

# Supporting Information

## Facile Synthesis of Ag@Pd Satellites-Fe<sub>3</sub>O<sub>4</sub> Core Nanocomposite as Efficient and Reusable Hydrogenation Catalysts

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## Experimental Section

### *Synthesis of Fe<sub>3</sub>O<sub>4</sub>-NH<sub>2</sub> MNPs*

The magnetic Fe<sub>3</sub>O<sub>4</sub> nanoclusters were prepared through a modified hydrothermal reaction<sup>1</sup> in a 3-neck flask. Typically, 2.12 g of FeCl<sub>3</sub>·6H<sub>2</sub>O, 8.0 g of sodium acetate and 8.5 mL of 1,6-hexadiazine were mixed in 60 ml of ethylene glycol (EG) with mechanical stirring at 700 rpm for 0.5 h at 50 °C. Then the obtained homogeneous dark orange solution was further heated to 180 °C and kept for another 14 h at 300 rpm. After this hydrothermal treatment process, the product was magnetically separated and washed successively with acetone, ultra pure water and ethanol separately for 3 times. Finally, the nanoclusters were transferred and dispersed into 40 mL of ethanol for storage.

### *Synthesis of PVP stabilized Ag@Pd NPs*

The core@shell structure nanocomposite was prepared through a successive sequential reduction.<sup>2</sup> Briefly, 5 mg of AgNO<sub>3</sub>, 48 mg of PVP was dissolved in 6 mL of EG, with N<sub>2</sub> bubbling for 0.5 h. Then the solution was slowly heated to 120 °C under N<sub>2</sub> atmosphere and kept for another 0.5 h. Once this clear yellow solution cooled to ambient temperature, it was mixed with 6 mL of a EG solution of PdCl<sub>2</sub> (containing 7.5 mg of PdCl<sub>2</sub>, 48 mg of PVP) and heated to 90 °C for 2 h under N<sub>2</sub> atmosphere. Once the synthesis was finished, the colloidal solution was cooled to ambient temperature for further usage.

### *Synthesis of PVP stabilized Pd and Ag-Pd alloy NPs*

The Pd and Ag-Pd alloy NPs were synthesized with the same procedure for preparing the Ag@Pd NPs, except for the different temperature control. Briefly, for the Pd NPs, 7.5 mg of PdCl<sub>2</sub> was mixed together with 48 mg of PVP in 6 mL of EG under N<sub>2</sub> bubbling for 0.5 h. Then the mixture was slowly heated to 120 °C under N<sub>2</sub> atmosphere and kept for 2 h. For the Ag-Pd alloy NPs, 5 mg of AgNO<sub>3</sub>, 7.5 mg of PdCl<sub>2</sub> and 96 mg of PVP was mixed in 12 mL of EG, with N<sub>2</sub> bubbling for 0.5 h. The reaction solution was slowly heated to 160 °C under N<sub>2</sub> atmosphere and kept for another 2 h. Once the synthesis was finished, the colloidal solution was cooled to ambient temperature for further usage.

### *Synthesis of Ag@Pd/Fe<sub>3</sub>O<sub>4</sub> nanocomposites*

Generally, to synthesize the Ag@Pd/Fe<sub>3</sub>O<sub>4</sub> nanocomposite, 4 ml of the as prepared Fe<sub>3</sub>O<sub>4</sub> suspension (ultrasonication for 15 min each time before use) was added into 50 mL of water. Then certain amount of the as-prepared Ag@Pd colloidal solution (depended on the different target metal loading) was added dropwisely under the ultrasonication and kept for 10 min. Afterwards the mixture was mechanically stirred for 20 h at 30 °C. The product was magnetically separated and washed successively with water and ethanol for 3 times, and stored in 4 mL of ethanol.

The synthesis of Ag-Pd alloy/Fe<sub>3</sub>O<sub>4</sub> and Pd/Fe<sub>3</sub>O<sub>4</sub> nanocomposite was achieved in the same procedure. Notably, with this method, different amounts of metal loadings can be realized by different ratios of Fe<sub>3</sub>O<sub>4</sub> suspension and colloidal solution.

### *Catalytic reduction of 4-NP over Ag@Pd/Fe<sub>3</sub>O<sub>4</sub> nanocomposite*

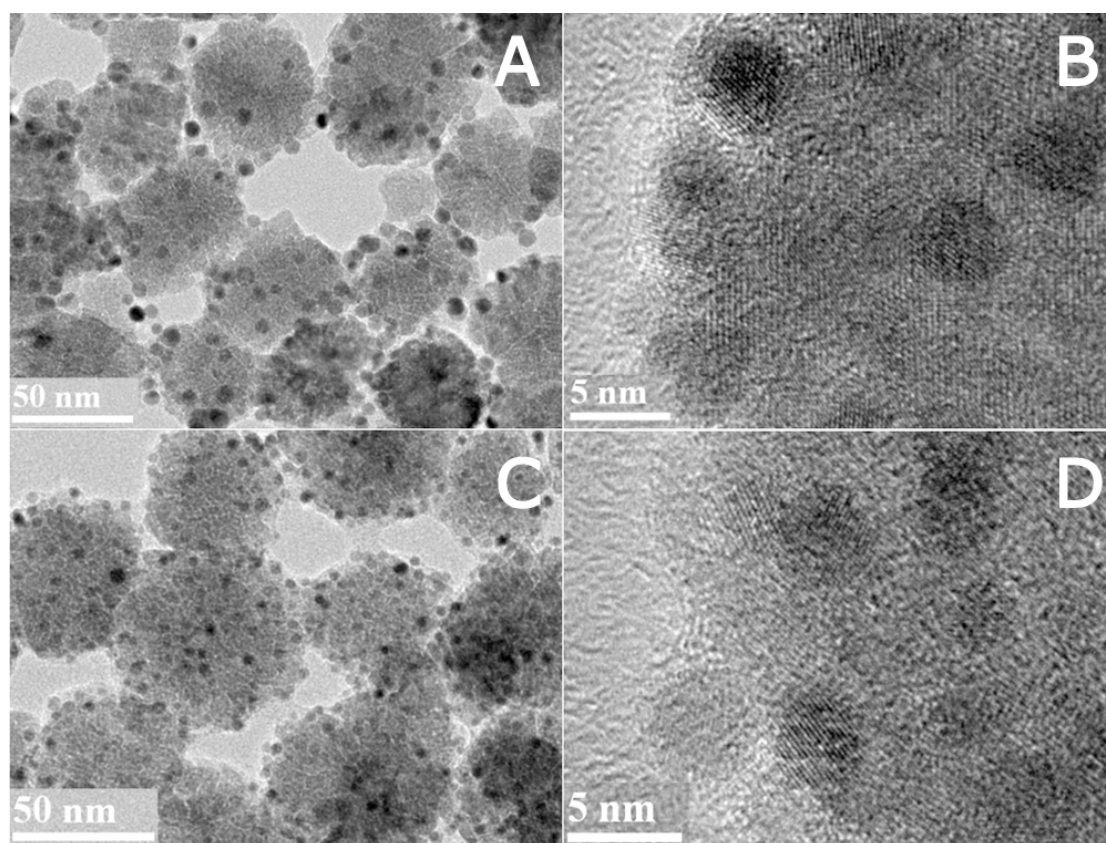
Firstly, 15.4 ppm of 4-NP solution with pH ~ 12 was prepared as the stock solution for further measurements. Then 20 µL of Ag@Pd/Fe<sub>3</sub>O<sub>4</sub> suspension (ultrasonication before use) was added to 2.6 mL of the stock solution, followed by the addition of 0.4 mL of 0.1 M NaBH<sub>4</sub>. After 10 s, an external magnetic field (Nd-Fe-B permanent magnet) was applied for 5 s to separate the magnetic catalyst and the upper solution was transferred to a quartz cuvette for UV-vis measurement. Once a spectrum was recorded, the solution was immediately transferred back to the previous bottle and shaken for another 10 s for the sequential catalysis reaction. This procedure was repeated during the UV-vis measurement. The catalytic reduction of 4-NP over Ag-Pd/Fe<sub>3</sub>O<sub>4</sub> nanocomposite was conducted with the same procedure except for different intervals. Control experiment to check the physical adsorption effect was carried out with the above same procedure except that 0.4 mL of H<sub>2</sub>O was added instead of 0.4 mL of NaBH<sub>4</sub> solution.

For the recycling tests, 50 µL of catalyst suspension was used to examine the reusability. After each cycle the catalyst was washed with water and then magnetically separated for the next cycle of test.

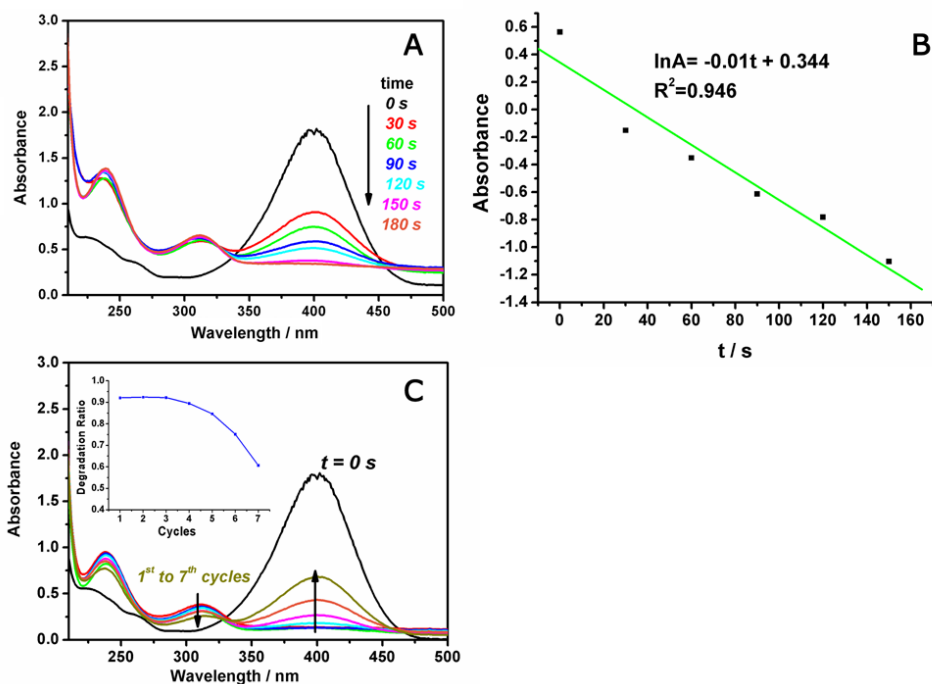
### *Characterization*

The UV-vis measurement was conducted with the Agilent 8453 UV-vis spectrometer. The compositions of the Ag@Pd/Fe<sub>3</sub>O<sub>4</sub> catalysts were analyzed by inductively coupled plasma-atomic

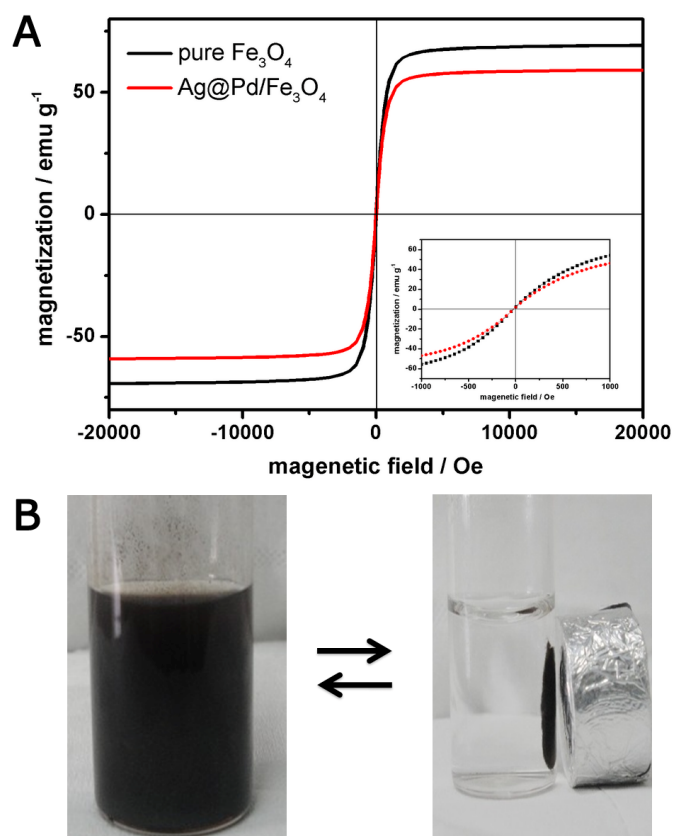
emission spectroscopy (ICP-AES) on a Thermo Elemental IRIS Intrepid. The crystalline structures were determined by X-ray diffraction (XRD) on a D8 Advance and Davinci.Design X-ray diffractometer with Cu K $\alpha$  radiation from 20° to 80°, and the particle sizes and dispersions were characterized by transmission electron microscopy (TEM) on a JEOL JEM-2010 microscope. Magnetic characterization was carried out by magnetometry at 300 K using a MPMS (SQUID) Quantum Design VSM superconducting quantum interference device (SQUID).



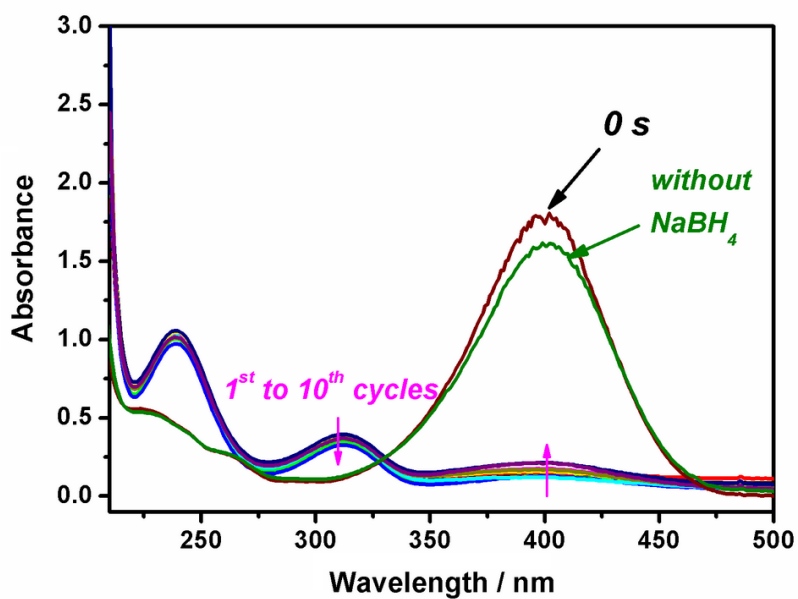
**Fig S1.** TEM and HRTEM images of the Ag-Pd alloy/Fe<sub>3</sub>O<sub>4</sub> (A, B) and Pd/Fe<sub>3</sub>O<sub>4</sub> nanocomposite (C, D), respectively.



**Fig. S2** (A) UV-Vis absorption spectra of the catalytic reduction of 4-NP over Ag-Pd alloy/ $\text{Fe}_3\text{O}_4$  nanocomposite; (B) variation of absorbance with time for the 400 nm band ascribed to 4-NP and the fit of the data to a first order kinetics; (C) UV-Vis spectra of the recycling performance of 4-NP reduction over magnetic Pd/ $\text{Fe}_3\text{O}_4$  catalyst, the spectra was acquired after hydrogenation for 60 s from 1<sup>st</sup> to 7<sup>th</sup> cycles.



**Fig. S3** (A) The hysteresis loops at 300 K of Fe<sub>3</sub>O<sub>4</sub>-NH<sub>2</sub> nanoclusters and Ag@Pd/Fe<sub>3</sub>O<sub>4</sub> nanocomposite, (B) photograph of a ethanol solution of Ag@Pd/Fe<sub>3</sub>O<sub>4</sub> nanocomposite in the absence (left) and presence (right) of a magnet.



**Fig. S4** UV-Vis spectra of the physical adsorption and recycling performance of 4-NP reduction over magnetic Ag@Pd/Fe<sub>3</sub>O<sub>4</sub> catalyst, the spectra was acquired after physical adsorption or hydrogenation for 120 s from 1<sup>st</sup> to 10<sup>th</sup> cycles.



**Table S1** The absorbance at 400 nm and the corresponding conversion ratio (C.R.) obtained from Fig. S4

	NPs Only	1 <sup>st</sup> cycle	2 <sup>nd</sup> cycle	3 <sup>rd</sup> cycle	4 <sup>th</sup> cycle	5 <sup>th</sup> cycle
<b>A<sub>400 nm</sub></b>	1.471	0.128	0.150	0.126	0.125	0.118
<b>C.R.</b>	7.5%	92.6%	91.2%	92.6%	92.6%	93.2%

	6 <sup>th</sup> cycle	7 <sup>th</sup> cycle	8 <sup>th</sup> cycle	9 <sup>th</sup> cycle	10 <sup>th</sup> cycle
<b>A<sub>400 nm</sub></b>	0.173	0.157	0.168	0.212	0.210
<b>C.R.</b>	90.1%	90.1%	90.4%	87.8%	88.1%

## References

1. L. Y. Wang, J. Bao, L. Wang, F. Zhang and Y. D. Li, *Chem-eur J*, 2006, **12**, 6341-6347.
2. K. Tedsree, T. Li, S. Jones, C. W. A. Chan, K. M. K. Yu, P. A. J. Bagot, E. A. Marquis, G. D. W. Smith and S. C. E. Tsang, *Nat Nanotechnol*, 2011, **6**, 302-307.