Electronic Supplementary Information

Semicondutor-Redox Catalysis Promoted by Metal-Organic Frameworks for CO_2 Reduction

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Experimental section

Chemicals. Chemical reagents for the preparation of samples and the reactions are all purchased from Alfa Aesar and used without further purification, including cobalt nitrate hexahydrate ($Co(NO_3)_2{\bullet}6H_2O$), benzimidazole (H-PhIM), bipyridine (bpy), triethanolamine (TEOA), N,N-dimethylformaide (DMF), dichloromethane (DCM), Acetonitrile (MeCN), tetrahydrofuran (THF) and dimethylsulfoxide (DMSO). Carbon dioxide gas, supplied by Fuzhou Lianzhong Industrial Gases Co., Ltd, is super grade purity (99.999%). The $^{13}CO_2$ is 97% enriched.

Preparation of Co-ZIF-9. In the preparation of Co-ZIF-9 [$Co(PhIM)_2$],[1] $Co(NO_3)_2{\bullet}6H_2O$ (0.210 g) and benzimidazole (0.060 g) were dissolved in 18 ml DMF. The resulted solution was stirred for 30 min and was capped in a 20 ml glass vial. The vial was placed in a programmed oven, heated to 135°C from room temperature by a rate of 5 °C/min and held at this temperature for 48h. Then the vial was cooled to room temperature by a rate of 0.4 °C/min. The purple cubic crystals were separated from the mother liquor, washed several times with DMF and DCM, and dried under vacuum in air.

Synthesis of $g\text{-}C_3N_4$. Mesoporous graphitic carbon nitride ($g\text{-}C_3N_4$) was prepared according to the reported procedure.[2] In a typical preparation, 5 g of cyanamide was dissolved a 40 %

dispersion of 12-nm SiO_2 particles (Ludox-HS40, Aldrich) in water with stirring at 80 °C until removal of water. The resulting mixtures were heated at a rate of 2.3 °C/min up to 550 °C and held at this temperature for 4h. The resulting yellow powders were treated with 4M NH_4HF_2 and washed with deionized water and ethanol for several times. Finally, the yellow powders were dried under vacuum at 80 °C for 12 h.

Characterizations. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer using Cu $K_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å), 40 KV, 40 mA with a scanning speed of 0.2°(2θ)/min. The fourier transform infrared (FTIR) spectra in the range of 4000-500 cm^{-1} were obtained on a Nicolet 670 FTIR spectrometer in KBr at a concentration of ca. 1%wt. Photoluminescence (PL) spectra were performed on an Edinburgh FL/FS900 spectrophotometer at room temperature. CO_2 adsorption properties of Co-ZIF-9 were determined at 0 °C on Micromeritics ASAP 2020 and the micropore surface areas were calculated by the Dubinbin-Radushkevich method. Before analysis the sample was degassed under vacuum at 200 °C for 8 hours to eliminate the guest molecules adsorbed on the surface and within the pores of the sample. Photocurrent measurements were performed with a CHI Electrochemical System in the mixture of MeCN and H_2O (v/v = 3/2) without any bias potential. A graphite rod and an Ag/AgCl (3 M KCl) electrode were used as the counter electrode and reference electrode, respectively. The working electrodes were irradiated from the back side to minimize the influence of the semiconductor layer.

Measurements. Gas chromatographic analysis was carried out on an Agilent 7820A gas chromatography equipped with a thermal conductivity detector (TCD) and a TD-01 packed column. The oven temperature was held constant at 50 °C. Inlet and detector temperature were set at 120 °C and 200 °C, respectively. A HP 5973-Agilent 6890 gas chromatography mass spectrometry (GC-MS) was employed to analyze the products of the $^{13}CO_2$ isotopic experiment.

Photocatalytic activity testing. The photocatalytic reactions were performed in an 80 ml reactor at 30 °C controlled by cooling water and 1bar CO_2 partial pressure. The reaction system containing C_3N_4 (20 mg), Co-ZIF-9 (4 µmol, 1 mg), bipyridine (10 mg), solvent (5 ml, acetonitrile: H_2O = 3: 2), TEOA (1 ml) by stirring with a magnetic stirrer and irradiated under a Xe lamp with a 420 nm cutoff filter. Agilent 7820A gas chromatography was employed to analyze the gases after reactions. Before the photocatalytic reactions, the Co-ZIF-9 sample were activated by thermal treatment under vacuum to eliminate the guest molecules trapped on the surface and in the channels of Co-ZIF-9 as described in the Supporting Information of the literature.[3] The formula of $Co(PhIM)_2$ was used to quantify the micromole of Co-ZIF-9 in the reactions. In the controlled experiments, the used amount of Co^{2+} and the precursors of Co-ZIF-9 were the same micromole as that of Co-ZIF-9.

Quantum yield measurement. A LED lamp (low-power 420 nm-LED, Shenzhen LAMPLIC Science Co. China) was employed as the light source for measuring the apparent quantum yield (AQY) for CO/H_2 evolution on the same photochemical experimental setup. The intensity of the incident monochromatic light (420 nm) was determined as 24.6 mW/cm^2 measured by a Newport 842-PE Power/Energy Meter with photodiode detectors. The irradiated area was controlled at 1.0 cm^2. The reaction temperature was 40 ^oC and the reaction time was 1 h. The calculation procedures of apparent quantum yield are in the following:

$2H^+ \rightarrow H_2$	$2e^-$	1h	0.4 µmol
$CO_2 \rightarrow CO$	$2e^-$	1h	1.0 µmol

Major parameters:
Light intensity: $I = 24.6\ mW/cm^2$
$P = I \times t \times S$, ($t = 3600s$, $S = 1\ cm^2$)
$E = n \times h \times \nu$, ($h = 6.626 \times 10^{-34}$ j·s, $\lambda = 420$ nm)

$$AQY\ (\%) = \frac{(\text{number of the produced molecule}) \times 2}{(\text{number of photons})} \times 100\%$$

So, AQY = 0.9 %

Table S1. Photocatalytic performance of Co-ZIF-9 and g-C_3N_4 based CO_2 reduction system as a function of system components.[a]

Entry	CO / µmol	H_2 / µmol	CO+H_2 / µmol	Sel.$_{CO}$ [b] / [%]
1	20.8	3.3	24.1	86.3
2[c]	n.d.[d]	n.d.	-	-
3[e]	n.d.	n.d.	-	-
4[f]	n.d.	n.d.	-	-
5[g]	0.1	0.3	0.4	25.0
6[h]	n.d.	n.d.	-	-
7[i]	n.d.	0.9	0.9	-
8[j]	15.6	4.5	20.1	77.6
9[k]	14.4	2.4	16.8	85.7

[a] Reaction conditions: g-C_3N_4 (20 mg), Co-ZIF-9 (4 µmol, 1 mg), bpy (10 mg), solvent (5 ml, MeCN: H_2O = 3: 2), TEOA (1 ml), λ>420 nm, 30 °C, 2 h. [b] Sel.$_{CO}$ = mol(CO)/mol(CO+H_2). [c] In the dark. [d] No detectable. [e] Without g-C_3N_4. [f] Without Co-ZIF-9. [g] Without bpy. [h] Without TEOA. [i] Using Ar instead of CO_2. [j] Using Co^{2+} instead of Co-ZIF-9. [k] Using precursors (H-PhIM and $Co(NO_3)_2 \cdot 6H_2O$) to replace Co-ZIF-9.

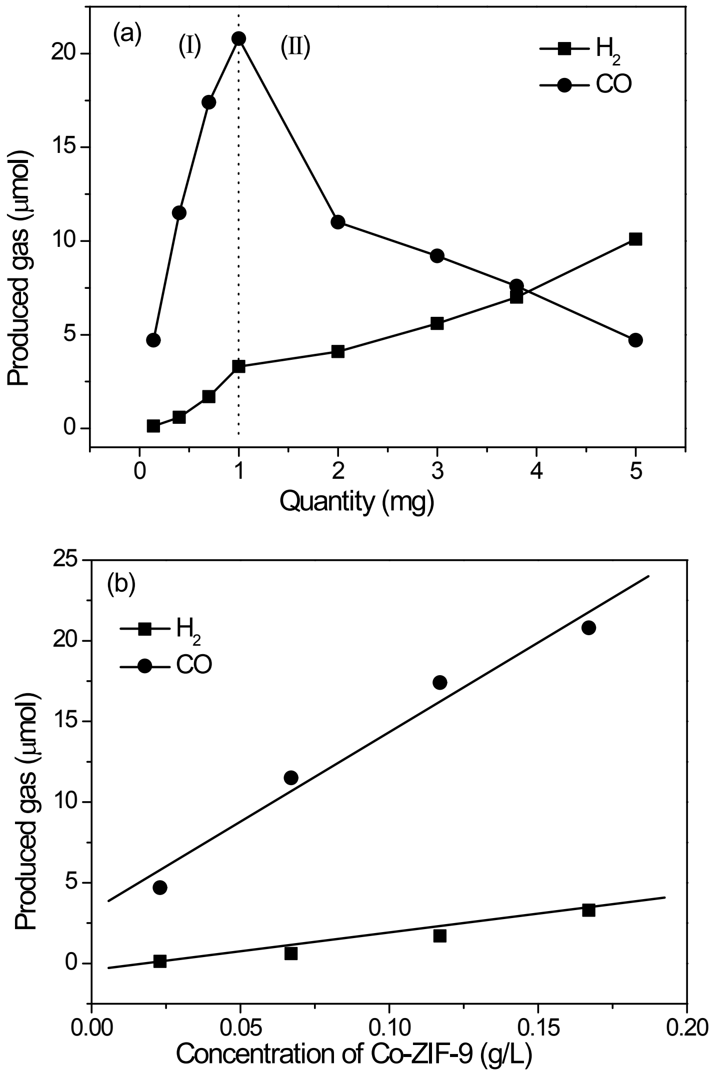

Fig. S1. (a) The production of CO and H_2 as a function of the adding amount of Co-ZIF-9. (b) Initial production of CO and H_2 as a function of Co-ZIF-9 concentration. g-C_3N_4 (20mg), TEOA (1 ml), bpy (10 mg), solvent (5 ml, MeCN: H_2O = 3: 2), $\lambda > 420$ nm, 30 °C, 2 h. The reaction pathways for the evolution of CO and H_2 are different. In the region I, the reaction rate is largely determined by the diffusion of the reactants, while in the region II, the reaction rate is mainly limited by the electron-transfer kinetics.[4]

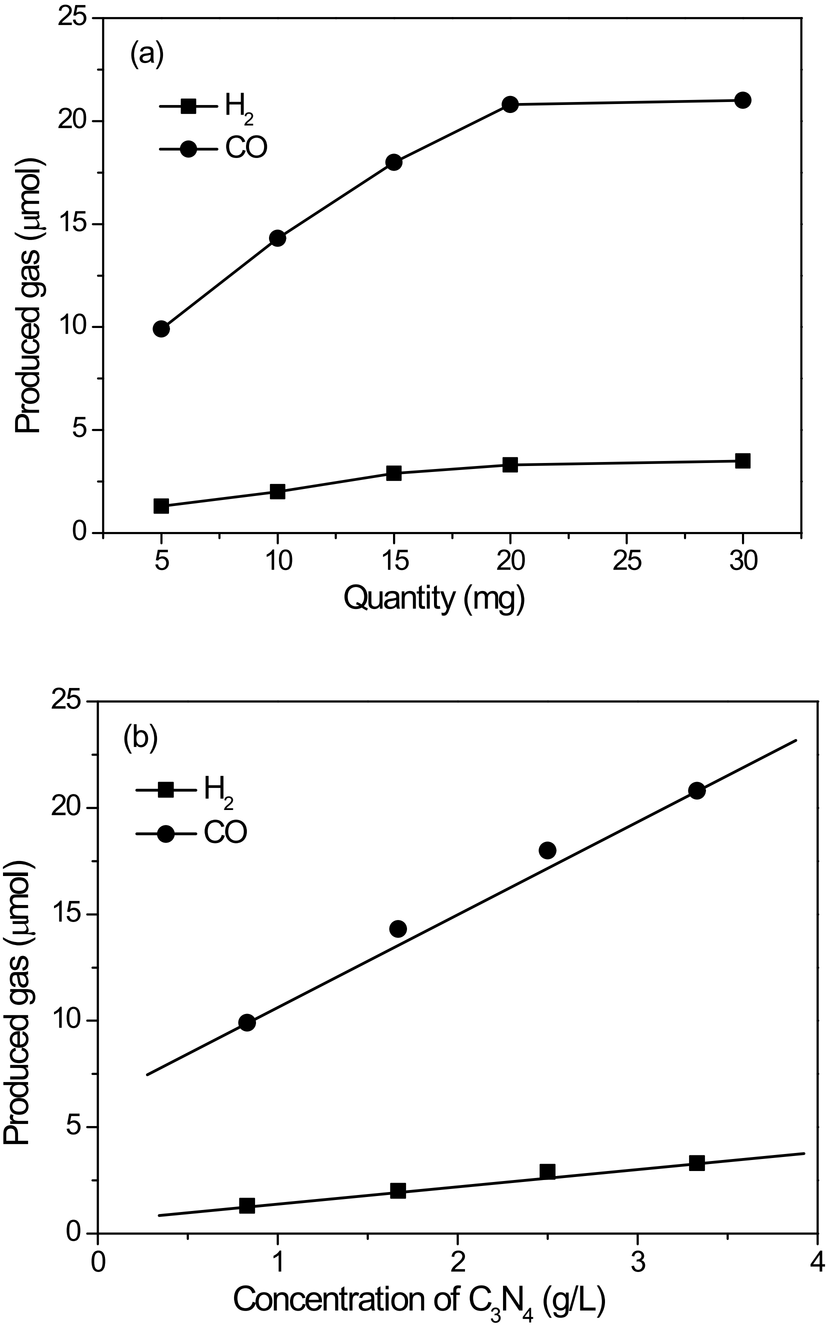

Fig. S2 (a) The production of CO and H_2 as a function of the adding amount of g-C_3N_4. (b) Initial production of CO and H_2 as a function of the concentration of g-C_3N_4. Co-ZIF-9 (1 mg), TEOA (1 ml), bpy (10 mg), solvent (5 ml, MeCN: H_2O = 3: 2), $\lambda > 420$ nm, 30 °C, 2 h.

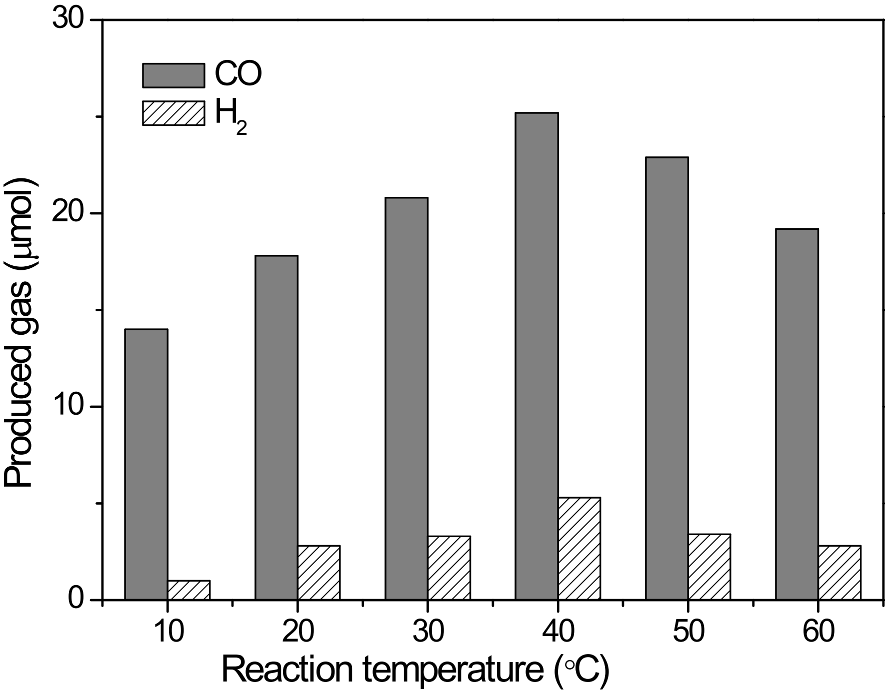

Fig. S3 The relationship between the reaction temperature and the catalytic efficiency of the CO_2 photoreduction system.

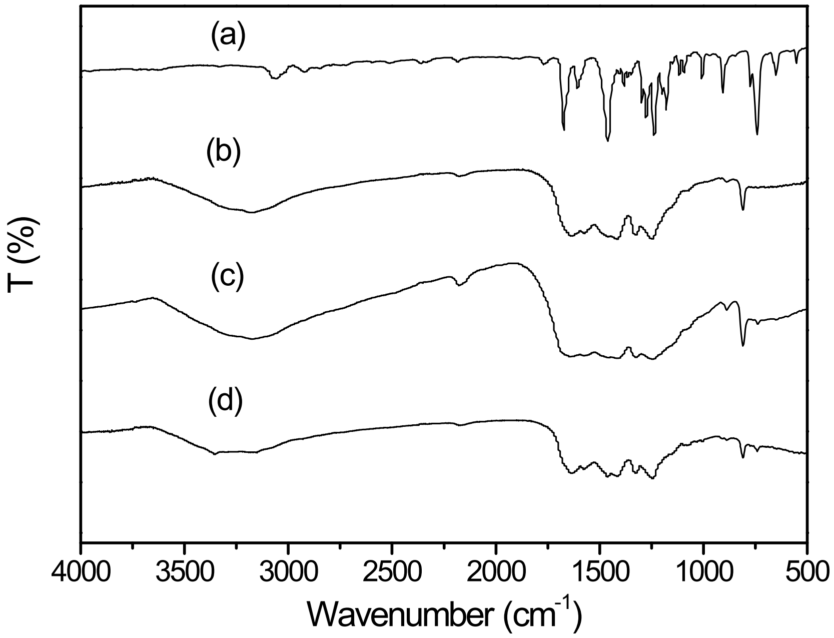

Fig. S4 FTIR spectra of Co-ZIF-9 (a), g-C_3N_4 (b), the fresh (c) and the used (d) mixture of Co-ZIF-9 and g-C_3N_4.

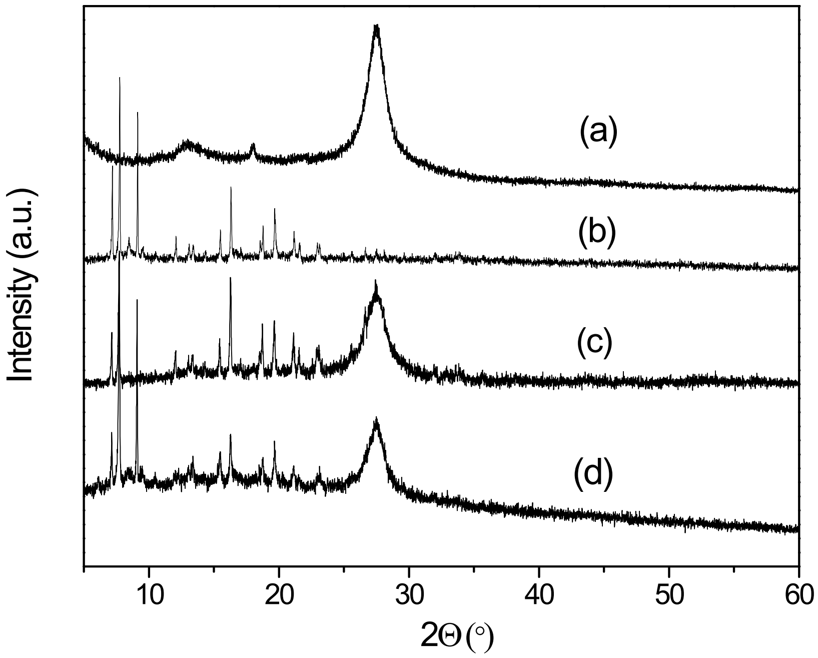

Fig. S5 XRD patterns of g-C_3N_4 (a), Co-ZIF-9 (b), the fresh (c) and used (d) mixture of Co-ZIF-9 and g-C_3N_4.

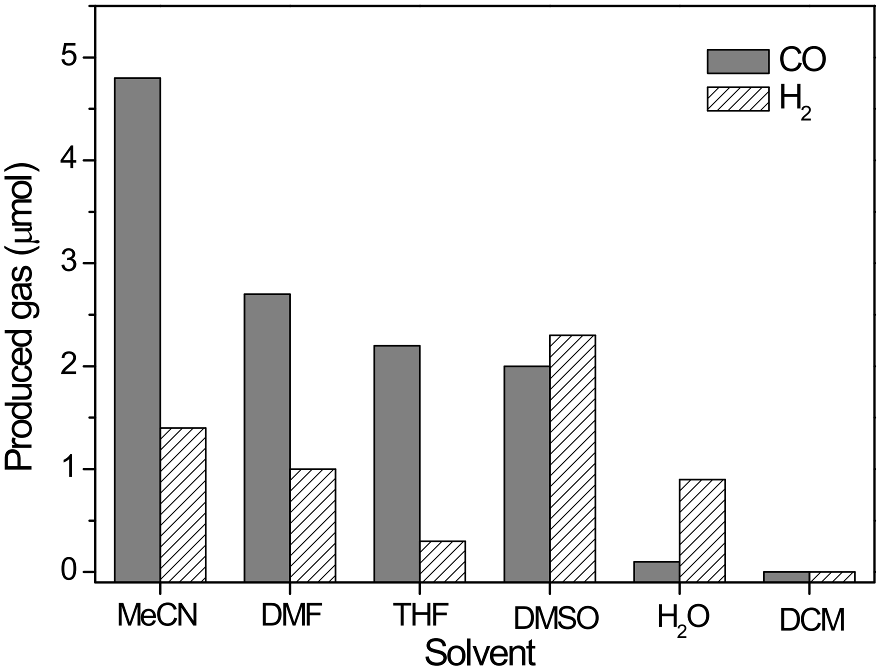

Fig. S6 The production of CO and H_2 in various reaction mediums (MeCN: acetonitrile, DMF: N, N-dimethylformaide, THF: tetrahydrofuran, DMSO: dimethylsulfoxide, DCM: dichloromethane).

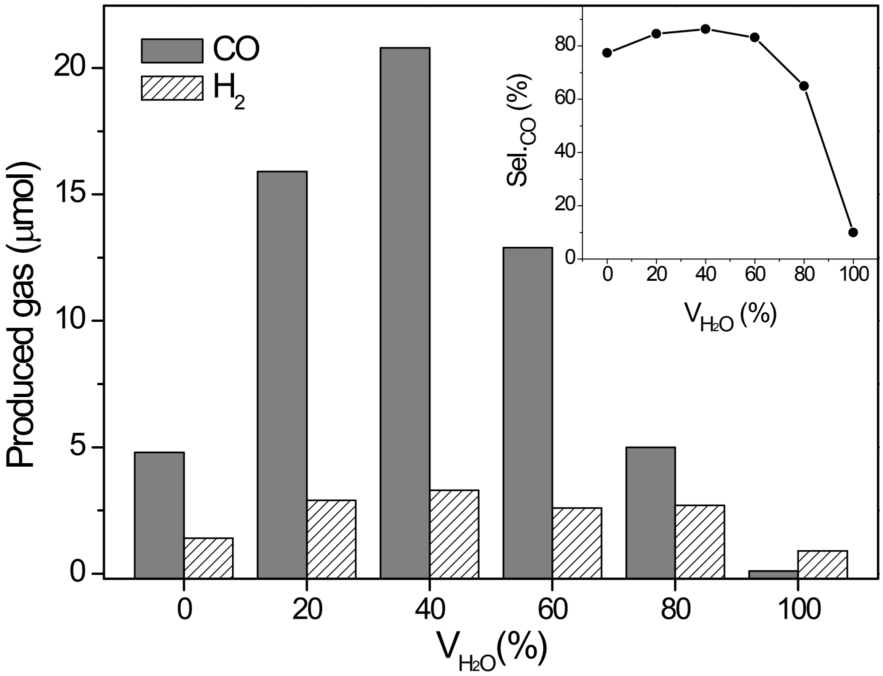

Fig. S7 The effects of the amount of water contained in reaction system on the catalytic performance of CO_2 conversion. Insert: Plot of CO selectivity *vs.* the ratio of water.

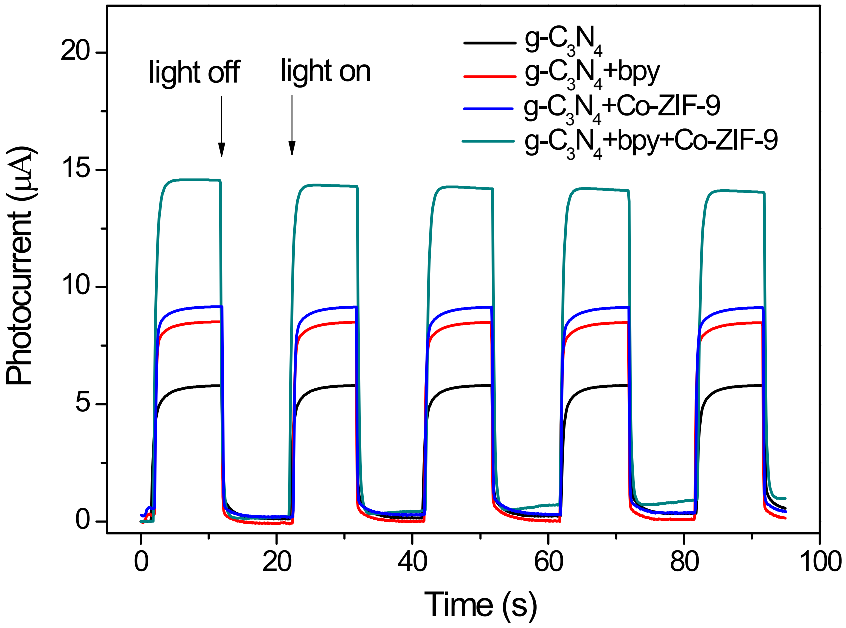

Fig. S8. Transient photocurrent response of the reaction system under visible light irradiation (λ > 420 nm).

References

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[3] S. Wang, W. Yao, J. Lin, Z. Ding, X. Wang, *Angew. Chem. Int. Ed.*, 2014, **53** 1034.

[4] T. Maschmeyer, M. Che, *Angew. Chem. Int. Ed.*, 2010, **49**, 1536.