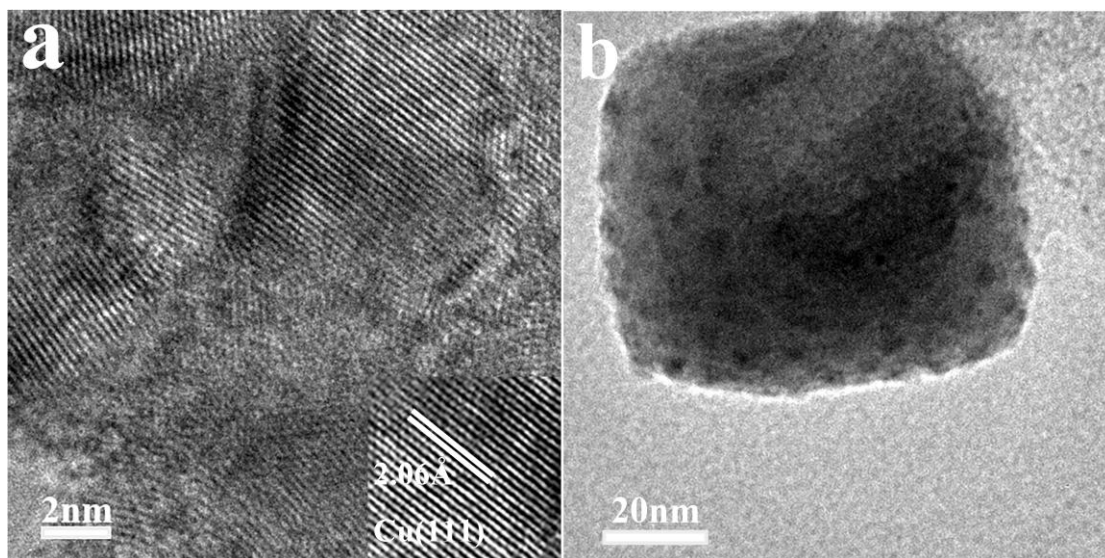


Fig. S7 (a) The HRTEM image of 5Cu/C-2Pt, and the inset is the enlarged figure; (b) The TEM image of Pt nanoparticles decorated Cu nanoparticle.