

Supporting Information

A general approach towards multi-faceted hollow oxide composites using zeolitic imidazolate frameworks

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S1

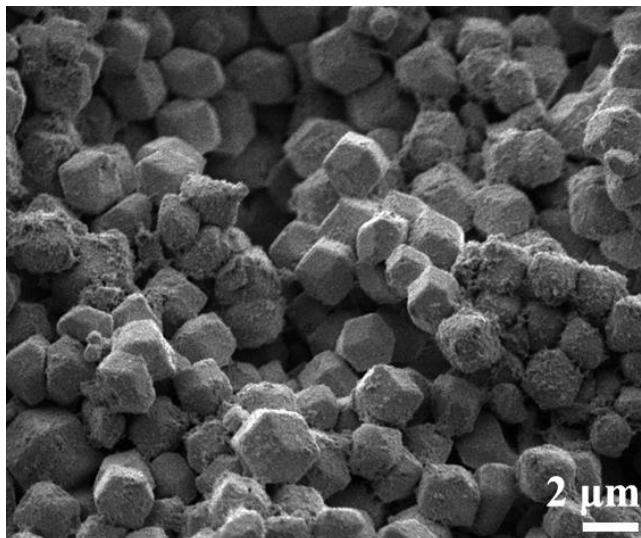


Fig. S1 An FESEM image of XRD patterns of $\text{Co}_3\text{O}_4/\text{SiO}_2$ hollow dodecahedra.

S2

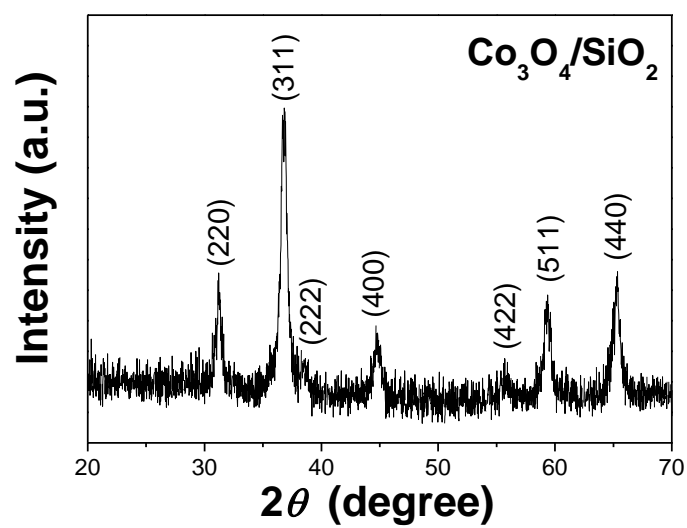


Fig. S2 XRD patterns of Co₃O₄/SiO₂ hollow dodecahedra.

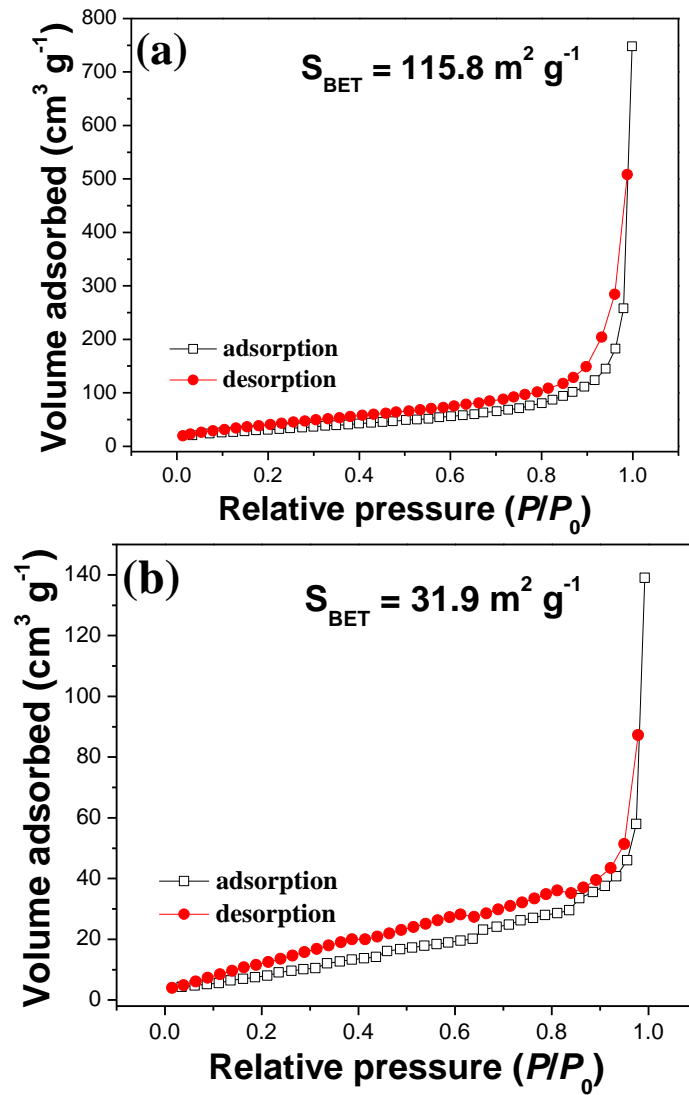


Fig. S3 Nitrogen adsorption-desorption isotherms of (a) $\text{Co}_3\text{O}_4/\text{SiO}_2$ -100 hollow dodecahedra and (b) Co_3O_4 nanostructures

S4

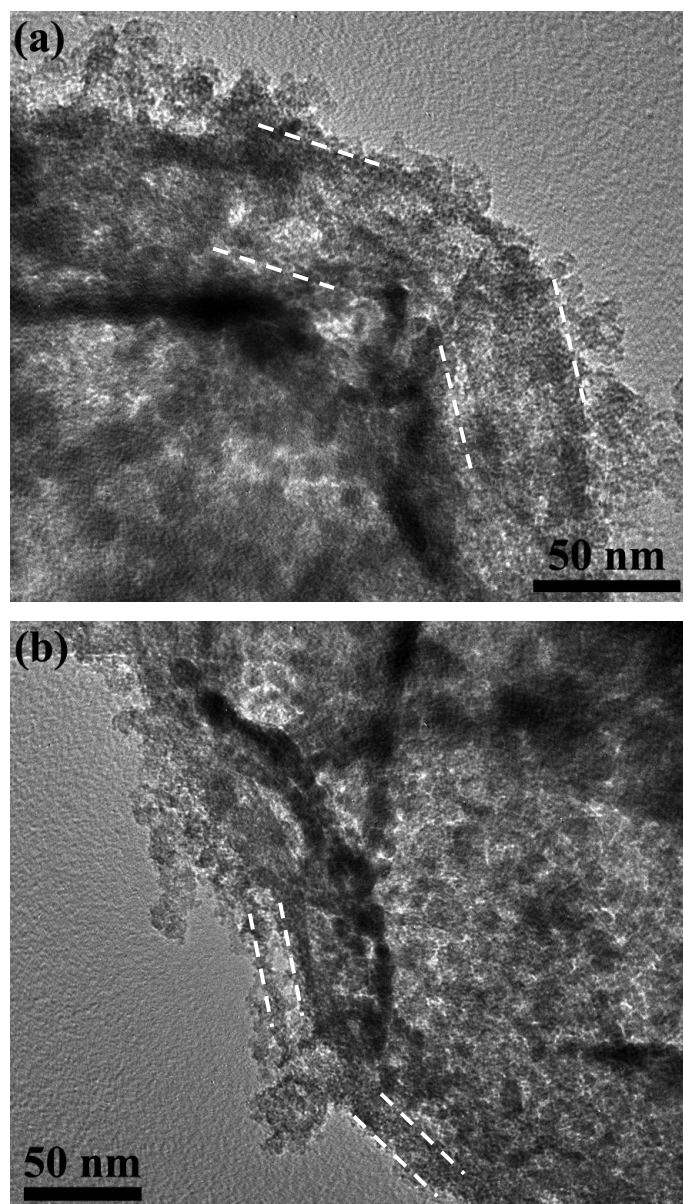


Fig. S4 TEM images of the $\text{Co}_3\text{O}_4/\text{SiO}_2$ hollow dodecahedra with different SiO_2 shell thicknesses obtained by adding different amounts of TEOS in the sol-gel process: (a) 60 μL and (b) 30 μL .

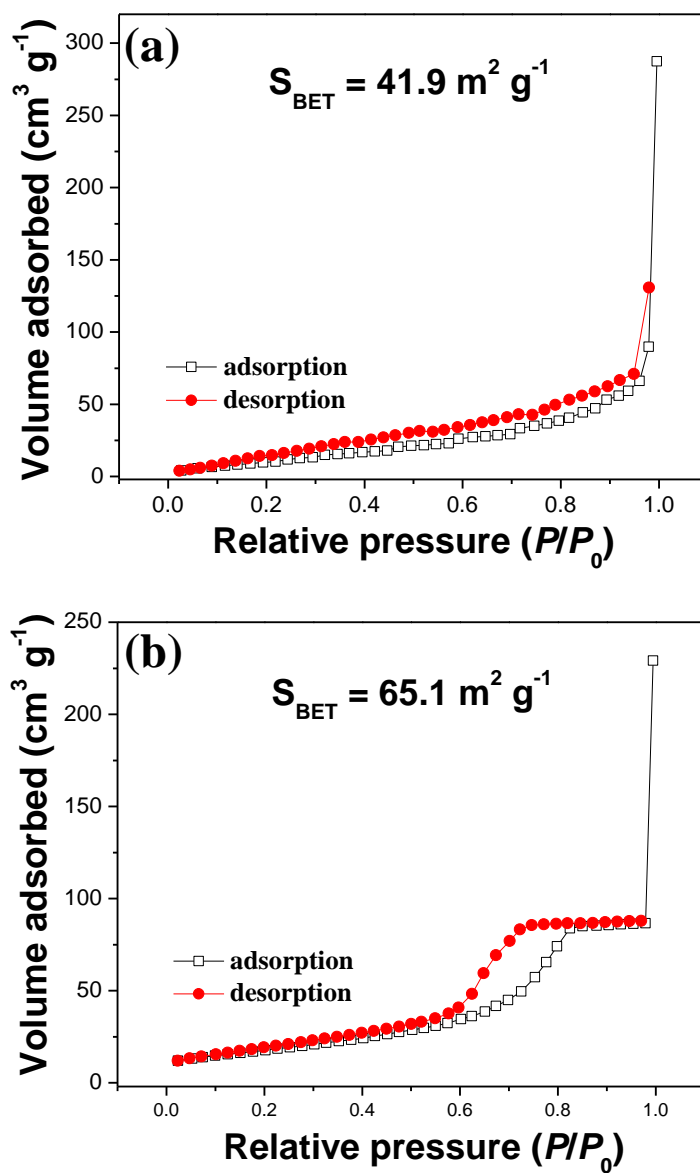


Fig. S5 Nitrogen adsorption-desorption isotherm curves of (a) $\text{Co}_3\text{O}_4/\text{TiO}_2$ hollow dodecahedra and (b) TiO_2 .

S6

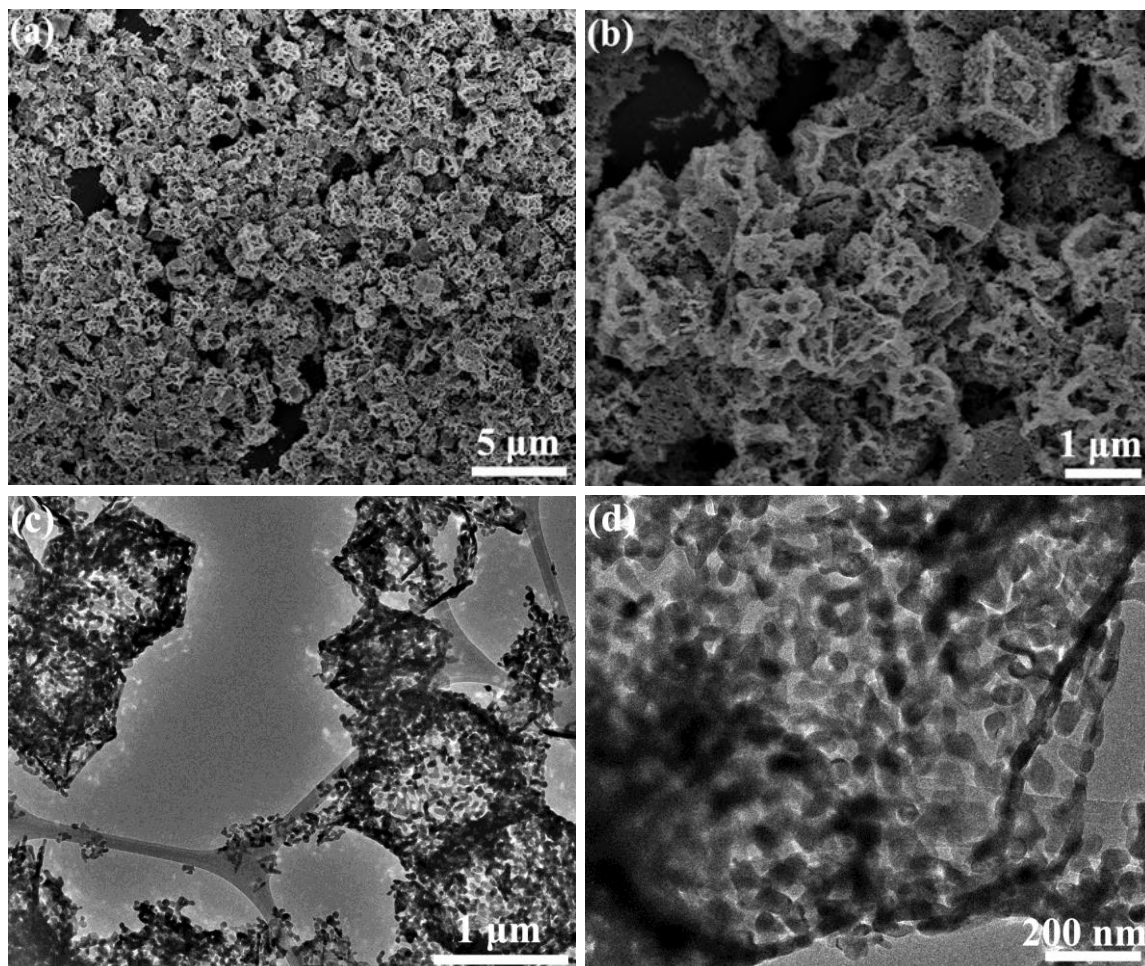


Fig. S6 (a) Low- and (b) high-magnified FESEM images, and (c) low- and (d) high-magnified TEM images of Co_3O_4 nanostructures obtained by directly heating bare ZIF-67 templates.

S7

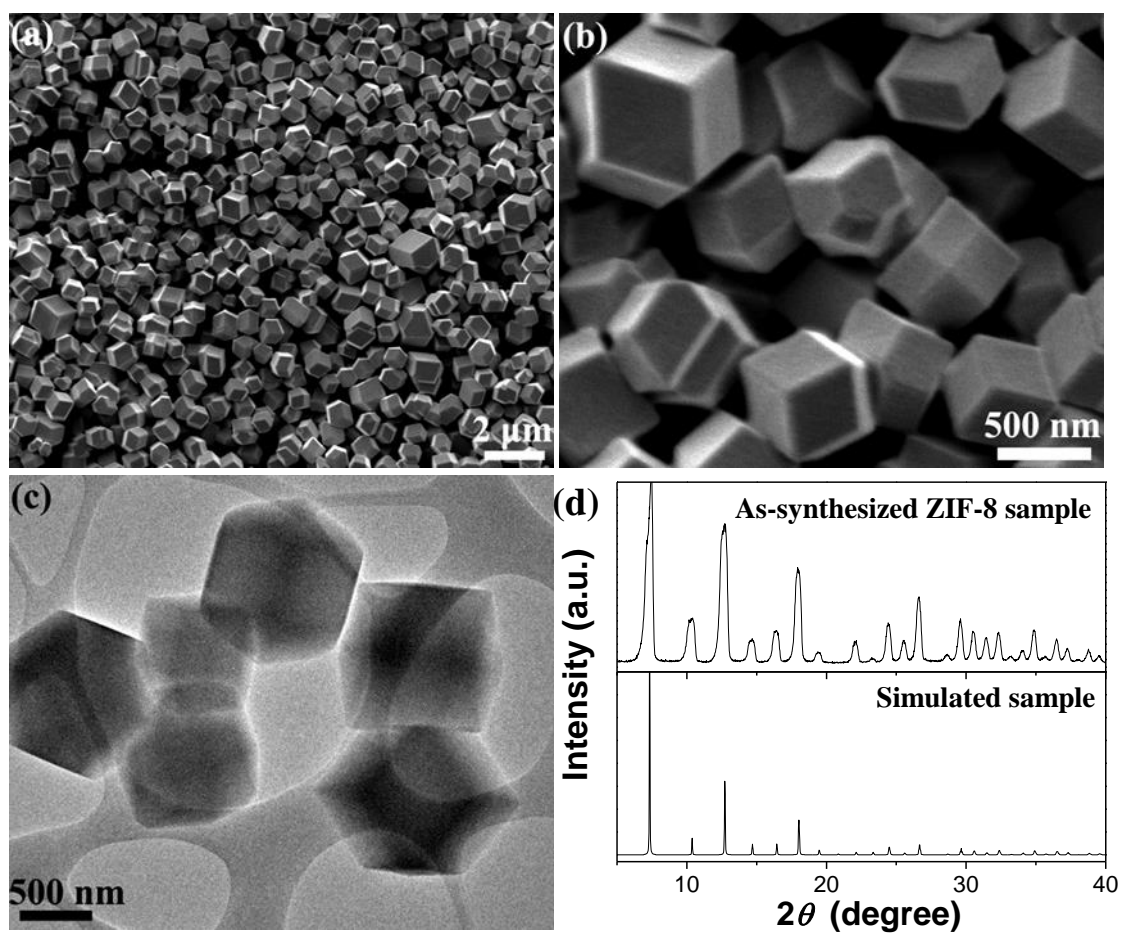


Fig. S7 (a) Low- and (b) high-magnified FESEM images, and (c) TEM image of ZIF-8; (d) experimental and simulated XRD patterns of ZIF-8.

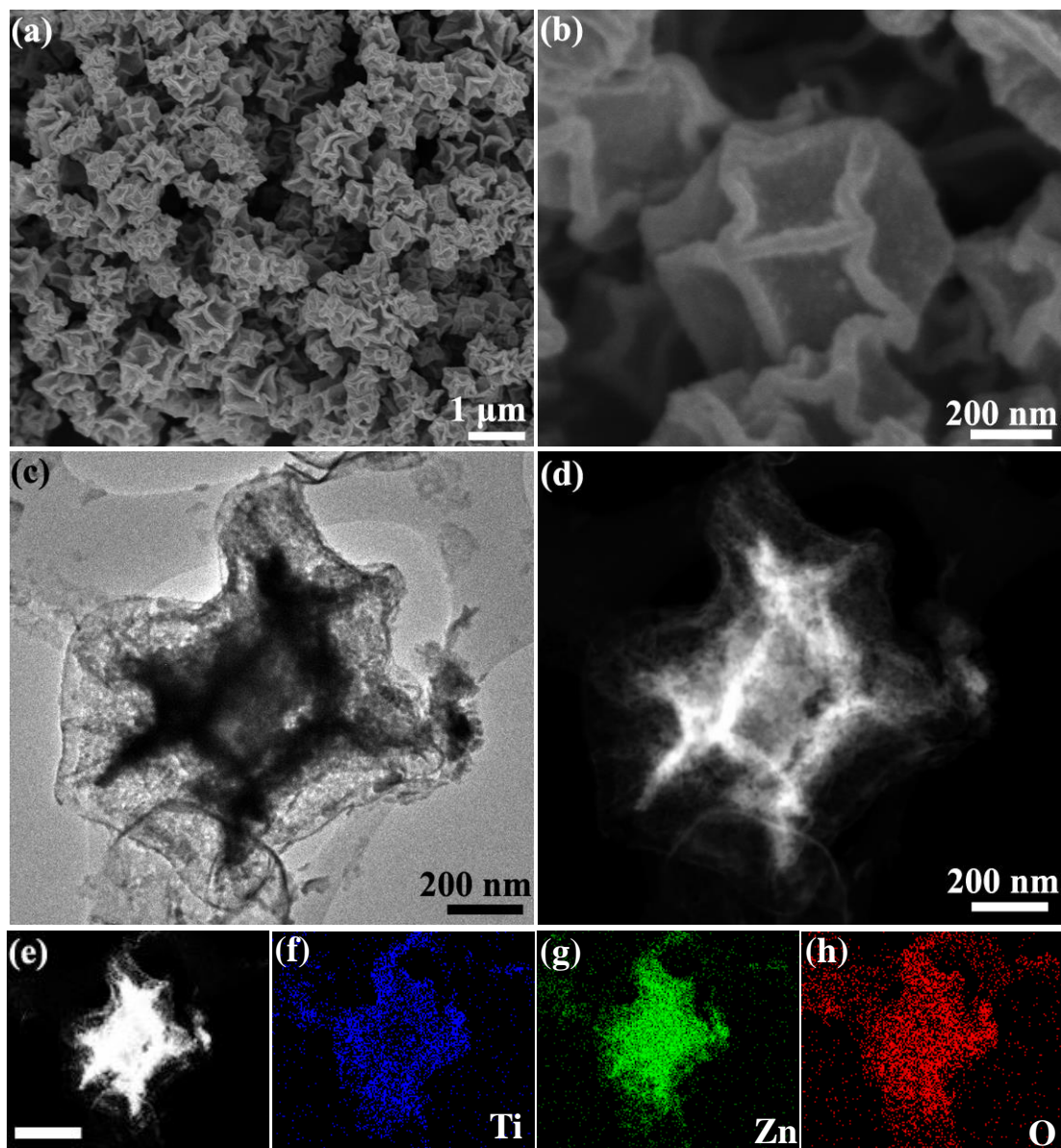


Fig. S8. (a) Low- and (b) high-magnified FESEM images of ZnO/TiO₂ hollow dodecahedra, (c) TEM image and (d) HAADF-STEM image of a single ZnO/TiO₂ hollow dodecahedron, (e)-(h) EDX-elemental mapping images of a single ZnO/TiO₂ hollow dodecahedron, the scar bar in (e) is 500 nm.

S9

Turnover frequency was calculated based on the total Co species added into reactor, assuming all the Co atoms present evolved in the photocatalytic reaction.¹⁻⁴

Turnover frequency calculation as follows:

$$\text{Turnover frequency} = \frac{\text{Produced oxygen in first 10 mins (mol/s)}}{\text{Active sites number (mol)}}$$
$$\text{Active sites number (mol)} = 3 \times \frac{m_{\text{Co}_3\text{O}_4}}{M_{\text{Co}_3\text{O}_4}}$$

Table S1. Turnover frequencies for all catalyst

Catalyst	Co ₃ O ₄ (wt.%)	O ₂ yield as in 1 st 10 mins (μmol)	Turn frequencies (s ⁻¹ per Co atom) × 10 ⁴
Co ₃ O ₄	100	17.7 ± 1.5	2.4
Co ₃ O ₄ + SiO ₂	70.3	14.4 ± 2.0	2.8
Co ₃ O ₄ -30	80.7	19.1 ± 2.3	3.2
Co ₃ O ₄ -60	70.3	48.3 ± 2.6	9.2
Co ₃ O ₄ -100	63.8	34.6 ± 1.4	7.3

References

- [1] J. Feng; F. Heinz, *Angew. Chem. Int. Ed.* **2009**, 48, 1841.
- [2] Y. Surendranath, M. W. Kanan, D. G. Nocera, *J. Am. Chem. Soc.* **2010**, 132, 16501.
- [3] R. Jonathan, S. H. Gregory, J. Feng, *J. Am. Chem. Soc.* **2013**, 135, 4516.
- [4] R. Zheng, G. Yanbing, Z. H. Zhang, C. H. Liang, P. Gao. *J. Mater. Chem. A*, **2013**, 1, 9897.