Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Synthesis of core-shell ZIF-67@Co-MOF-74 catalyst with controllable shell thickness and enhanced photocatalytic activity for visible light-driven water oxidation

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1. Experimental

1.1 Materials and Reagents

Cobalt (II) nitrate hemipentahydrate ($Co(NO_3)_2$•$6H_2O$), 2-methylimidazole (2-MI), 2,5-dihydroxyterephthalic acid (DHTP), 1,4-dicarboxybenzene (H_2BDC), 2-aminoterephthalic acid (NH_2-H_2BDC), benzene-1,3,5-tricarboxylic acid (H_3BTC), methanol were purchased from Adamas-beta, Sigma-Aldrich and used as received.

1.2 Synthesis of $[Ru(bpy)_3](ClO_4)_2$

$[Ru(bpy)_3](ClO_4)_2$ was synthesized according to reference 2.The 4 M $HClO_4$ was adding to an aqueous solution of $[Ru(bpy)_3]Cl_2$ and then separated by filtration.

2. N_2 adsorption/desorption isotherms

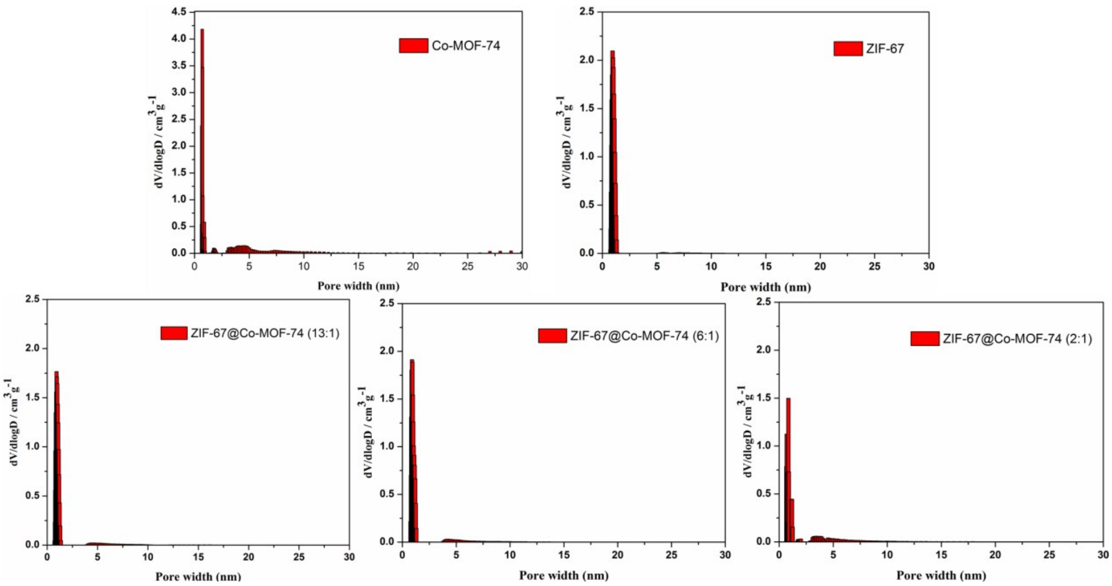

Figure S1. DFT method pore size distribution of the Co-MOF-74, ZIF-67 and core-shell ZIF-67@Co-MOF-74 catalyst with different shell thickness.

Table S1. Values of the catalyst estimated from the N_2 adsorption/desorption isotherms.

Sample	S_{BET} ($m^2 \cdot g^{-1}$)	V_{pore} ($cm^3 \cdot g^{-1}$)	Pore size (nm)
ZIF-67	2129	0.72	0.93
ZIF-67@Co-MOF-74 (13:1)	1878	0.71	0.93
ZIF-67@Co-MOF-74 (6:1)	1848	0.71	0.89
ZIF-67@Co-MOF-74 (2:1)	1647	0.70	0.85
Co-MOF-74	882	0.65	0.79

3. Catalytic performance optimization

3.1 Different sodium persulfate concentration

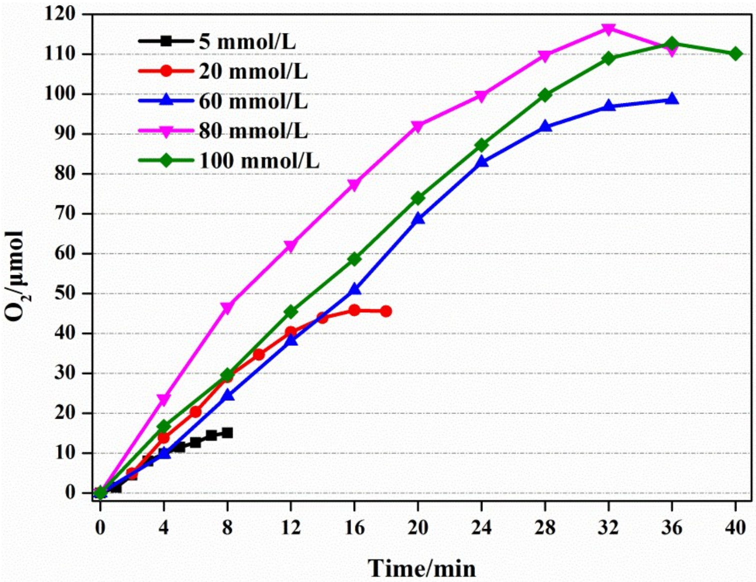

Figure S2 Kinetics of O_2 evolution of the photocatalytic system with core-shell ZIF-67@Co-MOF-74 with different shell thickness as catalysts. Conditions: Xe lamp (l Z 420 nm, 26.4 mW cm^{-2}); catalyst (1 mg); 1.0 mM $[Ru(bpy)_3](ClO_4)_2$, $Na_2S_2O_8$ (5/20/60/80/100 mmol/L), and 80 mM sodium borate buffer (initial pH, 9.0); total reaction volume: 10 mL.

3.2 Different PH value

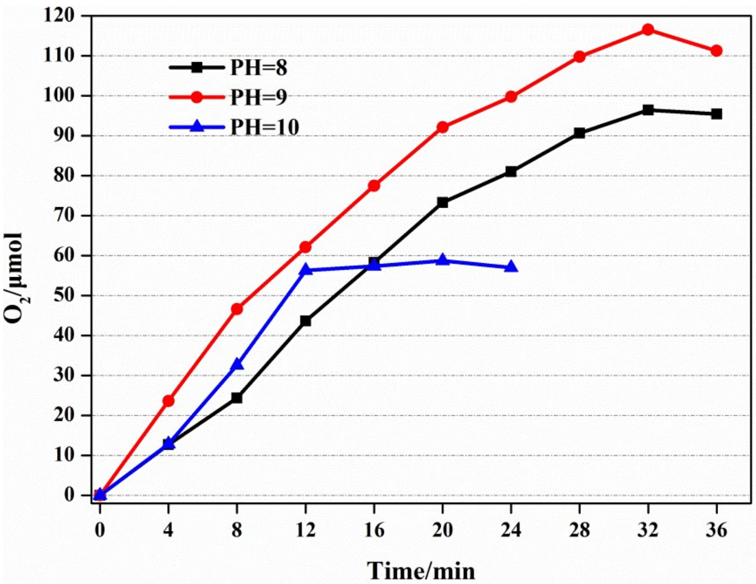

Figure S3 Kinetics of O_2 evolution of the photocatalytic system with core-shell ZIF-67@Co-MOF-74 with different shell thickness as catalysts. Conditions: Xe lamp (l Z 420 nm, 26.4 mW cm^{-2}); catalyst (1 mg); 1.0 mM $[Ru(bpy)_3](ClO_4)_2$, 80.0 mM $Na_2S_2O_8$, and 80 mM sodium borate buffer (initial pH, 8.0, 9.0, 10.0); total reaction volume: 10 mL.

3.3 The different amount of catalyst

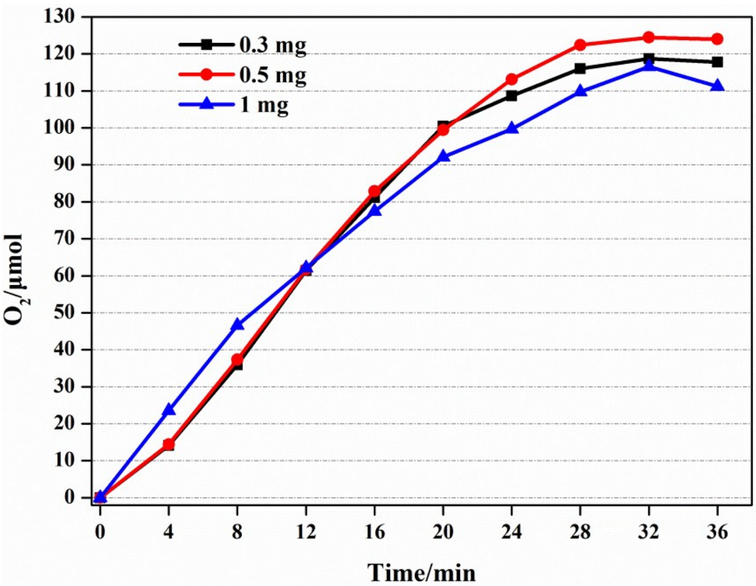

Figure S4 Kinetics of O_2 evolution of the photocatalytic system with ZIF-67, Co-MOF-74 and core-shell ZIF-67@Co-MOF-74 with different shell thickness as catalysts. Conditions: Xe lamp (l Z 420 nm, 26.4 mW cm^{-2}); catalyst (0.3/0.5/1 mg); 1.0 mM $[Ru(bpy)_3](ClO_4)_2$, 80.0 mM $Na_2S_2O_8$, and 80 mM sodium borate buffer (initial pH, 9.0); total reaction volume: 10 mL.

4. Stability studies

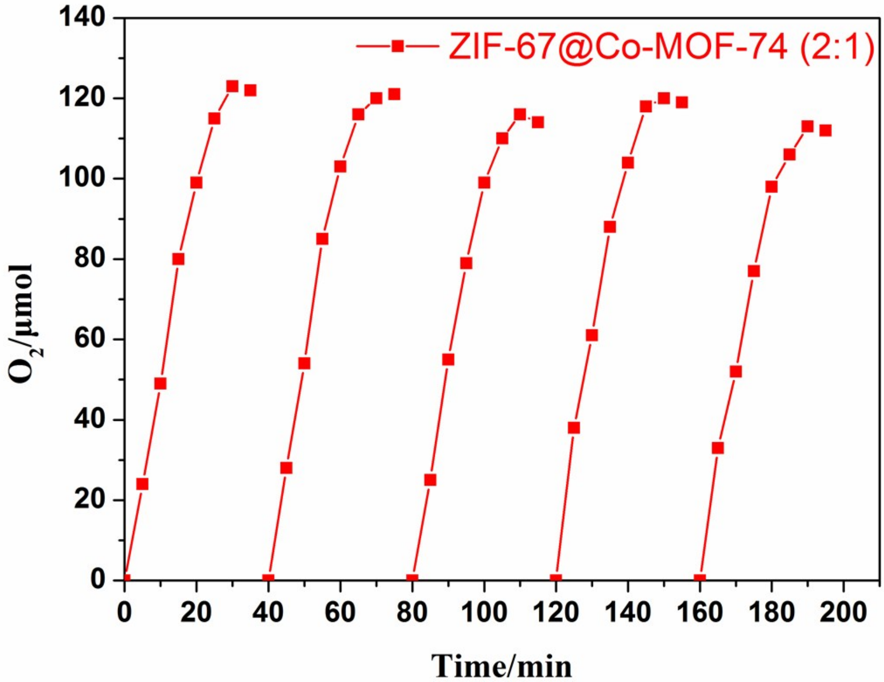

Figure S5. Kinetics of O_2 formation in the photocatalytic system using core-shell ZIF-67@Co-MOF-74 (2:1) and recovered catalysts. Conditions: Xe lamp (l Z 420 nm, 26.4 mW cm^{-2}); catalyst (0.5 mg); 1.0 mM $[Ru(bpy)_3](ClO_4)_2$, 80.0 mM $Na_2S_2O_8$, and 80 mM sodium borate buffer (initial pH, 9.0); total reaction volume: 10 mL.

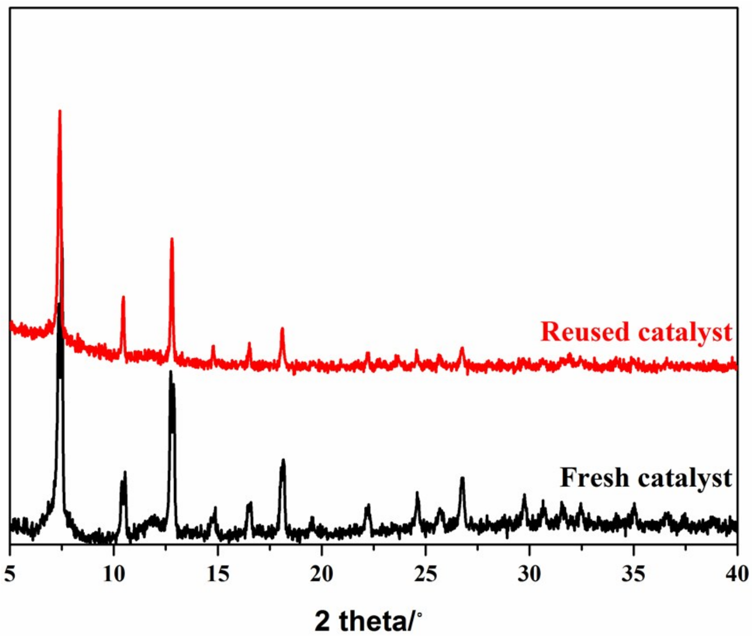

Figure S6. PXRD of the fresh and reused ZIF-67@Co-MOF-74 (2:1) catalyst.

5. Quantum yield calculation

The initial quantum yield (Φ) of photon-to-oxygen generation was calculated by the expression[S1-S3]:

AR (the photic area of reactor) = d·h = 2×3.5 cm^2 = 7.0 cm^2

E = 52.8 mW·cm^{-2}

P = E ·AR

= 52.8×7.0 mW

= 369.6 mW

$$\text{Photon flux} = \frac{P\lambda}{hc} = \frac{52.8 \times 10^{-3} \times 7 \times 60 \times 28 \times 420 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 1.3 \times 10^{21}$$

$$\Phi_{QY\ (initial)} = 2 \times \frac{Number\ of\ evolved\ O2\ molecules}{Number\ of\ absorbed\ photons} \times 100\ \%$$

$$= 2 \times \frac{122.38 \times 10^{-6} \times 6.02 \times 10^{23}}{1.3 \times 10^{21}} \times 100\ \%$$

= 11.3%

6. References

[S1] S. Goberna-Ferrón, W. Y. Hernández, B. Rodríguez-García and J. R. Galán-Mascarós, *ACS Catal*. **2014**, *4*, 1637−1641.

[S2] F. Song, Y. Ding, B. Ma, C. Wang, Q. Wang, X. Du, S. Fu and J. Song, *Energy Environ. Sci*. **2013**, *6*, 1170–1184.

[S3] J. Liu, Y. Liu, N. Liu, Y. Han, X. Zhang, H. Huang, Y. Lifshitz, S. T. Lee, J. Zhong, Z. Kang, *Science*. **2015**, *347*, 970-974.