Supporting Information (for New Journal of Chemistry)

Novel Prussian-blue-analogue microcuboid assemblies and their derived catalytic performance for effective reduction of 4-nitrophenol

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1 Influence factors for the formation of Co-Fe MCBs

For a chemical reaction, there are vavious factors that can influence the evolution process. Herein, the amount of surfactant, solvent and temperature (as well as reaction time, see below) were taken into consideration. When double amount of PVP (200 mg) was used in the solvothermal reaction, the Co-Fe MCBs can form for a longer time (150 h), see in Fig. S1a; whereas less amount of PVP (50 mg) was used, the obtained cuboids were short and many small cubes remained in the product (Fig. S1b). This phenomenon indicated that the PVP wrapping around Co-Fe PBA cubes can finely tune the decomposition rate of the initial cubes into smaller cubes. Along with the XRD analysis of Co-Fe MCBs, it can be inferred that PVP also can help to adjust the self-assembly of these smaller cubes to form the final cuboid along the preferred orientation. Another factor that influence the self-assembly process was the reaction solvent. In the synthesis of Co-Fe MCBs EG was chosen as the solvent, because EG possessed higher boiling point (197.4 °C) and good dispersibility. If DI water was used instead, no cuboid formed in the finall solution (Fig. S1c), demonstrating the critical role of EG in the self-assembly process of the *in-situ* formed small cubes into cuboids. In addition, temperature was also important for the formation of micro-sized cuboids. When the temperature increased higher than the boiling point of EG, only closely-packed short cuboids were observed (Fig. S1d).



Figure S1 SEM images showing Co-Fe MCBs prepared at different conditions. (a) 200 mg PVP, 40 mL EG, reaction time 150 h, reaction temperature 180 °C, (b) 50 mg PVP, 40 mL EG, reaction time 120 h, reaction temperature 180 °C, (c) 100 mg PVP, 40 mL H₂O, reaction time 120 h, reaction temperature 180 °C (d) 100 mg PVP, 40 mL EG, reaction time 120 h, reaction temperature 200 °C.

2 SEM and TEM images of Ni-Fe PBA cubes

Ni-Fe PBA cubes were synthesized using a similar procedure as Co-Fe PBA cubes. Figure S2a showed the SEM image of the as-synthesized Ni-Fe PBA cubes,¹ which exhibited uniform cubic shape as their counterpart Co-Fe PBA cubes. From the TEM image shown in Fig. S2b, it can be seen these solid cubes possessed a size of 160 nm. Figure S3 displayed the XRD pattern of the obtained Ni-Fe PBA cubes, which can be well indexed to the F-43m space group with a composition of $Ni_3[Fe(CN)_6]_2$ 10H₂O (JCPDS 00-046-0906). Note here the peak intensity of (422) crystal plane was much lower than other peaks.



Figure S2 (a) SEM and (b) TEM images of Ni-Fe PBA cubes prepared at the same condition as Co-Fe PBA cubes.



3 XRD pattern of Ni-Fe PBA cubes

Figure S3 XRD pattern and the corresponding JCPDS card (no. 00-046-0906) profile for Ni-Fe PBA cubes.

4 Time-dependent SEM images of Co-Fe MCBs



Figure S4 The time-dependent SEM images showing the growth process of Co-Fe MCBs. (a) 12 h, (b) 24 h, (c) 48 h, (d) 72 h, (e) 96 h, (f) 120 h.



5 Morphology and crystal structure characterizations of CoFe/NC-NCs

Figure S5 (a) SEM, (b) TEM and (c) XRD patterns of the annealed catalyst CoFe/NC-MCBs.

6 XPS profiles of CoFe/NC-MCBs catalyst

XPS spectra were performed in order to gain insight into the chemical valence of the catalyst. As shown in Fig. S6a, the Fe2p peak was split into totally four peaks in the high resolution spectrum. The energy binding located at 710.72 eV was ascribed to Fe²⁺-N/O species, and the peak at 723.80 eV was considered to Fe³⁺-N/O species and

was attributed to FeN_x and Fe₃O₄,² indicating the partial oxidation of the product. The two peaks at 717.72 and 732.95 eV were considered as the satellite peaks of Fe²⁺ and Fe³⁺, respectively. For the Co2p spectrum (Fig. S6b), the peak located at 780.20 eV was assigned to the $2p_{2/3}$ of Co, which can be further split into two peaks, 780.06 and 782.20 eV, belonging to the Co³⁺ and Co²⁺ coordinated to N or O species, respectively.³ Another dominant peak at 795.20 eV can be attributed to the $2p_{1/2}$ of Co, and the other two peaks at 785.44 and 803.39 eV were satellite peaks. The C1s can be deconvoluted into three peaks as shown in Fig. S6c. The peak at 284.77 eV was attributed to C-C/C=C species, and the peak located at 286.33 eV was assigned to C-N/C-O species.⁴ The out-of-plane sp³ carbon was shifted to 288.75 eV.⁵ Figure S6d displayed the O1s spectrum, according to the location these peaks can be clarified into three types. The peak at 529.81 eV belonged to the oxygen coordinated to Fe²⁺/Co²⁺, the peak at 531.90 eV was ascribed to oxygen vacancies on the surface, and the peak at 533.30 eV can be assigned to the chemisorbed oxygen.⁶ The small peak at 534.25 eV may be attributed to the satellite peak.



Figure S6 High-resolution XPS profiles of the catalyst CoFe/NC-MCBs. (a) Fe2p, (b) Co2p, (c) C1s, (d) O1s.

7 UV-Vis profiles of 4-NP after the addition of NaBH₄



Figure S7 UV-Vis spectra of 4-NP in the presence of NaBH₄ without adding catalyst.

8 Catalytic performance of CoFe/NC-NCs for the reduction of 4-NP

The catalytic properties of CoFe/NC-NCs for the reduction of 4-NP were also evaluated as shown in Fig. S8. In comparison with CoFe/NC-MCBs, it needed 32 min for CoFe/NC-NCs to completely convert 4-NP to 4-AP, and the obtained apparent rate constant, k_{app} , was 0.0524 min⁻¹, much lower than its counterpart. This may be caused by the larger particle size and lower crystallinity as shown in Fig. S8.



Figure S8 (a) UV-Vis spectra recording the reduction evolution of 4-NP under CoFe/NC-NCs. (b) Plot of ln (C₁/C₀) versus reaction

time.

9 Photographical images of collection of catalyst after reaction



Figure S9 Photograph of separating the catalyst from the solution after reduction by an external magnet.

10 Catalytic performance of CoFe/NC-MCBs and CoFe/NC-NCs for the reduction of MB



Figure S10 The chemical reaction route and the corresponding UV-Vis spectra for the reduction of MB. (a) Reduction reaction between MB (oxidized) and MB (reduced) in the presence of NaBH₄ and CoFe/NC-MCBs, and the photographs of the corresponding solution. (b) UV-Vis spectra of MB before (black) and after (red) adding NaBH₄ for 6 h. (c) UV-Vis spectra recording the reduction evolution of MB under catalyst. (d) Plot of ln (C_t/C_0) versus reaction time. (e) Recyclability of catalyst for the reduction of MB.



Figure S11 UV-Vis spectra recording the reduction evolution of MB under CoFe/NC-NCs.

11 Catalytic performance of CoFe/NC-MCBs for the reduction of RhB and MO

With the purpose of further extending the potential application of CoFe/NC-MCBs on reduction of other organic dyes, we also tested the catalytic performance of CoFe/NC-MCBs on another two common compounds, RhB and MO. Unfortunately, the results were undesirable. Note that RhB can be completely reduced by NaBH₄ within 6 min as shown in Fig. S12a, therefore, in the case of CoFe/NC-MCBs, NaBH₄ was absent during the reduction of RhB by CoFe/NC-MCBs. From Fig. 12b, it can be seen that after adding CoFe/NC-MCBs to the RhB solution for 60

min, the absorbance peak of RhB around 560 nm decreased only by 12%, which may be caused by the adsorption of RhB into the nanopores and surface of the catalyst. For the reduction of MO, similar phenomenon was observed (Fig. S13). The reason for the different reduction efficiency may be attributed to the different redox potential of this four organic dyes. The electrochemical redox potential of 4-NP, MB, RhB and MO was located at -1.02,⁷ -0.18,⁸ 1.43,⁹ 1.48⁹ V vs NHE, respectively. The lowest redox potential of 4-NP facilitate the fast reduction process in the presence of NaBH₄, similar situation happened to MB. But in the case of RhB and MO it was difficult for CoFe/NC-MCBs to completely reduce them taking into account of their high redox potentials. Further experiment on tuning the morphology and composition of the final catalyst is need to make a clear understanding of the reduction mechanism.



Figure S12 UV-Vis spectra recording the reduction evolution of RhB under (a) NaBH4 and (b) CoFe/NC-MCBs.



Figure S13 UV-Vis spectra recording the reduction evolution of MO under CoFe/NC-MCBs in the presence of NaBH4.

References

- 1. M. Hu, S. Ishihara, K. Ariga, M. Imura and Y. Yamauchi, *Chem. Eur. J.*, 2013, **19**, 1882-1885.
- 2. Y. Wang, D. Liu, Z. Liu, C. Xie, J. Huo and S. Wang, *Chem. Commun.*, 2016, **52**, 12614-12617.
- 3. H. S. Jeon, M. S. Jee, H. Kim, S. J. Ahn, Y. J. Hwang and B. K. Min, ACS Appl. Mater. Interfaces, 2015, 7, 24550-24555.
- 4. Y. Tong, X. Yu, H. Wang, B. Yao, C. Li and G. Shi, *ACS Catal.*, 2018, **8**, 4637-4644.
- 5. H.-x. Zhong, Q. Zhang, J. Wang, X.-b. Zhang, X.-l. Wei, Z.-j. Wu, K. Li, F.-l. Meng, D. Bao and J.-m. Yan, *ACS Catal.*, 2018, **8**, 3965-3970.
- 6. R. Wei, M. Fang, G. Dong, C. Lan, L. Shu, H. Zhang, X. Bu and J. C. Ho, *ACS Appl. Mater. Interfaces*, 2018, **10**, 7079-7086.
- 7. Amatore, C.; Capobianco, G.; Farnia, G.; Sandona, G.; Saveant, J. M.; Severin, M. G.; Vianello, E., Kinetics and mechanism of self-protonation reactions in organic electrochemical processes. *J. Am. Chem. Soc.* **1985**, *107*, 1815-1824.
- 8. Ghosh, S. K.; Kundu, S.; Mandal, M.; Pal, T., Silver and gold nanocluster catalyzed reduction of methylene blue by arsine in a micellar medium. *Langmuir* **2002**, *18*, 8756-8760.
- 9. Yan, S.; Li, Z.; Zou, Z., Photodegradation of rhodamine B and methyl orange over boron-doped g-C3N4 under visible light irradiation. *Langmuir* **2010**, *26*, 3894-3901.