Electronic Supplementary Information

Fabrication of magnetic bimetallic Fe₃O₄@Au–Pd hybrid nanoparticles with recyclable and efficient catalytic properties

Qingdong Xia, Shanshan Fu, Guojuan Ren, Fang Chai, * Jingjie Jiang * and Fengyu Qu *

Key Laboratory of Design and Synthesis of Functional Materials and Green Catalysis, Colleges of Heilongjiang Province, College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150025, P. R. China. E-mail: fangchai@gmail.com, jiangjingjie80@163.com, qufengyuchem@hrbnu.edu.cn



Fig. S1 EDS spectrum analysis of Fe₃O₄@Pd NPs.



Fig. S2 TEM images of Fe₃O₄@Au nanoseeds.



Fig. S3 The size distribution of Au NPs of (a) Fe₃O₄@Au nanoseeds and (b) Au-Pd NPs of Fe₃O₄@Au-Pd NPs.



Fig. S4 SEM images of Fe₃O₄ hollow spheres.

Specific surface areas of the samples were determined using N_2 adsorption–desorption isotherms at 77 k (Micromeri–tics TriStar II 3020) with the Brunauer–Emmett–Teller (BET) method. Fig. S5 shows the nitrogen adsorption desorption isotherms.



Fig. S5 N₂ adsorption/desorption isotherm of (a) Fe₃O₄ hollow spheres, (b) Fe₃O₄@Pd NPs, (c) Fe₃O₄@Au-Pd NPs.



Fig. S6 The UV-vis characteristic peaks of freshly prepared 4-nitrophenol and 4-nitrophenolate ion aqueous solution at 317 and 400 nm, respectively.



Fig. S7 (a) Absorption spectra of aqueous mixture solutions of 4-NP and NaBH₄ at different concentrations of 4-NP. (b) Plot of the peak absorbance against the concentration of 4-NP.

Table S1 Rates of reaction and turnover frequencies (TOF)^a for the reduction of 4-NP by catalyst. ^a The TOF is defined as the moles of reduced 4-NP molecules per mole of the surface noble metal atoms per second.

Catalyst	Туре	Rate constant (s ⁻¹)	TOF ^a (s ⁻¹)	References
Fe ₃ O ₄ @Au-Pd NPs	Supported	28.90 3 10 ⁻³	8.78 3 10-2	This work
Fe ₃ O ₄ @Pd NPs	Supported	14.50 ¢ 10 ⁻³	3.28 ¢ 10 ⁻²	This work
Au-Pd carbon spheres	Nanocomposites	14.60 3 10 ⁻³	3.37 ¢ 10 ⁻³	1
Fe _x O _y /Pd@mSiO ₂	yolk-shell	1.60 \$ 10-3	2.19 1 0-3	2
Pd/Fe ₃ O ₄ /polypyrrol	hollow capsules	2.03 ¢ 10 ⁻³	1.47 ¢ 10 ⁻²	3
Pd@Au CSNTPs	core-shell	2.31 \$ 10-3	2.46 ¢ 10 ⁻²	4
PdAu/Fe ₃ O ₄	nanocomposites	5.47 ¢ 10 ⁻³	4.91 ¢ 10 ⁻²	5
Fe ₃ O ₄ @SiO ₂ @CeO ₂ @Au-Pd	nanocomposites	4.0 ¢ 10 ⁻³	5.69 3 10-2	6

References:

- 1. S. C. Tang, S. Vongehr, G. R. He, L. Chen and X. K. Meng, J. Colloid. Interf. Sci., 2012, 375, 125–133.
- 2. T. J. Yao, T. Y. Cui, X. Fang, F. Cui and J. Wu, Nanoscale, 2013, 5, 5896–5904.
- T. J. Yao, Q. Zuo, H. Wang, J. Wu, B. F. Xin, F. Cui and T. Y. Cui, J. Colloid. Interf. Sci., 2015, 450 366–373.
- 4 R. P. Zhao, M. X. Gong, H. M. Zhu, Y. Chen, Y. W. Tang and T. H. Lu, *Nanoscale*, 2014, 6, 9273–9278.
- 5 Y. Tuo, G. F. Liu, B. Dong, J. T. Zhou, A. J.Wang, J. Wang, R. F. Jin, H. Lv, Z. Dou and W. Y. Huang, *Sci. Rep-UK.*, DO i: 10.1038/srep13515.
- 6 Q. Wang, W. J. Jia, B. C. Liu, A. Dong, X. Gong, C. Y. Li, P. Jing, Y. J. Li, G. R. Xu and J. Zhang, J. Mater. Chem. A., 2013, 1, 12732–12741.



Fig. S8 The UV-vis spectra and kinetic rate of reduction of 4-NP by NaBH₄ under the catalysis of Fe₃O₄@Pd NPs for 1-6 times.



Fig. S9 The UV-vis spectra and kinetic rate of reduction of 4-NP by NaBH₄ under the catalysis of Fe₃O₄@Au-Pd NPs for 1-6 times.



Fig. S10 The SEM (a, c, e) and EDX (b, d, f) of the Fe₃O₄@Au-Pd NPs as catalyst after reused 1^{st} , 3^{rd} , 6^{th} times, respectively.



Fig. S11 UV-vis spectra of the reduction of $K_3Fe(CN)_6$ solution upon the addition of NaBH₄ recorded at different times from 1 min to12 h at 25 °C, [[Fe(CN)₆]³⁻]=3×10⁻³ M, [BH⁴⁻]=0.04 M in the absence of catalyst.



Fig. S12 The UV-vis spectra and kinetic rate of reduction of K₃Fe(CN)₆ by NaBH₄ under the catalysis of Fe₃O₄@Pd NPs for 1-9 times.



Fig. S13 The UV-vis spectra and kinetic rate of reduction of K₃Fe(CN)₆ by NaBH₄ under the catalysis of Fe₃O₄@Au-Pd NPs for 1-9 times.



Fig. S14 UV-vis spectra of the reduction of 2-NP by NaBH₄ in the presence of Fe₃O₄@Au-Pd NPs, $(2 \text{ mL H}_2\text{O}, 90 \text{ }\mu\text{L} 10 \text{ mM} 2\text{-NP}, 600 \text{ }\mu\text{L} 0.5 \text{ M} \text{ NaBH}_4)$.



Fig. S15 UV-vis spectra of the reduction of 3-NP by NaBH₄ in the presence of Fe₃O₄@Au-Pd NPs, (2 mL H₂O, 150 μ L 10 mM 3-NP, 1 mL 0.5 M NaBH₄).



Fig. S16 UV-vis spectra of the reduction of 4-NTP by NaBH₄ in the presence of Fe₃O₄@Au-Pd NPs, (2 mL H₂O, 25 μ L 10 mM 4-NTP, 200 μ L 0.5 M NaBH₄).