

Fabrication of Co@SiO₂@C/Ni submicrorattles as Highly Efficient catalysts for 4-nitrophenol reduction

Xiaohui Guo^a, Min Zhang^{*a}, Jing Zheng^a, Jingli Xu^a, Tasawar Hayat^b, Njud S. Alharbi^c, Baojuan Xi^d, and Shenglin Xiong^{*d}

^aCollege of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai 201620, PR China Email: zhangmin@sues.edu.cn

^bDepartment of Mathematics, Quaid-I-Azam University, Islamabad 44000, Pakistan NAAM Research Group, King Abdulaziz University, Jeddah, Saudi Arabia

^cBiotechnology Research Group, Department of Biological Sciences, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia

^d Key Laboratory of the Colloid and Interface Chemistry, Ministry of Education, and School of Chemistry and Chemical Engineering, Shandong University, Jinan, 250100, PR China. E-mail: chexsl@sdu.edu.cn

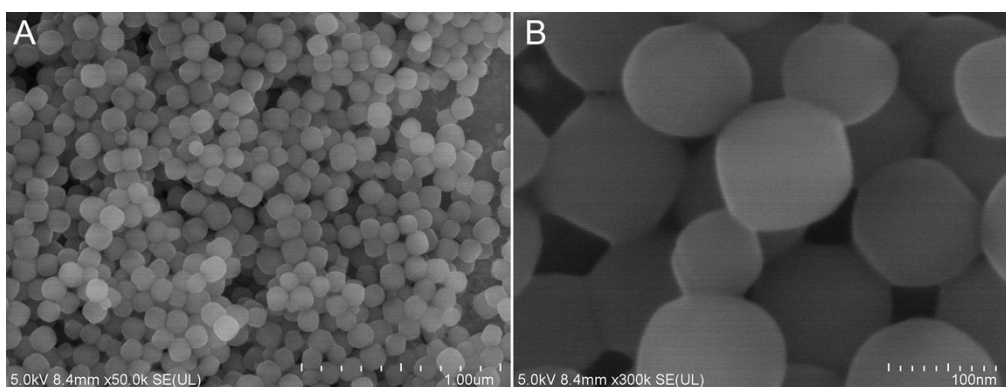


Figure S1. SEM images of $\text{Co}_3[\text{Co}(\text{CN})_6]_2$ cubes with different magnification

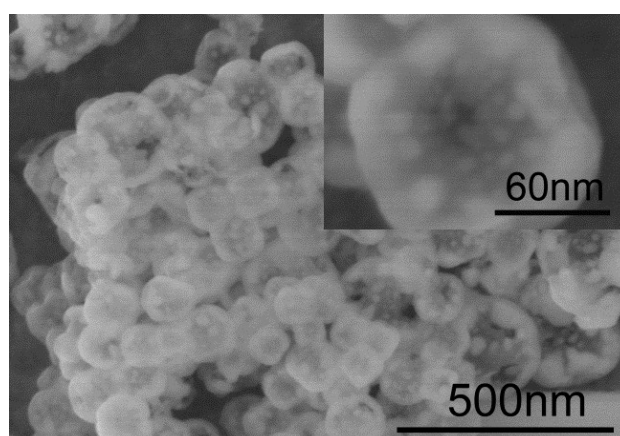


Figure S2. SEM images of $\text{Co}@\text{SiO}_2$ -500 submicrorattles.

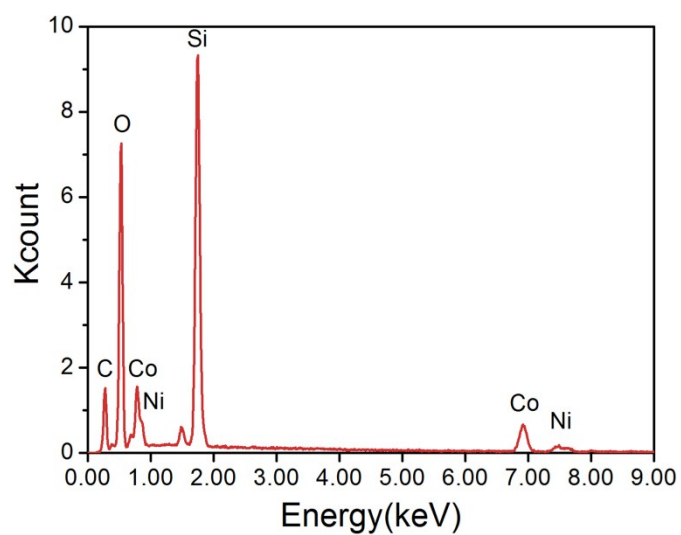


Figure S3. Energy-disperse X-ray spectrum (EDS) of Co@SiO₂@C/Ni-500 submicrorattles.

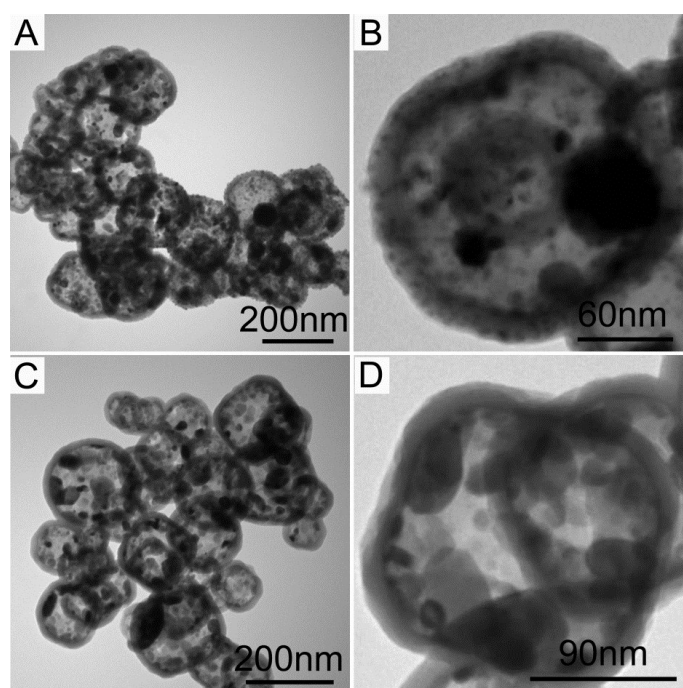


Figure S4. TEM images of (A, B) Co@SiO₂@C/Ni-500, (C,D) Co@SiO₂-500. (0.1 mL of TEOS was used.)

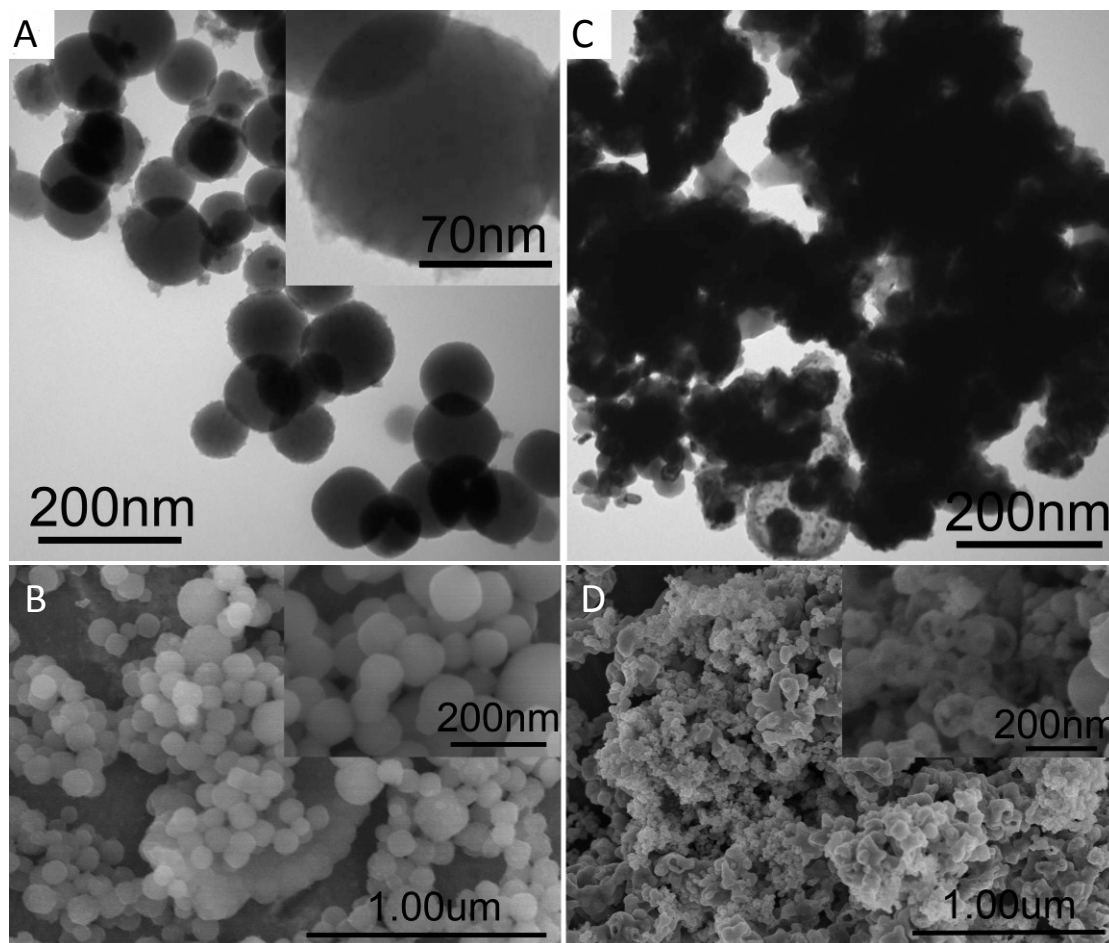


Figure S5. TEM and SEM images of (A,B) $\text{Co}_3[\text{Co}(\text{CN})_6]_2@\text{PDA-Ni}^{2+}$, (C,D) $\text{Co-Ni}@C$ composites annealed at 500 °C.

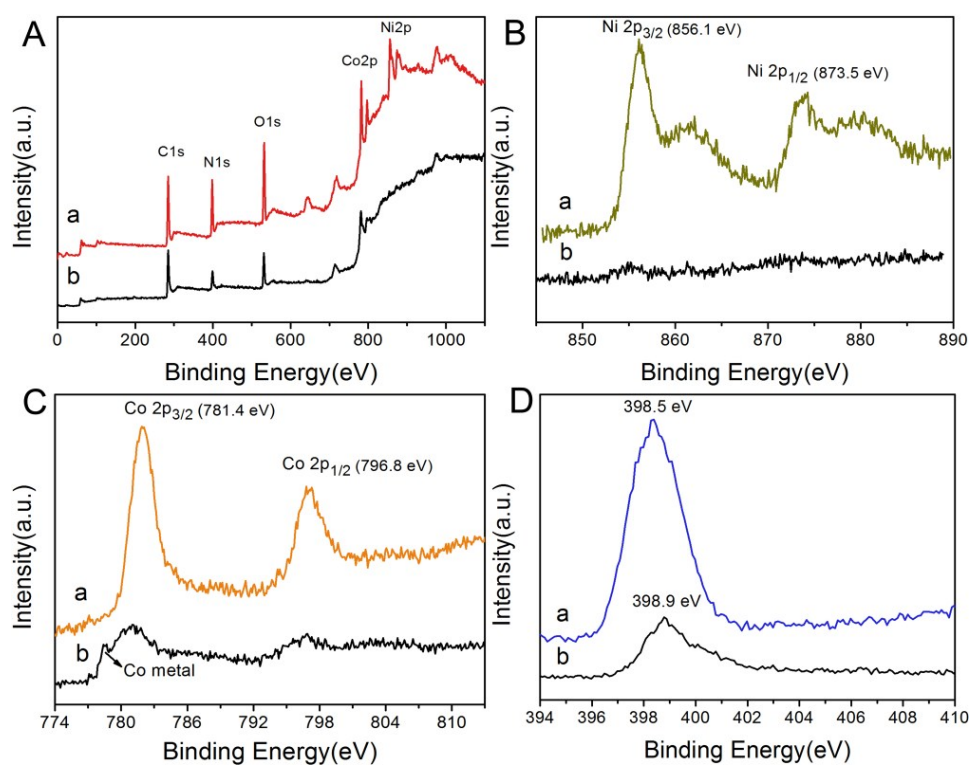


Figure S6. XPS spectra of $\text{Co}_3[\text{Co}(\text{CN})_6]_2@\text{PDA-Ni}^{2+}$ composite (a) and Co-Ni@C-500 composite: (A) the full survey scan, (B) Ni 2p, (C) Co 2p, and (D) N 1s.

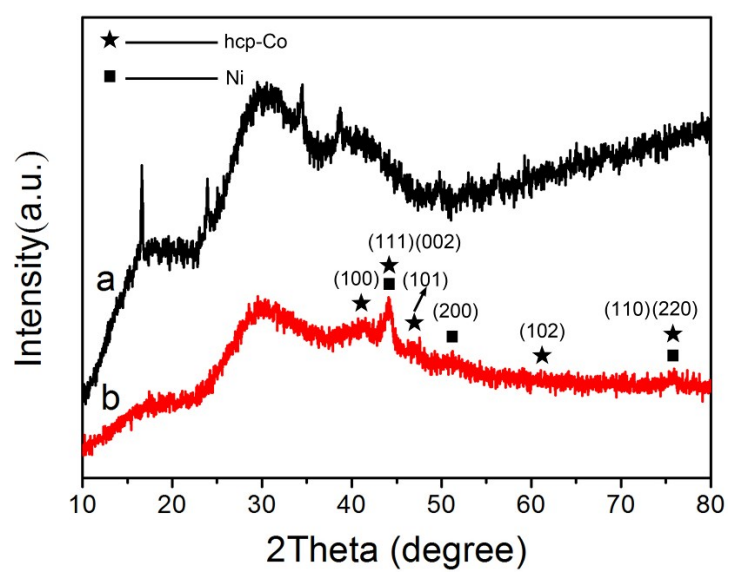


Figure S7. XRD patterns of $\text{Co}_3[\text{Co}(\text{CN})_6]_2@\text{PDA-Ni}^{2+}$ (a) and $\text{Co-Ni}@C-500$ (b).

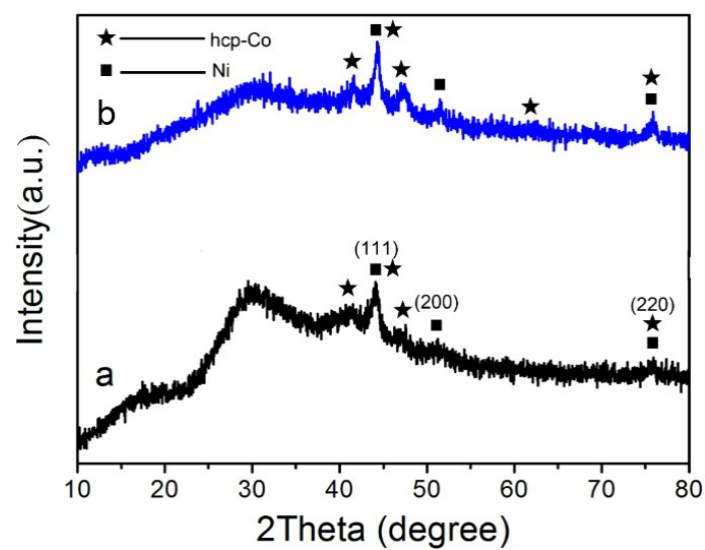


Figure S8. XRD patterns of Co@SiO₂@C/Ni-500 submicrorattles fabricated with the molar ratio of dopamine and nickel ion of 1:0.5 (a) and 1:3 (b).

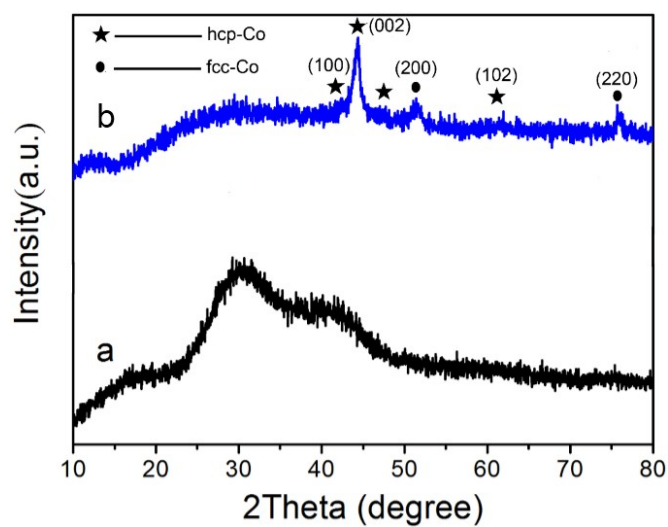


Figure S9. XRD patterns of Co@SiO₂@C/Ni submicrorattles annealed at 400 °C (a) and 700 °C (b).

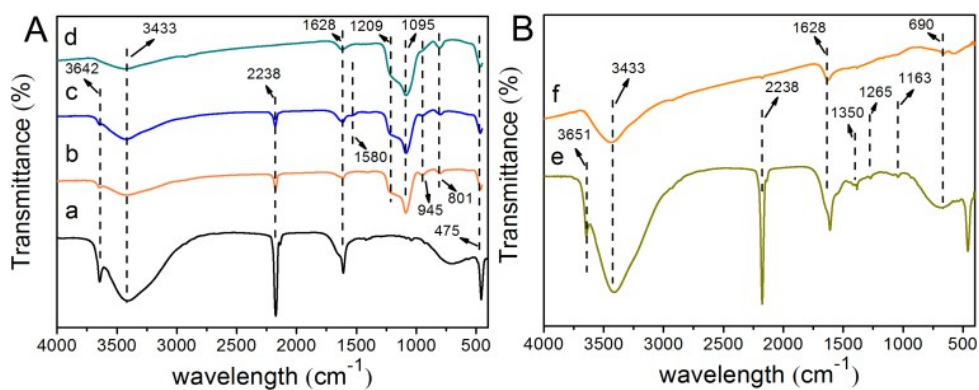


Figure S10. FTIR of Co₃[Co(CN)₆]₂ cubes (A), Co₃[Co(CN)₆]₂@SiO₂ (B), Co₃[Co(CN)₆]₂@SiO₂@PDA-Ni²⁺ (C), Co@SiO₂@C/Ni-500 submicrorattles (D),

$\text{Co}_3[\text{Co}(\text{CN})_6]_2@\text{PDA-Ni}^{2+}$ (E), $\text{Co-Ni}@C-500$ (F).

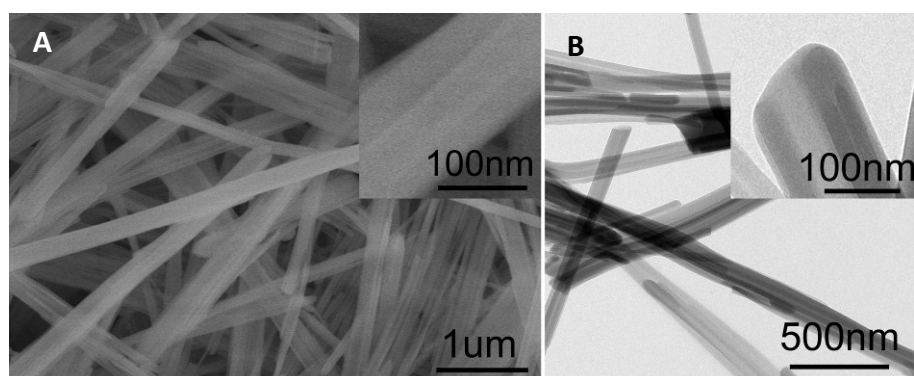


Figure S11. SEM and TEM images of Co-NTC nanowires.

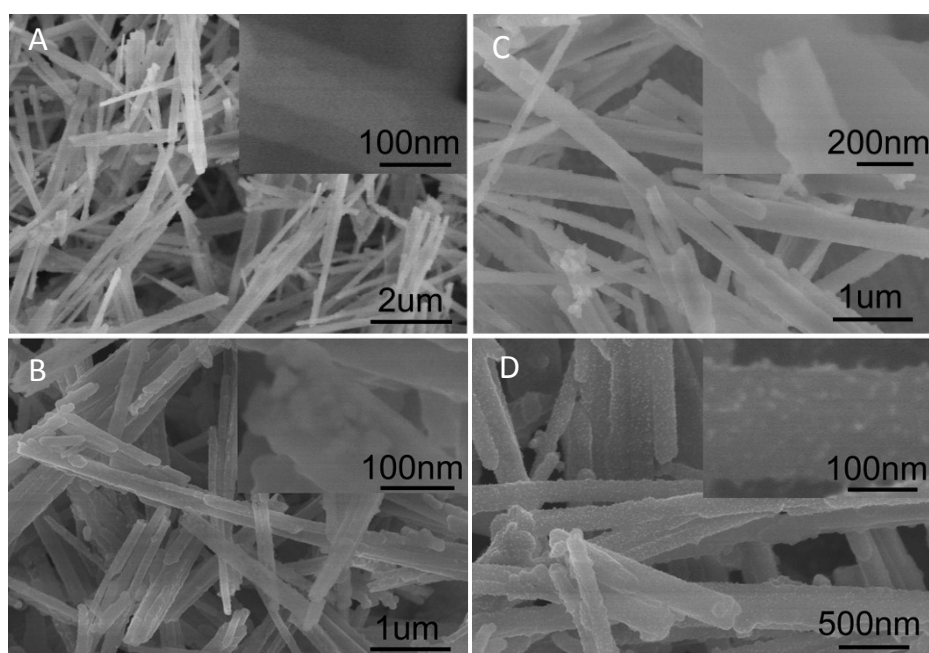


Figure S12. SEM images of (A) $\text{Co-NTC}@SiO_2$, (B) $\text{Co}@SiO_2$ nanocables, (C) $\text{Co-NTC}@SiO_2$ nanocables, (D) $\text{Co-NTC}@SiO_2$ nanocables.

NTC@SiO₂@PDA-Ni²⁺, (D) Co@SiO₂@C/Ni.

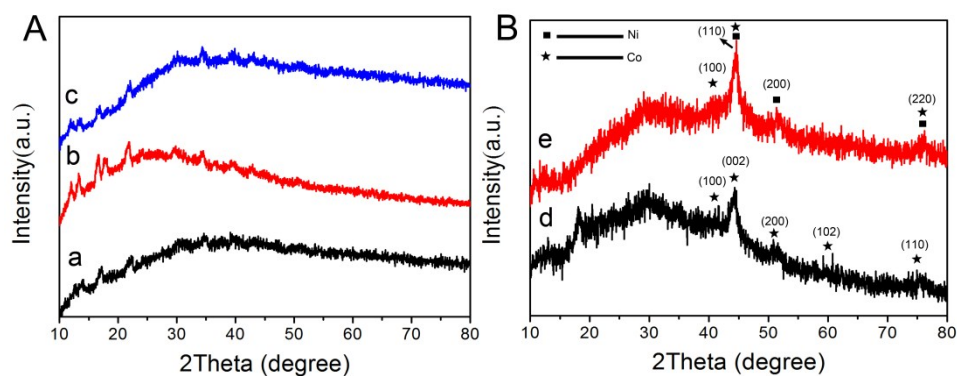


Figure S13. XRD patterns of Co-NTC nanowires (a), Co-NTC@SiO₂ (b), Co-NTC@SiO₂@PDA-Ni²⁺ (c), Co@SiO₂ (d), Co@SiO₂@C/Ni nanotubes (e).

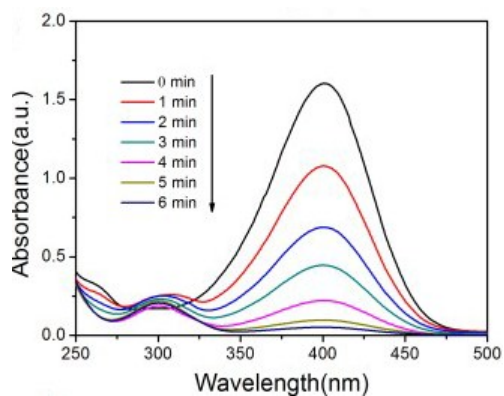


Figure S14. UV-vis absorption spectra of 4-NP at different reaction time during the

reduction by NaBH_4 catalyzed by $\text{Co@SiO}_2\text{/C/Ni-700}$.

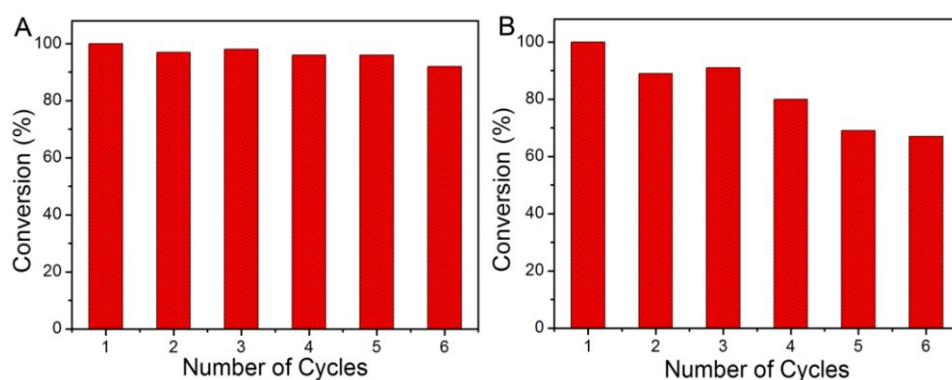


Figure S15. The reusability of $\text{Co@SiO}_2\text{/C/Ni-700}$ (a) and Co-Ni@C-700 (b) as the catalyst for the reduction of 4-NP with NaBH_4 .

Table S1. ICP data of $\text{Co@SiO}_2\text{-700}$, $\text{Co@SiO}_2\text{/C/Ni-700}$ and Co-Ni@C-700 .

Catalyst	Co ($\mu\text{g/mg}$)	Ni ($\mu\text{g/mg}$)
Co@SiO_2	201.25	/
$\text{Co@SiO}_2\text{/C/Ni}$	132.25	67.25
Co-Ni@C	417.75	159.75

Table S2. A full comparison of $\text{Co@SiO}_2\text{/C/Ni}$ submicrorattles catalysis activity and test condition with other cobalt and noble metal catalysts.

Catalyst	K (min^{-1})	$\kappa(\text{mg}^{-1}\text{min}^{-1})$	TOF/ h^{-1}	Conversion ratio	Ref.
----------	-------------------------	---	----------------------	------------------	------

Co@SiO ₂ -700	0.38	1.63	27.69	100%	This work
Co@SiO ₂ @C/Ni-700	0.583	7.74	136.71	100%	This work
Co-Ni@C-500	0.63	1.18	17.82	100%	This work
Au nanoparticles	0.06	0.72	12.13	100%	S1
Pd nanocatalysts	0.732	0.36	6.11	100%	S2
Fe ₃ O ₄ @SiO ₂ -Au@mSiO ₂	0.53	6.43	123.76	100%	S3
Au@meso-SiO ₂	0.08	2.51	39.02	100%	S4
Ni/SiO ₂ (230 nm)	0.504	1.06	18.95	100%	S5
BNNS/Ag-3	0.163	0.96	17.93	100%	S6
Cu ₂ O-Cu-CuO	0.624	1.242	18.81	100%	S7
P _{PAA}	0.9276	2.306	31.72	100%	S8
Pd/MIL-100(Cr) NCs	1.13	1.506	21.82	100%	S9
Cu ₂ O@Ag	0.4368	1.094	16.39	100%	S10
Ir/IrOx	0.033	0.71	10.76	100%	S11
2Au@2Ag	0.18	0.632	9.57	100%	S12
reduced Co ₃ O ₄	1.49	2.26	34.23	100%	S13

- S1. K. B. Narayanan and N. Sakthivel, *Journal of Hazardous Materials*, 2011, 189, 519-525.
- S2. X. Lu, X. Bian, G. Nie, C. Zhang, C. Wang and Y. Wei, *Journal of Materials Chemistry*, 2012, 22, 12723-12730.
- S3. 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.
- S4. J. Chen, Z. Xue, S. Feng, B. Tu and D. Zhao, *Journal of Colloid and Interface Science*, 2014, 429, 62-67.
- S5. Z. Niu, S. Zhang, Y. Sun, S. Gai, F. He, Y. Dai, L. Li and P. Yang, *Dalton Transactions*, 2014, 43, 16911-16918.
- S6. H. Shen, C. Duan, J. Guo, N. Zhao and J. Xu, *Journal of Materials Chemistry A*, 2015, 3, 16663-16669.
- S7. A. K. Sasmal, S. Dutta and T. Pal, *Dalton Transactions*, 2016, 45, 3139-3150.
- S8. C. Kästner and A. F. Thünemann, *Langmuir*, 2016, 32, 7383-7391.
- S9. R. Li, Y. Yang, R. Li and Q. Chen, *ACS Applied Materials & Interfaces*, 2015, 7, 6019-6024.
- S10. S. Kandula and P. Jeevanandam, *European Journal of Inorganic Chemistry*, 2016, 2016, 1548-1557.
- S11. 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, 16738-16749.
- S12. X. Zhang and Z. Su, *Advanced Materials*, 2012, 24, 4574-4577.

- S13. H. Chen, M. Yang, S. Tao and G. Chen, *Applied Catalysis B: Environmental*, 2017, 209, 648-656.