

Rationally Designed Hierarchical nickel-enabled magnetic yolk-like nanospindles for enhanced catalysis and protein adsorption

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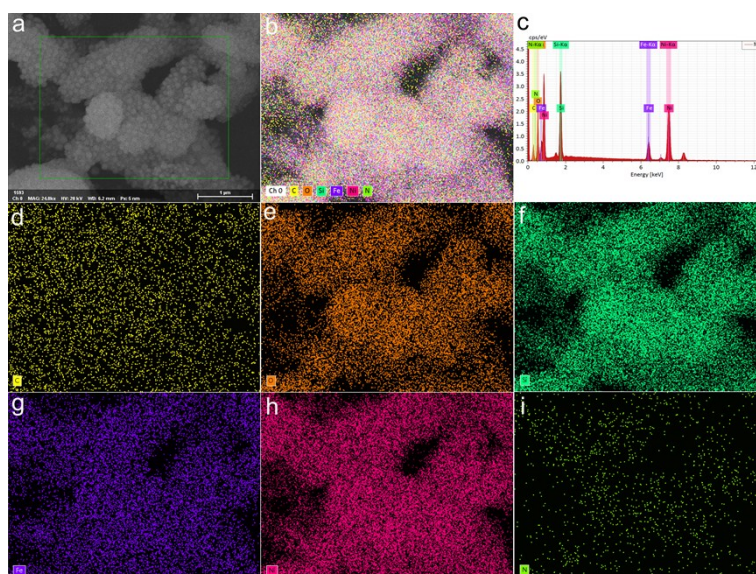


Fig. S1 Energy-disperse X-ray spectrum (EDS) mapping imagines and EDX spectrum of FeOx@SiO₂@C-Ni/900(c). (d) C, (e) O, (f) Si, (g) Fe, (h) Ni, (i) N

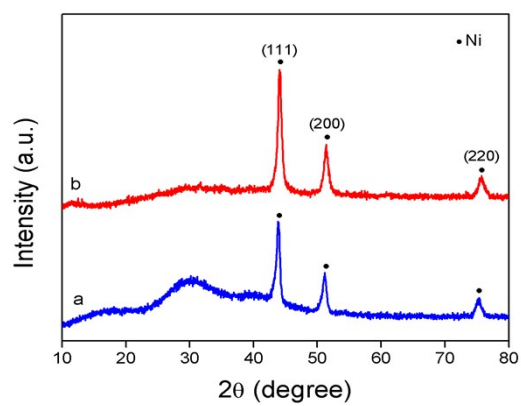


Fig. S2 The XRD Pattern of $\text{Fe}_2\text{O}_3@NS@PDA$ calcinated in nitrogen environment at 700 °C (a), and 900 °C (b).

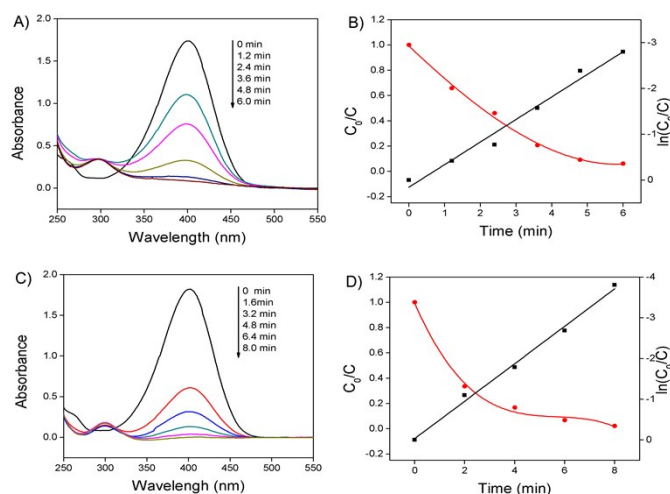


Fig. S3 (A) successive reduction of 4-NP using $\text{FeO}_x@\text{SiO}_2@\text{C-Ni}/700$ as catalysts; (B) C/C_0 and $\ln(C/C_0)$ versus time for the reduction of 4-NP over 1 mg $\text{FeO}_x@\text{SiO}_2@\text{C-Ni}/700$ catalysts; (C) successive reduction of 4-NP using $\text{FeO}_x@\text{SiO}_2@\text{C-Ni}/900$ as catalysts; (D) C/C_0 and $\ln(C/C_0)$ versus time for the reduction of 4-NP over 1 mg $\text{FeO}_x@\text{SiO}_2@\text{C-Ni}/900$ catalysts.

Table S1. The ICP data of the resultant products with different calcination temperature before and after catalytic reaction.

Catalysts	Ni ($\mu\text{g}\cdot\text{mg}^{-1}$)
$\text{FeO}_x@\text{SiO}_2@\text{C-Ni}/500$	256.67
$\text{SiO}_2@\text{C-Ni}/700$	394.69
$\text{SiO}_2@\text{C-Ni}/900$	474.32

Table S2. A full comparison of $\text{FeO}_x@\text{SiO}_2@\text{C-Ni}$ nanospindles catalysis activity and test condition with other nickel and noble metal catalysts.

Catalyst	Type	$K(\times 10^{-3}\text{s}^{-1})$	$\kappa(\text{g}^{-1}\text{s}^{-1})$	Ref.
$\text{FeO}_x@\text{SiO}_2@\text{C-Ni}/500$	nanospindles	46	179.22	This work
$\text{SiO}_2@\text{C-Ni}/700$	nanospindles	8.21	20.85	This work
$\text{SiO}_2@\text{C-Ni}/900$	nanospindles	7.66	16.15	This work
Au nanoparticles	nanoparticles	0.06	0.72	S1
Pd nanocatalysts	nanoparticles	0.73	0.36	S2
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Au}@m\text{SiO}_2$	Core-shell	7.0	105	S3
$\text{Au}@m\text{eso-SiO}_2$	Hollow spheres	0.08	2.51	S4
Ni/SiO_2	Core-shell	2.8	0.94	S5
$\text{Cu}_2\text{O}@Ag$	Core-shell	0.44	1.09	S6

RGO-Ni	Nanosheets	0.25	0.04	S7
C-Ni/600	Nanoparticles	18.6	449	S8
Ni/SNTs	Nanotube	84	91	S9
Fe ₃ O ₄ @SiO ₂ -Ag	nanospheres	7.67	7.67	S10
Ni (modified)	Nanoparticles	2.4	0.80	S11
Ni/MC-550	Bottle-neck	1.51	338	S12

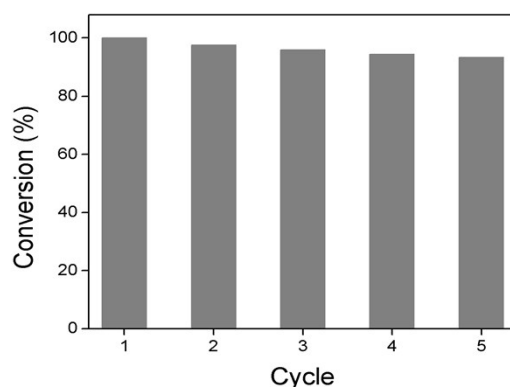


Fig. S4 The reusability of FeO_x@SiO₂@C-Ni/500 as the catalyst for the reduction of 4-NP with NaBH₄.

Table S3. Properties of different adsorbents for His-rich proteins capture.

Adsorbent	Type	Capacity (mg g ⁻¹)	Ref.
FeO _x @SiO ₂ @C-Ni/500	nanospindles	1893.0	This work
FeO _x @SiO ₂ @C-Ni/700	nanospindles	952.4	This work
FeO _x @SiO ₂ @C-Ni/900	nanospindles	724.6	This work
CNTs/Fe ₃ O ₄ @Cu Silicate	nanotubes	302.3	S13
Cu-IDA-silica-coated Fe ₃ O ₄	microspheres	418.6	S14
Magnetic HCNTs	nanotubes	2200	S15
Fe ₃ O ₄ @PVBC@IDA-Ni	core-shell	1988	S16
Fe ₃ O ₄ /Cys	nanospheres	53.2	S17
Fe ₃ O ₄ @SiO ₂ @LDH	Microspheres	239	S18
MnFe ₂ O ₄ @SiO ₂ @NH ₂ @2AB-Ni	nanoparticles	220	S19
Fe ₃ O ₄ @NiSiO ₃	Yolk-shell	220	S20
Fe ₃ O ₄ @SiO ₂ -IDA-Cu	nanoparticles	38.2	S21
P(PEGDMA-VI)@ECA	microspheres	22.0	S22
Fe ₃ O ₄ @SiO ₂ @C/Ni	nanoparticles	409.8	S23

$\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{IL}$	microspheres	2150	S24
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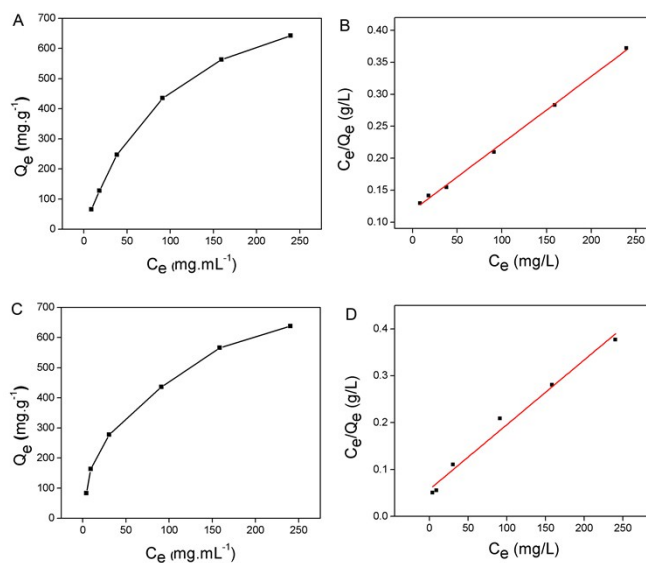


Fig. S5 Adsorption isotherms of protein BHB and Linear fitting of adsorption isotherms plots based on Langmuir model for $\text{FeO}_x@\text{SiO}_2@\text{C-Ni}/700$ (A,B), $\text{FeO}_x@\text{SiO}_2@\text{C-Ni}/900$ (C,D).

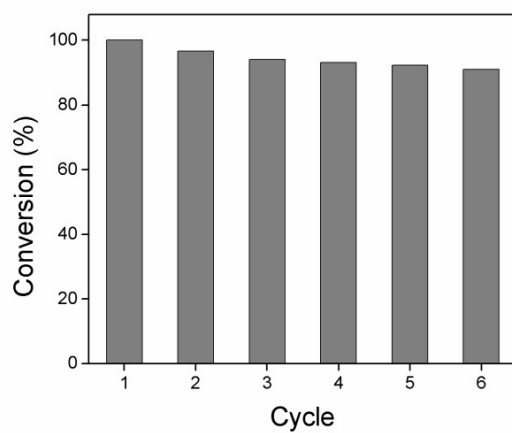


Fig. S6 The reusability of $\text{FeO}_x@\text{SiO}_2@\text{C-Ni}/500$.

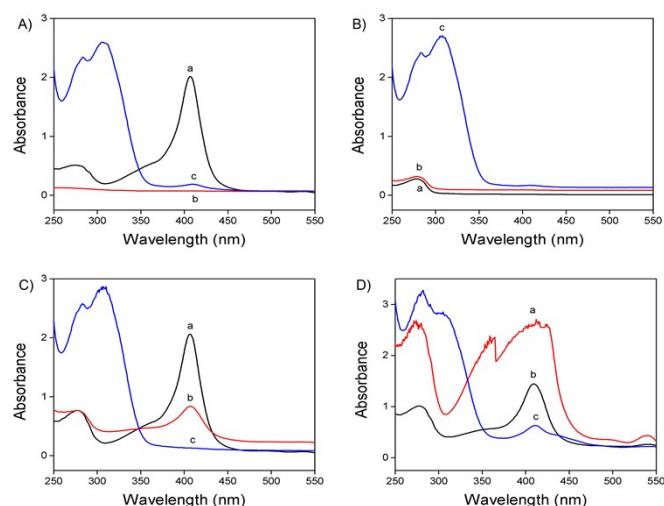


Fig. S7 Curve a is UV-vis spectra of 0.4 mg mL⁻¹ of the BHb (A), BSA (B), BHb and BSA mixture (C), and 500-fold diluted bovine blood (D) before adsorbed by FeO_x@SiO₂@C-Ni/500 adsorbents. Curve b is the UV-vis spectra of the supernatant of the above BHb (A), BSA (B), BHb and BSA mixture (C), and 100-fold diluted bovine blood (D) after adsorption by adsorbents. Curve c is the UV-vis spectra of desorption solution of the adsorbed protein by adsorbents in BHb (A), BSA (B), BHb and BSA mixture (C) and 100-fold diluted bovine blood (D) using a concentration of 0.2 g mL⁻¹ of imidazole solution as the eluent.

Notes and references

- S1. K. B. Narayanan and N. Sakthivel, *J. Hazard. Mater.*, 2011, **189**, 519-525.
- S2. X. Lu, X. Bian, G. Nie, C. Zhang, C. Wang and Y. Wei, *J. Mater. Chem.*, 2012, **22**, 12723-12730.
- S3. Y. H. Deng, Y. Cai, Z. K. Sun, J. Liu, C. Liu, J. Wei, W. Li, C. Liu, Y. Wang and D. Y. Zhao, *J. Am. Chem. Soc.*, 2010, **132**, 8466.
- S4. J. Chen, Z. Xue, S. Feng, B. Tu and D. Zhao, *J. Colloid Interface Sci.*, 2014, **429**, 62-67.
- S5. Z. Jiang, J. Xie, D. Jiang, J. Jing and H. Qin, *Cryst Eng Comm.*, 2012, **14**, 4601.
- S6. S. Kandula and P. Jeevanandam, *Eur. J. Inorg. Chem.*, 2016, **10**, 1548-1557.
- S7. Z. Ji, X. Shen, G. Zhu, H. Zhou and A. Yuan, *J. Mater. Chem.*, 2012, **22**, 3471-3477.
- S8. L. Ding, M. Zhang, Y. W. Zhang, J. B. Yang, J. Zheng, Tasawar Hayat, Njud S. Alharbi and J. L. Xu, *nanotechnology.*, 2017, **34**, 345601-345610.
- S9. Y. Chi, Q. Yuan, Y. J. Li, J. C. Tu, L. Zhao, N. Li, X. T. Li, *J. Colloid Interface Sci.*, 2012, **383**, 96-102.
- S11. Jiang Z, Xie J, Jiang D, Wei X and Chen M, *Cryst Eng Comm.*, 2013, **15**, 560-569.

- S12. Y. Yang, Y. Ren, C. Sun and S. Hao, *Chem. Soc. Rev.*, 2014, **41**, 5577-5578.
- S13. M. Zhang, Y. Wang, Y. Zhang, L. Ding, J. Zheng and J. L. Xu, *Appl. Surf. Sci.*, 2016, **375**, 154-161.
- S14. M. Zhang, D. Cheng, X. W. He, L. X. Chen and Y. K. Zhang, *Chem. Asian J.*, 2010, **5**, 1332-1340.
- S15. M. Zhang, B. Wang, Y. Zhang, W. Li, W. Gan and J. Xu, *Dalton Trans.*, 2016, **45**, 922-927.
- S16. J. L. Cao, X. H. Zhang, X. W. He, L. X. Chen, Y. K. Zhang, *J. Mater. Chem. B*, 2013, **1**, 3625-3632.
- S17. X. Y. Zou, K. Li, Y. B. Zhao, Y. Zhang, B. J. Li and C. P. Song, *J. Mater. Chem. B*, 2013, **1**, 5108-5113.
- S18. M. F. Shao, F. Y. Ning, J. W. Zhao, M. Wei, David G. Evans and X. Duan, *J. Am. Chem. Soc.*, 2012, **134**, 2,1071-1078.
- S19. Z. Rashid, H. Naeimi, A. H. Zarnani, M. Nazari, M. R. Nejadmoghaddam and R. Ghahremanzadeh, *RSC Adv.*, 2016, **6**, 36840-36848.
- S20. Y. Wang, G. C. Wang, Y. Xiao, Y. L. Yang and R. K. Tang, *ACS Appl. Mater. Inter.*, 2014, **6**, 19092-19099.
- S21. G. Q. Jian, Y. X. Liu, X. W. He, L. X. Chen and Y. K. Zhang, *Nanoscale*, 2012, **4**, 6336-6342.
- S22. C. B. Du, N. Zhang, S. C. Ding, X. M. Gao, P. Guan and X. L. Hu, *Polym. Chem.*, 2016, **7**, 1-3.
- S23. Y. W. Zhang, M. Zhang, J. B. Yang, L. Ding, J. Zheng, J. L. Xu, and S. L. Xiong, *Name.*, 2016, **8**, 15978-15988.
- S24. Y. Wei, Y. Li, A. Tian, Y. Fan, X. Wang, *J. Mater. Chem. B*, 2013, **1**, 2066-2071.