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Supporting Information

Formation of Uniform magnetic C@CoNi alloy hollow hybrid composites with excellent performance on catalysis and protein adsorption

Yang Ling,[a] Min Zhang,*[a] Jing Zheng,[a] Jingli Xu,[a] Tasawar Hayat,[b] Njud S. Alharbi[c]

Preparation of CPS@Ni-Al

In a typical reaction, 120mg of the as-prepared CPS particles, $Ni(NO_3)_2{\cdot}6H_2O$ (0.058g), $Al(NO_3)_2{\cdot}9H_2O$ (0.075g), hexamethylenetetramine (HMT) (0.28g), and trisodium citrate (0.012g) were added into a mixed solvent of DI water (300 mL)and ethanol (20 mL). After vigorous stirring and ultra-sonication, the suspension was then transferred to a round-bottom flask and kept in a nitrogen atmosphere at 90 °C for 6 h. After cooling, the product was collected by centrifugation and washed with water and ethanol for several times before drying at 60°C overnight.

Preparation of CPS@Co-Mn

In a typical reaction, 120mg of the as-prepared CPS particles, $MnCl_2{\cdot}4H_2O$ (0.040g), $Co(NO_3)_2{\cdot}6H_2O$ (0.058g), hexamethylenetetramine (HMT) (0.28g), and trisodium citrate (0.012g) were added into a mixed solvent of DI water (300 mL)and ethanol (20 mL). After vigorous stirring and ultra-sonication, the suspension was then transferred to a round-bottom flask and kept in a nitrogen atmosphere at 90 °C for 6 h. After cooling, the product was collected by centrifugation and washed with water and ethanol for several times before drying at 60°C overnight.

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After cooling, the product was collected by centrifugation and washed with water and ethanol for several times before drying at 60°C overnight.

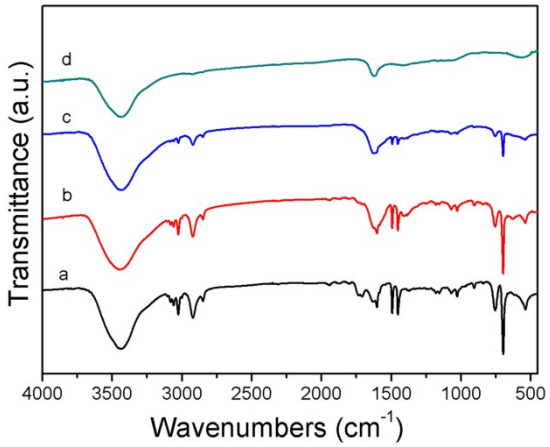

Fig. S1 FT-IR spectra of CP (a); CPS@Ni-Co (b); CPS@Ni-Co@PDA (c) and C@CoNi/500 (d).

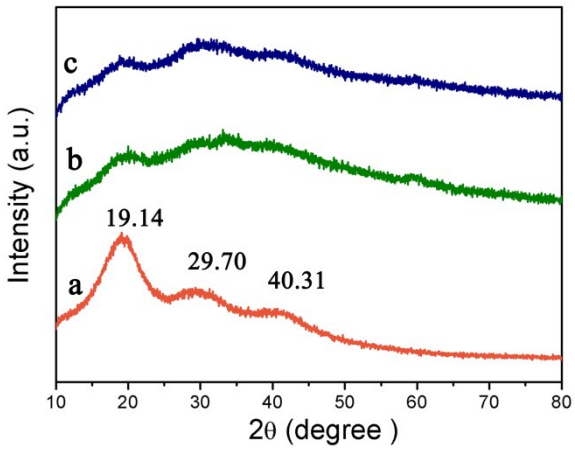

Fig . S2 XRD diffraction patterns of CPS (a); CPS@Ni-Co (b) and CPS@Ni-Co@PDA (c).

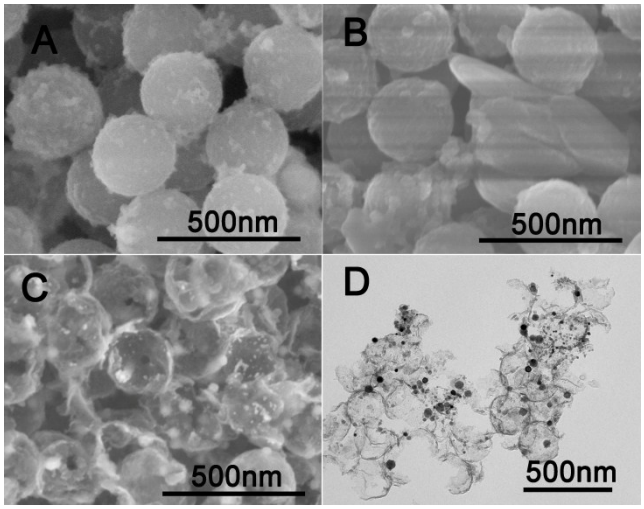

Fig. S3 SEM images of CPS@Ni-Al (A); CPS@Ni-Al@PDA (B); C@NiAl (C) and TEM image of C@NiAl (D).

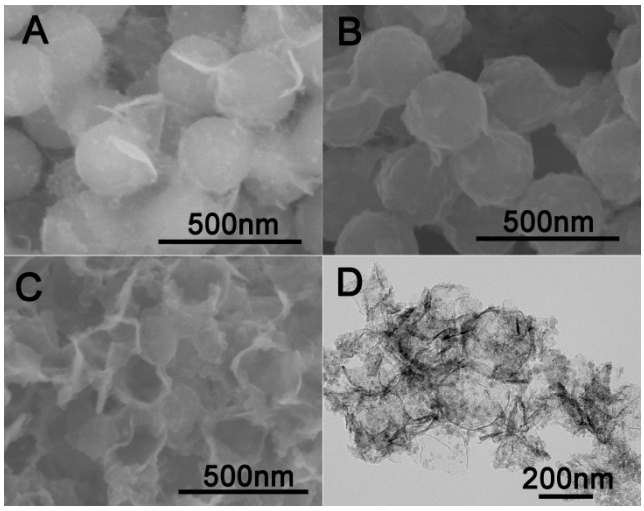

Fig. S4 SEM images of CPS@Co-Mn (A); CPS@Co-Mn@PDA(B); C@CoMn (C) and TEM image of C@CoMn (D).

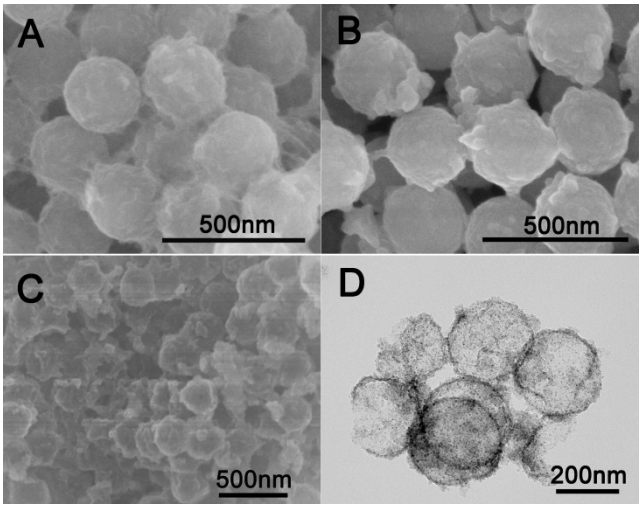

Fig. S5 SEM images of CPS@Ni-Mn (A); CPS@Ni-Mn@PDA (B); C@NiMn (C) and TEM image of C@NiMn (D).

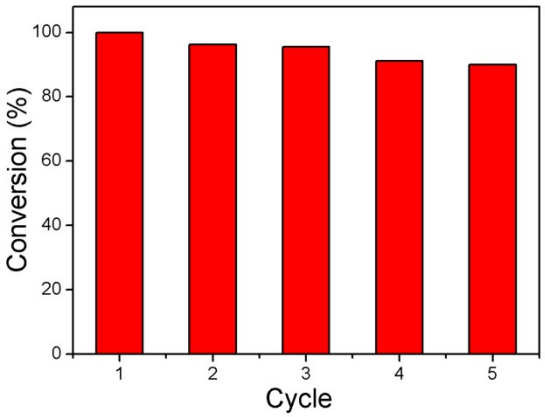

Fig. S6 The reusability of C@CoNi/500 as the catalyst for the reduction of 4-NP with $NaBH_4$.

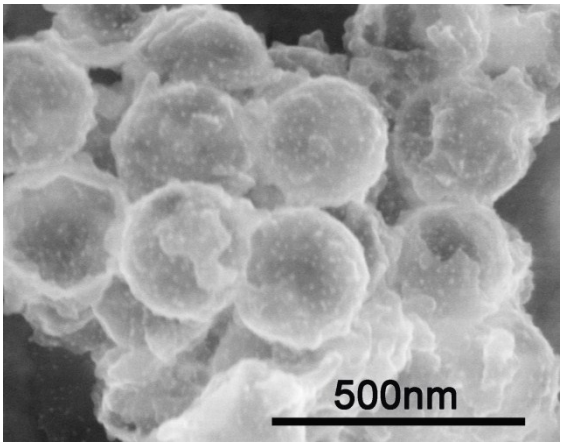

Fig. S7 SEM images of C@CoNi/500 after five catalytic reaction

Table S1. ICP data of C@CoNi/500, C@CoNi/700 and C@CoNi/900.

Catalyst	Co (μg/mg)	Ni (μg/mg)
C@CoNi/500	76.49	80.56
C@CoNi/700	129.58	101.35
C@CoNi/900	149.04	167.75

Table S2. A full comparison of the activity parameter κ of C@CoNi hollow hybrid composites with other noble metal catalysts

Catalyst	$K(\times 10^{-3} s^{-1})$	$k(\times 10^{-3} mg^{-1} s^{-1})$	References
C@CoNi/500	15.8	100.6	This work
C@CoNi/700	16.5	71.45	This work
C@CoNi/900	11.9	47.42	This work
Cu_2O/Ag	7.28	18.23	1
Au@Ag	3	10.38	2
Pd/MIL-100(Cr)NCs	18.83	25.1	3
P_{PAA}	15.46	38.43	4
Ir/IrOx	0.55	11.83	5
BNNS/Ag-3	2.72	16	6
Au@meso-SiO_2	1.33	41.8	7
Cu_2O-Cu-CuO	10.4	20.7	8
Fe_3O_4@SiO_2–Au@mSiO_2	7	105	9

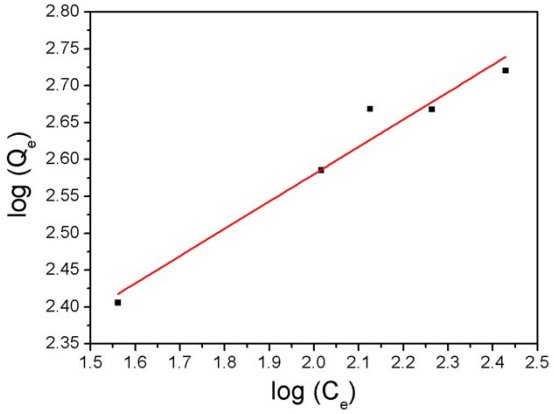

Fig. S8 Linear fitting of adsorption isotherms plots based on Freundlich model.

Table S3. the estimate of Langmuir model and Freundlich model

Langmuir			Freundlich		
Q_m	b	R^2	Q_m	n	R^2
628.93	0.0571	0.98832	69.21	2.70	0.94902

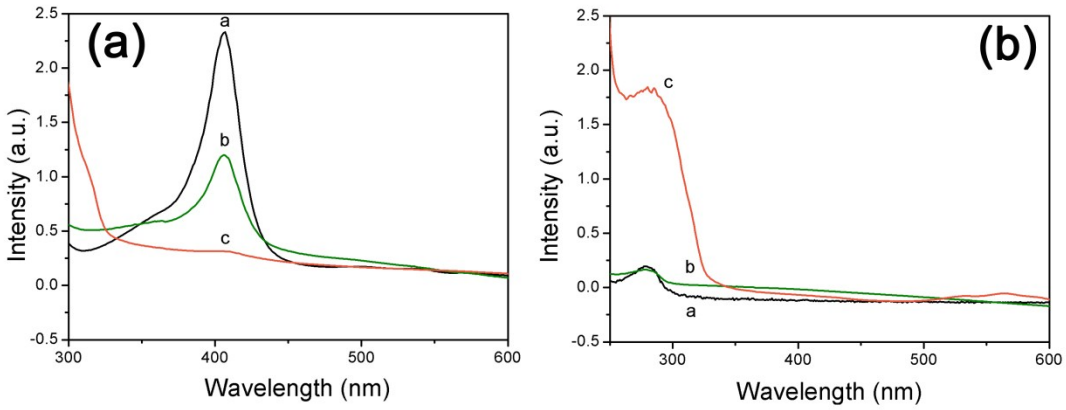

Fig. S8 Curve a is the UV-vis spectrum of 0.4 mg mL^{-1} of the BHb and BSA mixture (a), BSA (b) before adsorption by C@CoNi/500. Curve b is the UV-vis spectrum of supernatant of, BHb and BSA mixture (a), BSA (b) after adsorbed by C@CoNi/500. Curve c is the UV-vis spectrum of desorption solution of the adsorbed protein by C@CoNi/500 in, BHb and BSA mixture (a), BSA (b) using concentration of 0.2 g mL^{-1} of dimethyl imidazole solution as the eluent.

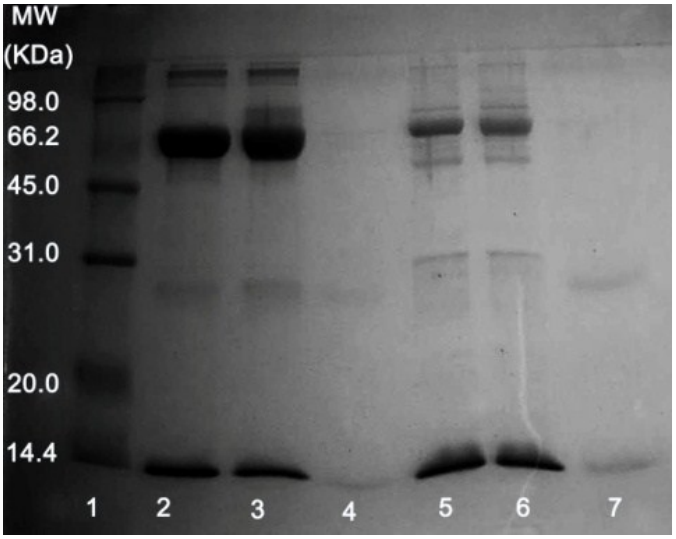

Fig. S9 SDS-PAGE analysis of adsorption by C@CoNi composites from solution. Lane 1, marker; lane 2, 1 $mg \cdot mL^{-1}$ of BHb and BSA binary solution; lane 3, remaining BHb and BSA solution after adsorption by C@CoNi composites; lane 4, the eluted BHb and BSA mixture by 0.2 $g \cdot mL^{-1}$ dimethyl imidazole solution; lane 5, 100-fold human whole blood; lane 6, remaining human whole blood solution after adsorption by C@CoNi composites; lane 7, the eluted 100-fold human whole blood by 0.2 $g \cdot mL^{-1}$ dimethyl imidazole solution.

References

1. S. Kandula and P. Jeevanandam, *European Journal of Inorganic Chemistry*, 2016, **2016**, 1548-1557.
2. X. Zhang and Z. Su, *Advanced materials*, 2012, **24**, 4574-4577.
3. L. Ran, Y. Yang, L. Ren and Q. Chen, *ACS applied materials & interfaces*, 2015, **7**, 6019.
4. C. Kästner and A. F. Thunemann, *Langmuir the Acs Journal of Surfaces & Colloids*, 2016, **32**, 7383.
5. D. Xu, P. Diao, T. Jin, Q. Wu, X. Liu, X. Guo, H. Gong, F. Li, M. Xiang and Y. Ronghai, *ACS applied materials & interfaces*, 2015, **7**, 16738.
6. H. Shen, C. Duan, J. Guo, N. Zhao and J. Xu, *Journal of Materials Chemistry A*, 2015, **3**, 16663-16669.
7. J. Chen, Z. Xue, S. Feng, B. Tu and D. Zhao, *J Colloid Interface Sci*, 2014, **429**, 62-67.
8. A. K. Sasmal, S. Dutta and T. Pal, *Dalton transactions*, 2016, **45**, 3139-3150.
9. Y. Deng, Y. Cai, Z. Sun, J. Liu, C. Liu, J. Wei, W. Li, C. Liu, Y. Wang and D. Zhao, *Journal of the American Chemical Society*, 2010, **132**, 8466-8473.