

## Supporting Information

### **Water-dispersible and magnetically recoverable Fe<sub>3</sub>O<sub>4</sub>/Pd@nitrogen-doped carbon composite catalysts for catalytic reduction of 4-nitrophenol**

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Shanghai 201620

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#### **Experimental**

##### **2.1 Synthesis of Fe<sub>3</sub>O<sub>4</sub>/Pd@nitrogen-doped carbon catalysts**

Fe<sub>3</sub>O<sub>4</sub> microspheres were synthesized using a modified solvothermal method.<sup>1</sup> Small Pd nanoparticles were synthesized according to a reported method using triblock Pluronic copolymer (P123) as the reductant and dispersed in 6.5 ml of distilled water.<sup>2</sup>

In order to functionalize Fe<sub>3</sub>O<sub>4</sub> microspheres with amino groups, 0.5 g of Fe<sub>3</sub>O<sub>4</sub> microspheres was added into a solution containing 90 ml of isopropanol and 0.75 ml of aminopropyltriethoxysilane (APTES) at 80 °C for 2 h under stirring. After washing with isopropanol twice *via* centrifugation and decantation, the resulting -NH<sub>2</sub> functionalized Fe<sub>3</sub>O<sub>4</sub> microspheres were dispersed in 25 ml of distilled water.

Fe<sub>3</sub>O<sub>4</sub>/Pd composite microspheres were prepared by adding 24.5 ml of Pd

nanoparticle suspension into 125 ml of aqueous solution containing 10 ml of  $-NH_2$  functionalized  $Fe_3O_4$  microspheres under sonication due to the presence of strong interactions between amine groups and metal.<sup>3, 4</sup> After 10 min, the black microspheres were collected by a magnet, washed with distilled water and then dispersed in 25 ml of distilled water.

5 mg of dopamine was added into the aqueous solution containing 30 mg of  $Fe_3O_4/Pd$  composite microspheres. Then, the pH of the solution was further adjusted to around 9 using 1 mol/L NaOH aqueous solution and stirred for 12 h. Finally, the  $Fe_3O_4/Pd@polydopamine$  ( $Fe_3O_4/Pd@PDA$ ) composite microspheres were collected by a magnet, washed with ethanol and dried at 100 °C in an oven. The  $Fe_3O_4/Pd@NC$  composite catalysts were obtained after calcining the  $Fe_3O_4/Pd@PDA$  composite microspheres at 500 °C for 1 h with a heating rate of 2 °C/min in  $N_2$  flow.

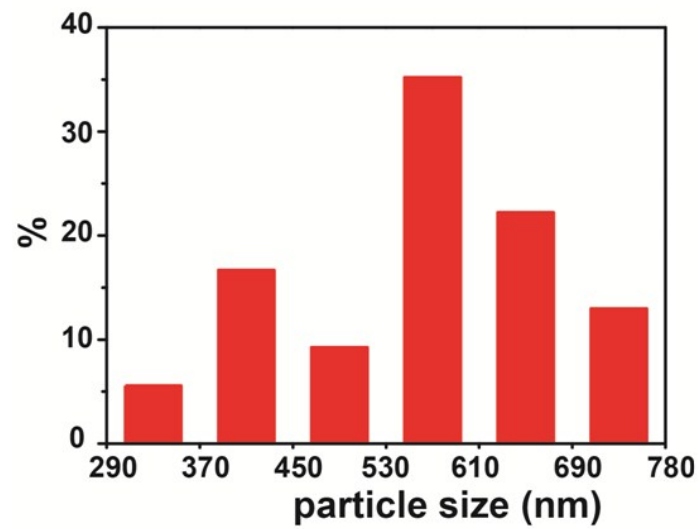
## **2.2 General procedures for catalytic reduction of 4-nitrophenol and its derivatives**

The catalytic reduction reactions were carried out in a quartz cell with a 1 cm path length at room temperature and monitored by Shimadzu UV-1800 UV-Vis spectrophotometer. An aqueous solution containing 1 mL of 0.05 mol/L  $NaBH_4$  solution and 2 mL of  $5 \times 10^{-5}$  mol/L 4-nitrophenol or its derivatives solution was added into the quartz cell. Then, 0.5 ml of 115 mg/L catalyst suspension was rapidly added into the solution and the absorption spectra were recorded immediately. The intensity change of the absorption peak at 400 nm was used to track the conversion process of

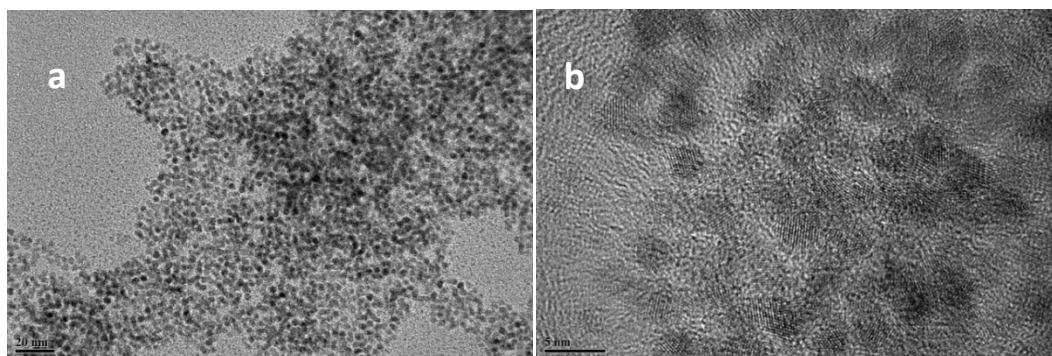
4-nitrophenol to 4-aminophenol. In a control experiment, the catalytic performances of commercial 5 wt% Pd/C catalysts (Sinopharm Chemical Reagent Com., Ltd) was tested following the procedure described above. The Pd molar concentration of both Fe<sub>3</sub>O<sub>4</sub>/Pd@NC and commercial Pd/C catalysts in reaction solution was kept the same in all experiment conditions. In order to evaluate the catalytic stability of catalysts, another 45 μL of 2.28×10<sup>-3</sup> mol/L 4-nitrophenol and 45 μL of 1.1 mol/L NaBH<sub>4</sub> were added to the reaction solution after each cycle of reaction.

### **2.3 Characterization**

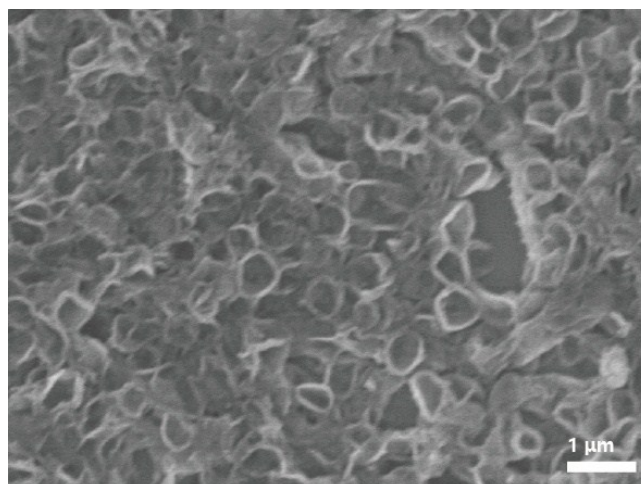
SEM and TEM images were taken on a Hitachi S-4800 scanning electron microscopy and a JEOL JEM-2100F high-resolution transmission electron microscopy, respectively. The Pd and Fe<sub>3</sub>O<sub>4</sub> contents were quantitatively analyzed by inductively coupled plasma optical emission spectrometer (Prodigy ICP-OES). Powder XRD pattern was collected on a Rigaku D/Max-2550PC X-ray diffractometer with Cu Kα radiation. The magnetic properties of four samples were evaluated by a vibrating sample magnetometer (VSM) at 300 K.



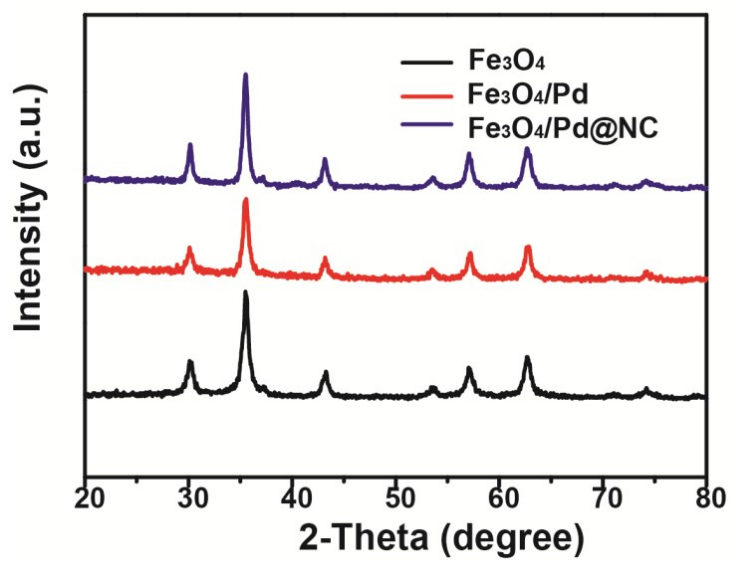
**Fig. S1** Particle size distribution of  $\text{Fe}_3\text{O}_4$  microspheres.



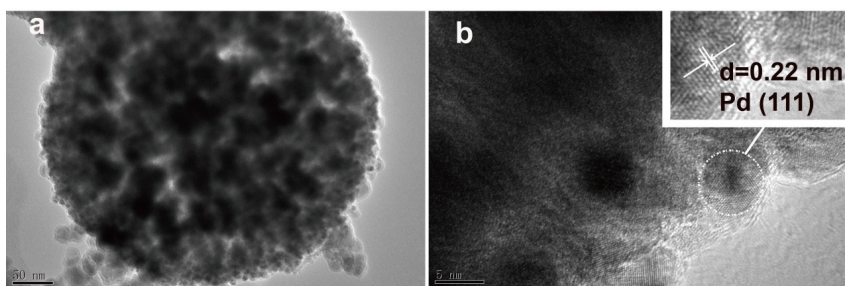
**Fig. S2** (a) TEM and (b) high-resolution TEM images of Pd nanoparticles.



**Fig. S3** SEM image of the Fe<sub>3</sub>O<sub>4</sub>/Pd@NC catalysts after reacting with HCl.



**Fig. S4** XRD patterns of the Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>/Pd and Fe<sub>3</sub>O<sub>4</sub>/Pd@NC composite microspheres.



**Fig. S5** (a and b) TEM images of  $\text{Fe}_3\text{O}_4/\text{Pd}@\text{NC}$  catalysts after six cycles. The inset in (b) is the high-resolution TEM image of Pd nanoparticles.

## Reference

1. Y. H. Deng, C. H. Deng, D. W. Qi, C. Liu, J. Liu, X. M. Zhang and D. Y. Zhao, *Adv. Mater.* 2009, **21**, 1377-1382.
2. Y. Z. Piao, Y. J. Jang, M. Shokouhimehr, I. S. Lee and T. Hyeon, *Small*, 2007, **3**, 255-260.
3. J. N. James, J. W. Han and D. S. Sholl, *Appl. Surf. Sci.*, 2014, **301**, 199-207.
4. Y. Huang, Z. Zheng, T. Liu, J. Lü, Z. Lin, H. Li and R. Cao, *Catal. Commun.*, 2011, **14**, 27-31.