Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Enhanced catalytic application of Au@polyphenol-metal nanocomposite synthesized by a facile and green method

Supplementary Information

Tao Zeng,[a] Xiaole Zhang,[a,b] Yuanyuan Guo,[a] Hongyun Niu,[a] and Yaqi Cai*[a]

[a] The State Key Laboratory of Environmental Chemistry and Ecotoxicology of Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China; E-mail: caiyaqi@rcees.ac.cn
[b] College of Life Science, Hebei United University, Tangshan, 063000, Hebei, China.

EXPERIMENTAL SECTION

Chemicals

Hydrogen tetrachloroaurate hydrate ($HAuCl_4 \cdot 4H_2O$), ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), 2-amino-2-hydroxymethylpropane-1,3-diol (Tris), 4-nitrophenol (4-NP), and sodium hydrate (NaBH4) were purchased from Sinopharm Chemistry Reagent Co. Ltd. (Beijing, China). Tannic acid (TA), (-)-Epigallocatechin gallate (EGCG), and gallic acid (GA) were obtained from Sigma-Aldrich. All chemicals were used as received without further purification. Ultrapure water was prepared in the laboratory using a Milli-Q SP reagent water system from Millipore (Milford, MA).

Synthesis of core-shell Au@ployphenol-Fe nanocatalyst

Au NPs were first prepared by simply mixing 1 mL of $HAuCl_4 \cdot 4H_2O$ (1mM) with 5 uL of TA (40 mg mL^{-1}) at room temperature. The suspension was vigorously mixed by a vortex mixer until the solution color changed red and kept constant. The obtained Au NPs were collected by centrifugation (10000 r min^{-1}) and washed with water to remove excess TA. To fabricate Au@ployphenol-Fe nanocatalyst, 10 uL of $FeCl_3 \cdot 6H_2O$ (1 mg mL^{-1}) was added into the 0.5 mL of Au NPs solution with a 30 s of vigorous mixing, followed by the addition of 10 uL of TA (4 mg mL^{-1}) with another 30 s mixing. After mingling of the above mixture with 0.5 mL Tris-HCl (pH = 8.5), the products were recovered by centrifugation and rinsed with water two times. The layer thickness can be controlled by selectively repeating the above cycle. For the assembly of other polyphenols-Fe layers, the synthetic procedures were same as described above except that EGCG and GA were used in place of TA at same concentration.

Catalytic reduction of 4-NP

The reduction of 4-NP in the presence of $NaBH_4$ was carried out to investigate the catalytic activity of the catalyst. Typically, 2 mL of deionized water, 1.0 mL of fresh $NaBH_4$ (0.2 M), and 0.1 mL 4-NP (5 mM) were added into a quartz cuvette in sequence, followed by the addition of 0.05 mL of catalyst (2 mM Au) to the mixture. The reaction progress was monitored by UV-vis spectroscopy at a certain time interval to obtain the successive information. When conduct the pH-dependent experiments, various buffer systems were applied to adjust the pH value: pH ~ 2, glycine - HCl (0.2 M); pH ~ 5.0, Na_2HPO_4 (0.2 M) - citric acid (0.1 M); pH ~ 8.5, Tris - HCl (10 mM).

Characterization

The size and morphology of the synthesized materials were surveyed by H-7500 transmission electron microscope (TEM, Tokyo, Japan) and Tecnai G2 F20 HRTEM with an energy dispersive X-ray spectrometry (HRTEM-EDX, FEI, Netherlands). X-Ray photoelectron spectroscopy (XPS) measurements were conducted by applying a Thermo Scientific ESCA-Lab-200i-XL spectrometer (Waltham, MA) with monochromatic Al Kα radiation (1486.6 eV). Zeta-potential measurements were conducted in water by using a Zetasizer Nano ZS (Malvern). UV-vis absorption tests were carried out on a 4802S UV-vis spectrophotometer (Shanghai Unico, China).

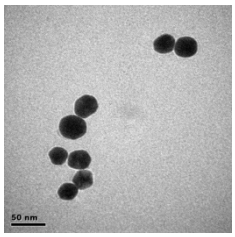

Fig. S1 TEM image of bare Au NPs.

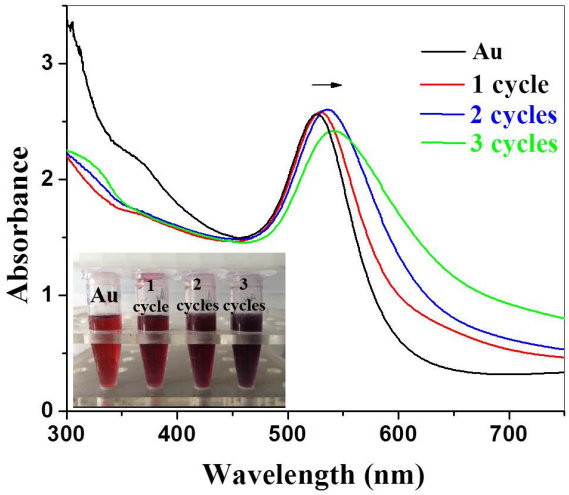

Fig. S2 UV-vis spectra of bare Au NPs, Au@TA-Fe composites with 1, 2, and 3 assembly cycles. The inset shows the color of the corresponding solution.

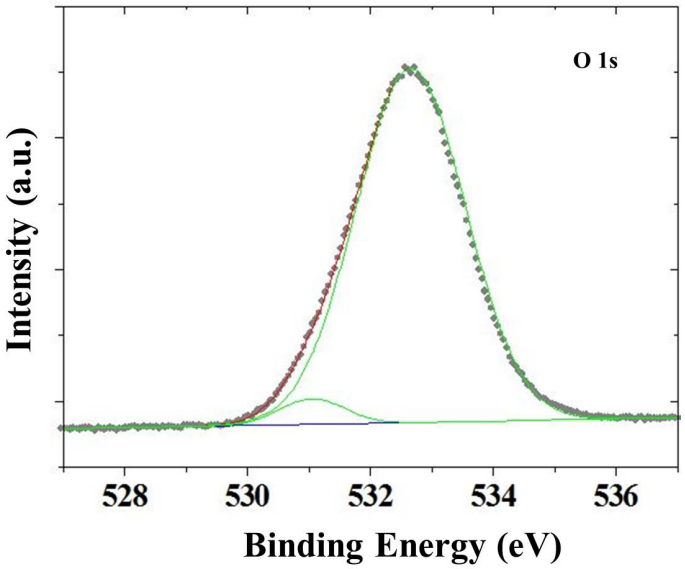

Fig. S3 XPS spectrum of O 1s core-level.

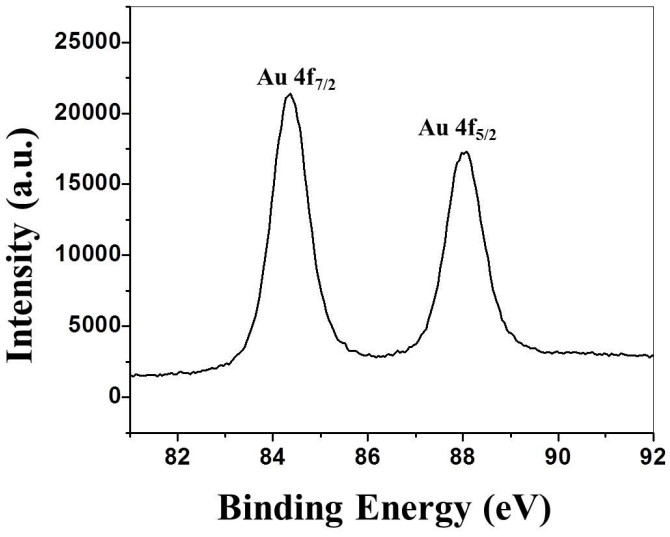

Fig. S4 XPS spectrum of Au 4f core-level.

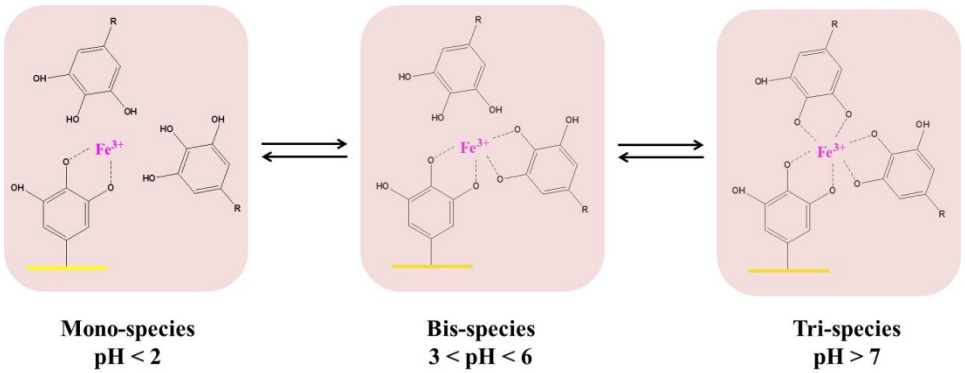

Fig. S5 pH-responsive character of TA-Fe^{3+} layer.

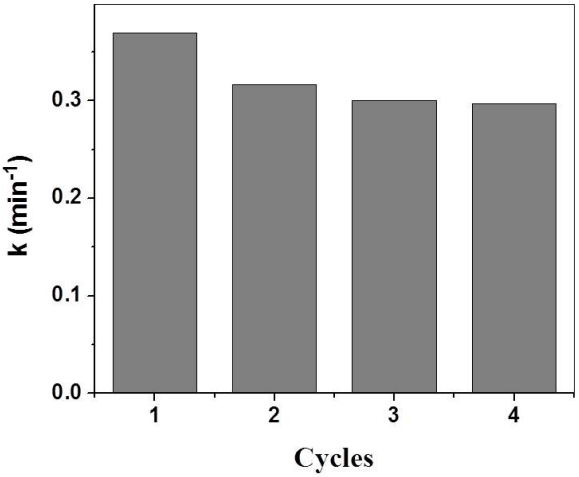

Fig. S6 Rate constant k of different reuse cycle.

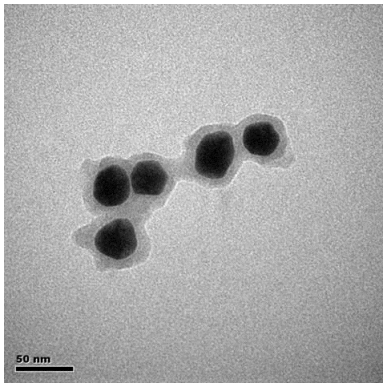

Fig. S7 TEM image of Au@TA-Fe nanocatalyst after used.

Table S1 Comparison of catalytic activity for 4-NP reduction by Au based nanocatalysts

Catalyst structure	k (min^{-1})	k_{nor} (min^{-1} μmol^{-1})	Ref. No.
Au NPs/SiO_2-NTs	0.64	0.638	1
Au NPs@[Na]-HAMS	0.31	-	2
AuNPs/Fe_3O_4-NPs	0.01	0.36	3
Fe_3O_4@SiO_2-Au@mSiO_2	0.35	1.05	4
Au NPs/TWEEN/GO	0.25	1.16	5
Au NPs/GO	0.18	-	6
Au@MIL-100(Fe)	0.33	-	7
Au-EGCG-CF	0.14	0.14	8
Dumbbell-like Fe3O4-Au	0.63	0.33	9
PLAL-AuNPs/CeO_2-NTs	0.14	0.84	10
Au@TA-Fe	0.37	3.7	This work

References:

[1] Z. Y. Zhang, C. L. Shao, P. Zou, P. Zhang, M. Y. Zhang, J. B. Mu, Z. C. Guo, X. H. Li, C. H. Wang and Y. C. Liu, *Chem. Commun.*, 2011, 47, 3906-3908.

[2] X. Fang, Z. Liu, M.-F. Hsieh, M. Chen, P. Liu, C. Chen, N. Zheng, ACS Nano 2012, 6, 4434.

[3] Y. C. Chang and D. H. Chen, *J. Hazard. Mater.*, 2009, 165, 664-669.

[4] Y. H. Deng, Y. Cai, Z. K. Sun, J. Liu, C. Liu, J. Wei, W. Li, C. Liu, Y. Wang, D. Y. Zhao, *J. Am. Chem. Soc.* 2010, *132*, 8466.

[5] Y. W. Zhang, S. Liu, W. B. Lu, L. Wang, J. Q. Tian and X. P. Sun, *Catal. Sci. Technol.*, 2011, **1**, 1142

[6] W. B. Lu, R. Ning, X. Y. Qin, Y. W. Zhang, G. H. Chang, S. Liu, Y. L. Luo and X. P. Sun, *J. Hazard. Mater.*, 2011, **197**, 320

[7] F. Ke, J. F. Zhu, L. G. Qiu and X. Jiang, *Chem. Commun.*, 2013, 49, 1267-1269.

[8] H. Wu, X. Huang, M. M. Gao, X. P. Liao, B. Shi, *Green Chem.,* 2011, *13*, 651.

[9] F. H. Lin, R. A. Doong, *J. Phys. Chem. C* 2011, *115*, 6591.

[10] J. M. Zhang, G. Z. Chen, M. Chaker, F. Rosei and D. L. Ma, Appl. Catal. B-environ, 2013, 132, 107-115.