

Supplementary Information

Co-ZIF-9/TiO₂ nanostructure for superior CO₂ photoreduction activity

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Preparation of ZIF_x/T films

The ZIF_x/T films used for the electrochemical test were prepared via a spin-coating method. 5 mg of ZIF_x/T samples were firstly dispersed into 3 mL of ethanol solvent by ultrasonic treatment for 30 min, then spin-coated on the ITO substrate layer by layer. In the procedure of spin coating, every drop of the ZIF_x/T suspension was about 0.05 mL, and 2 drops of suspension in total was dripped on the ITO substrate in each cycle. The spin speed and time were 200 rpm for 10 s followed with 600 rpm for 40 s. Finally, the coated films were heated to 110 °C at a rate of 1 °C/min and kept at this temperature for 4 h.

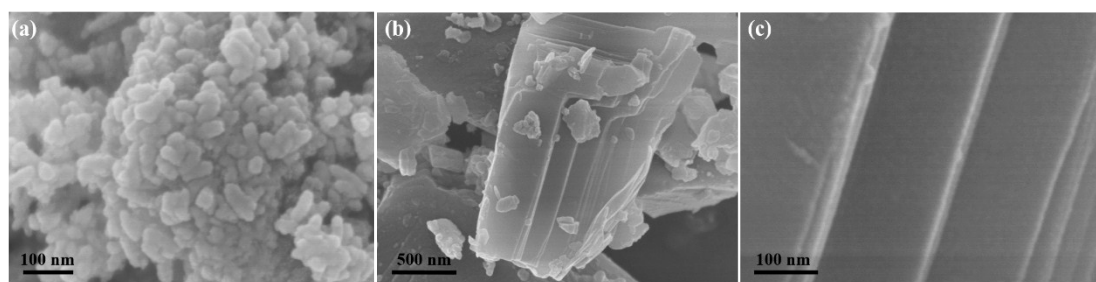


Fig. S1 SEM images of as-prepared TiO₂ (a), Co-ZIF-9 in low magnification (b) and high magnification (c).

The size and morphology of the as-prepared TiO₂ and Co-ZIF-9 were observed by the SEM. As shown in Fig. S1a, pure TiO₂ consists of large amounts of small nanoparticles aggregated together. The Co-ZIF-9 appears as the assembly of sheets with the length of ~2 μm (Fig. S1b-c), and the TEM image further confirmed that those sheets are only several nanometers in thickness (Fig. 3a).

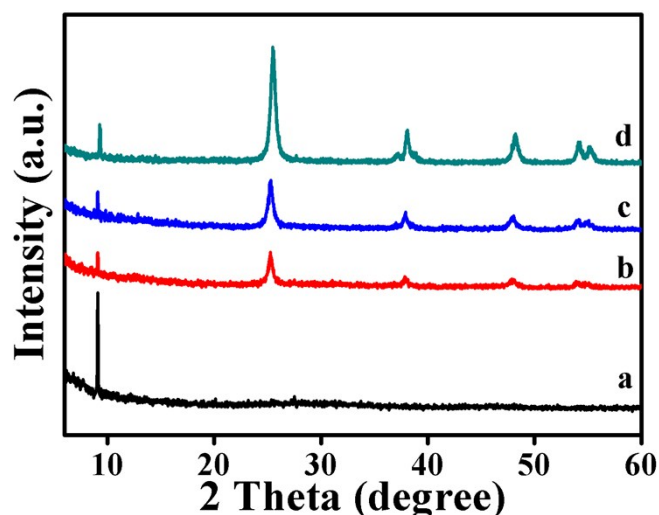


Fig. S2 XRD patterns of the intermediate products obtained at various crystal growth stages for ZIF_{0.10}/T composite. (a) hydrolysis of Ti precursor to obtain amorphous TiO₂ over Co-ZIF-9 after 12 h of magnetic stirring. (b-d) crystalline of TiO₂ after 3, 6, 12 h of solvothermal treatment.

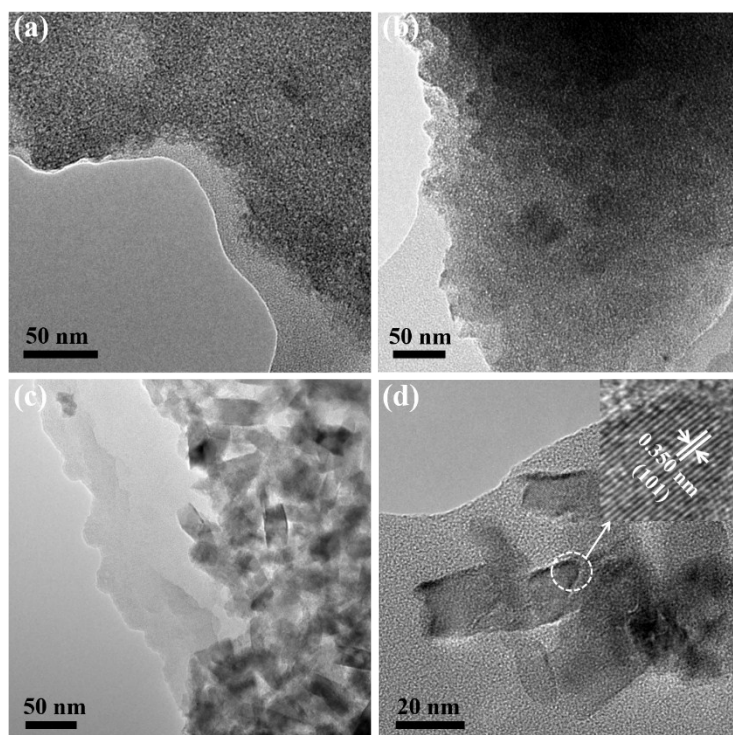


Fig. S3 TEM images of the intermediate products obtained at various crystal growth stages for ZIF_{0.10}/T composite. (a) hydrolysis of Ti precursor to obtain amorphous TiO₂ over Co-ZIF-9 after 12 h of magnetic stirring. (b-d) crystalline of TiO₂ after 3, 6, 12 h of solvothermal treatment.

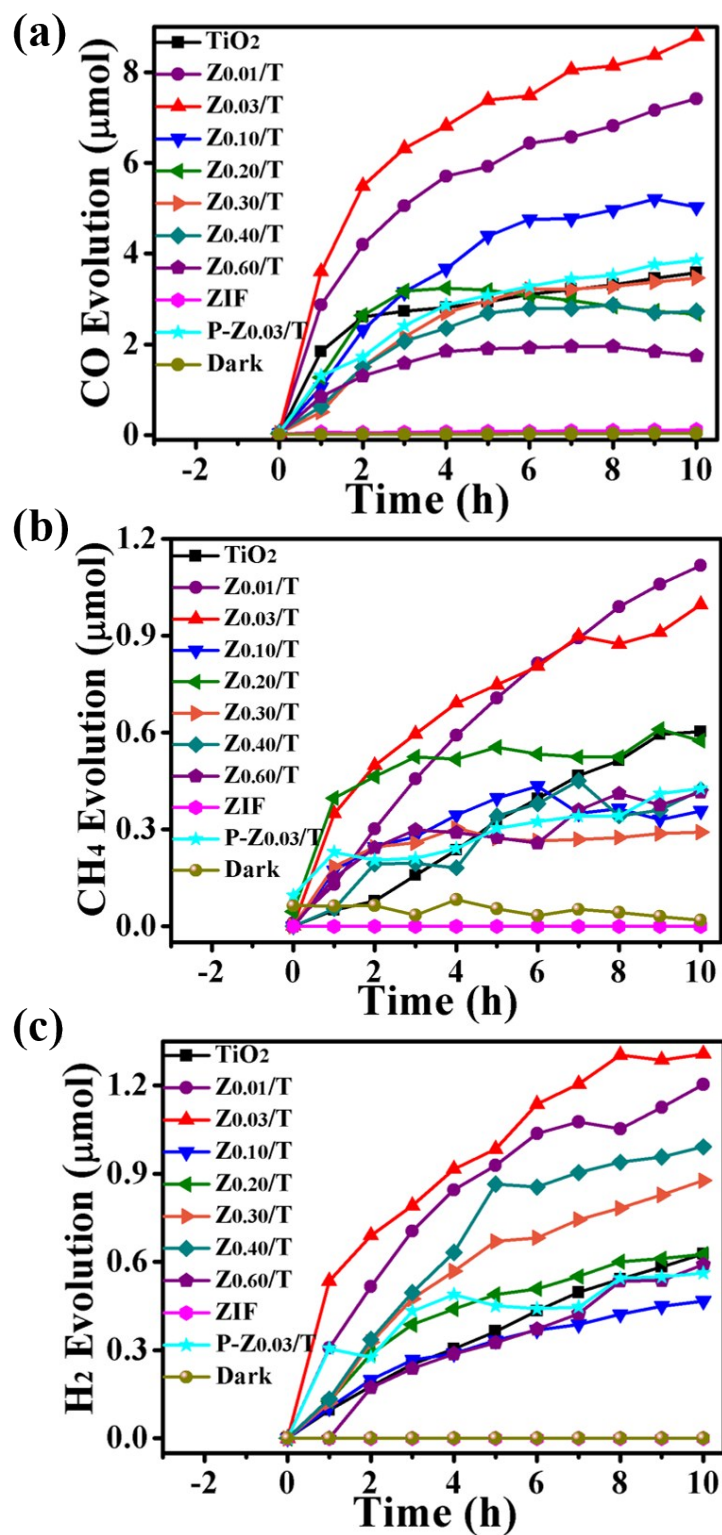


Fig. S4 CO₂ photoreduction activity of as-prepared TiO₂ and ZIF_x/T composites. (a) CO, (b) CH₄, and (c) H₂ evolution.

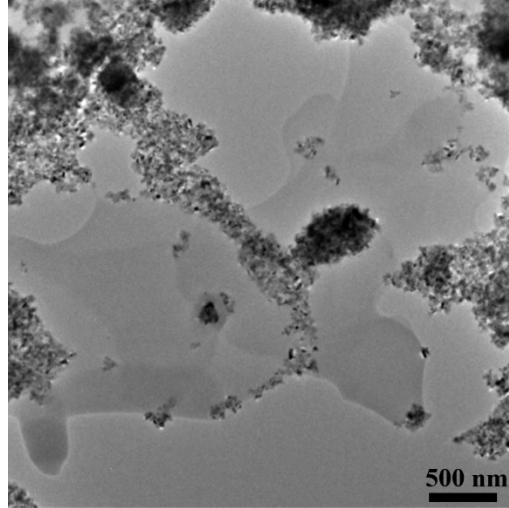


Fig. S5 TEM image of physically mixed Co-ZIF-9/TiO₂ composite (P-ZIF_{0.03}/T).

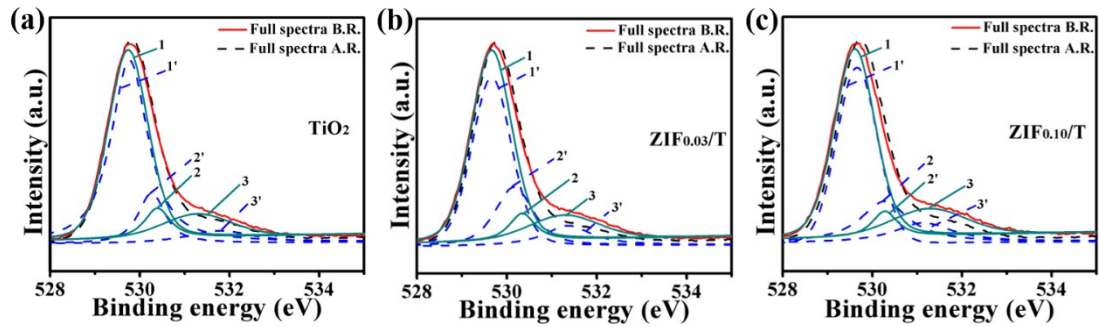


Fig. S6 O 1s XPS spectra of (a) TiO₂, (b) ZIF_{0.03}/T, and (c) ZIF_{0.10}/T before reaction (B. R., solid line) and after reaction (A. R., dashed line). Curves 1&1', curves 2&2', and curves 3&3' in (a, b, c) associate with lattice O, adsorbed O_2^- , and -OH, respectively.

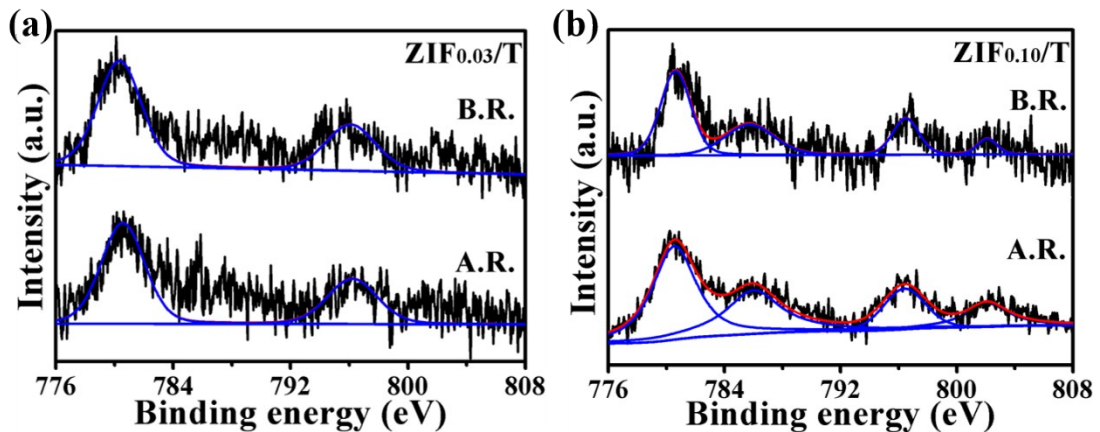


Fig. S7 Co 2p XPS spectra of (a) ZIF_{0.03}/T and (b) ZIF_{0.10}/T before reaction (B. R.) and after reaction (A. R.).

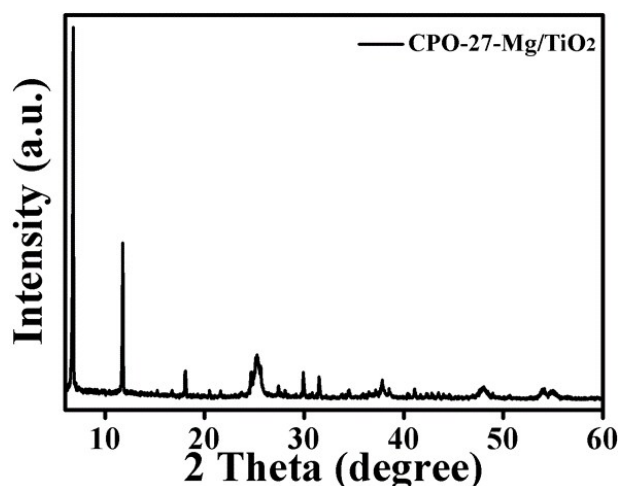


Fig. S8 XRD pattern of prepared CPO-27-Mg/TiO₂.

CPO-27-Mg/TiO₂ composite was prepared according to the procedure described in the literature [*Appl. Catal. B: Environ.*, 2016, 183, 47]. Firstly, 0.61 mmol of H₄DOBDC (BOBDC = 2,5-dioxido-1,4-benzenedicarboxylate) was dissolved in 18 mL of tetrahydrofuran in the 50 ml of Teflon inlet of autoclave, then 2.5 mL of NaOH (1 mol·L⁻¹) was added to this solution under constant stirring. After that, 2 mmol of TiO₂ and 1.21 mmol of Mg(NO₃)₂·6H₂O in 5 mL of de-ionized water was added to the above solution. After 30 min of vigorous stirring, the autoclave was sealed and heated at 110 °C for 72 h. The final product was collected by filtration, washed thoroughly with methanol and water for several times, then dried at 60 °C in vacuum.

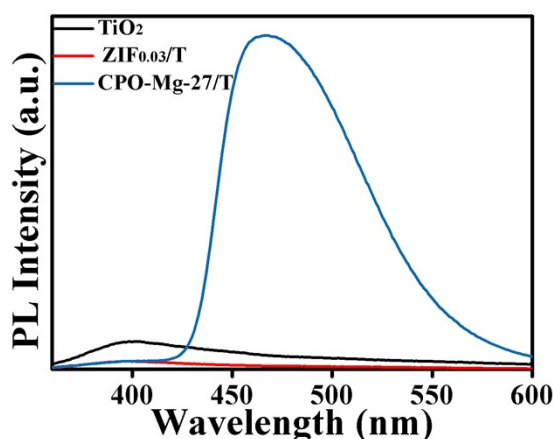


Fig. S9 Photoluminescence (PL) spectra of TiO₂, ZIF_{0.03}/T, and CPO-27-Mg/TiO₂.

Table. S1 Binding energy (eV) of Co 2p XPS spectra in ZIF_{0.03}/T and ZIF_{0.10}/T samples.

	Co 2p _{3/2}		Satellite peak 1		Co 2p _{1/2}		Satellite peak 2	
	B.R.	A.R.	B.R.	A.R.	B.R.	A.R.	B.R.	A.R.
ZIF _{0.03} /T	780.44	780.50	-	-	796.15	796.20	-	-
ZIF _{0.10} /T	780.63	780.54	785.72	785.90	796.49	796.40	802.08	802.12

Table S2 CO₂ photoreduction activity of ZIF_{0.03}/T in contrast to the Co(NO₃)₂/TiO₂ composite and the reported CPO-27-Mg/TiO₂ nanocomposite under the irradiation of Xe lamp in 10 h.

	CO (μmol)	CH ₄ (μmol)	H ₂ (μmol)	UPN (μmol)
TiO ₂	3.58	0.60	0.62	13.24
ZIF _{0.03} /T	8.79	0.99	1.30	28.17
Co(NO ₃) ₂ /TiO ₂	3.66	0.62	0.91	14.14
CPO-27-Mg/TiO ₂	5.56	1.19	0.21	21.15