Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

A Co_3O_4-embedded porous ZnO rhombic dodecahedron prepared using zeolitic imidazolate frameworks as precursors for CO_2 photoreduction

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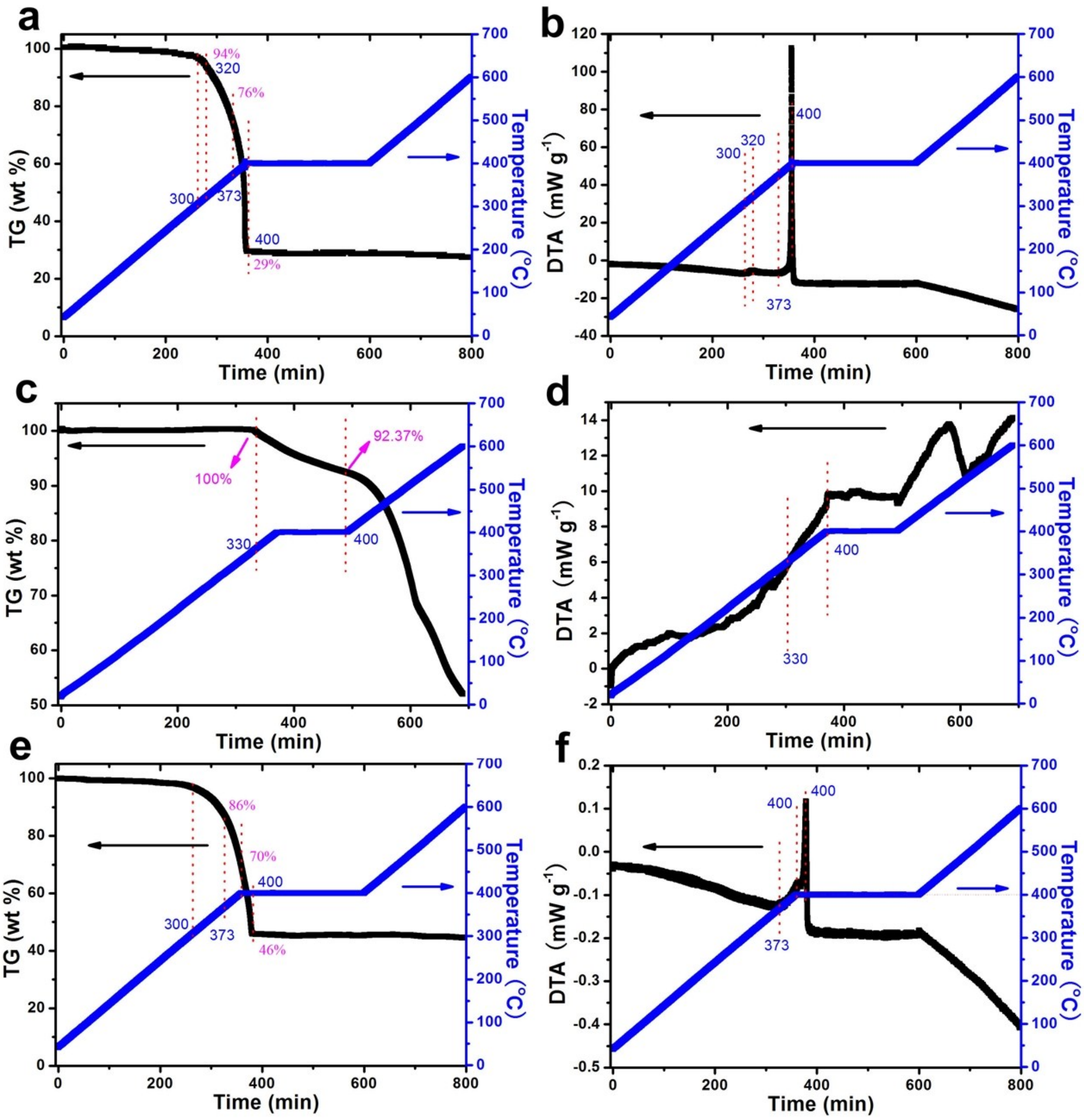

Fig. S1 (a,b) TG and DTA curves of ZIF-8 recorded in air (one-step calcination). (c,d) TG and DTA curves of ZIF-8@ZIF-67 recorded in N_2 (the first-step calcination in a N_2 atmosphere); (e,f) TG and DTA curves of ZIF-8@ZIF-67 recorded in air (the second-step calcination in an air atmosphere).

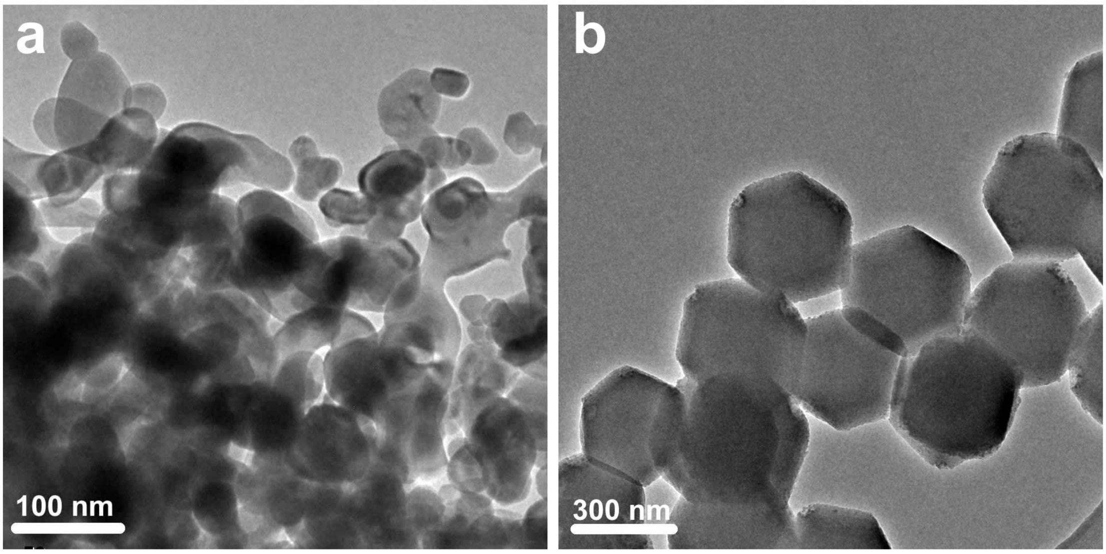

Fig. S2 TEM image of (a) ZnO-2 prepared from ZIF-8 *via* one-step calcination in an ambient atmosphere, (b) ZnO@Co_3O_4 precursor prepared from the core-shell ZIF-8@ZIF-67 crystals in a tubular furnace at 400 ^oC for 2 h under a N_2 atmosphere at a heating rate of 1 ^oC min^{-1} to obtain.

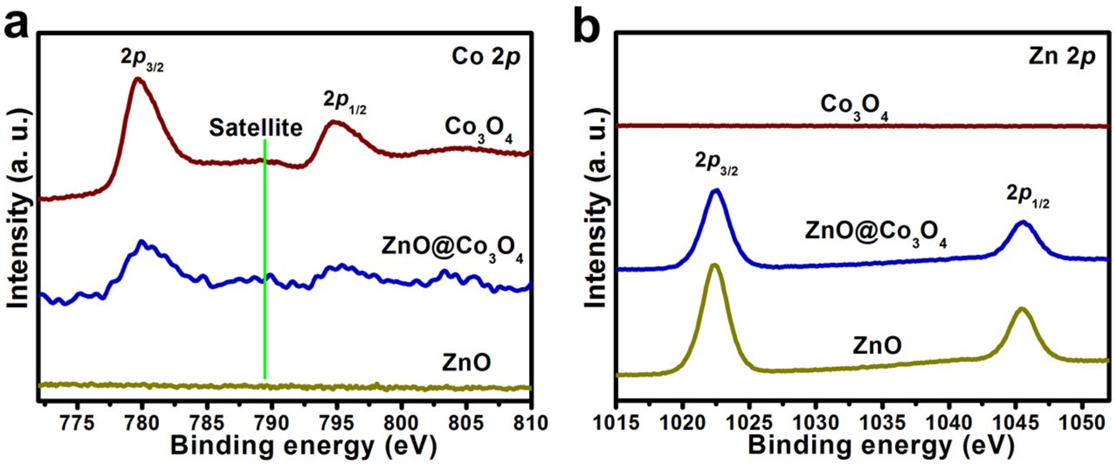

Fig. S3 High resolution XPS centered on (a) Co *2p* and (b) Zn *2p* for the ZIFs derived samples.

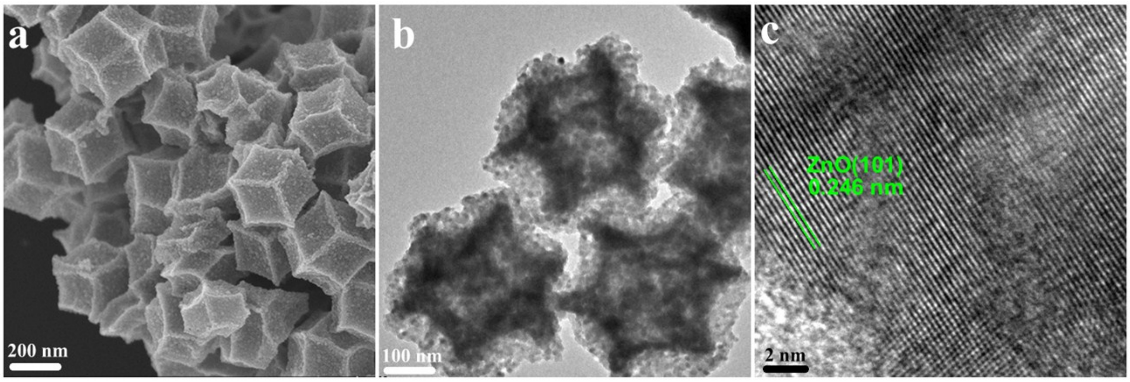

Fig. S4 (a) SEM, (b) TEM, and (C) high resolution TEM images of ZIF-8 derived ZnO.

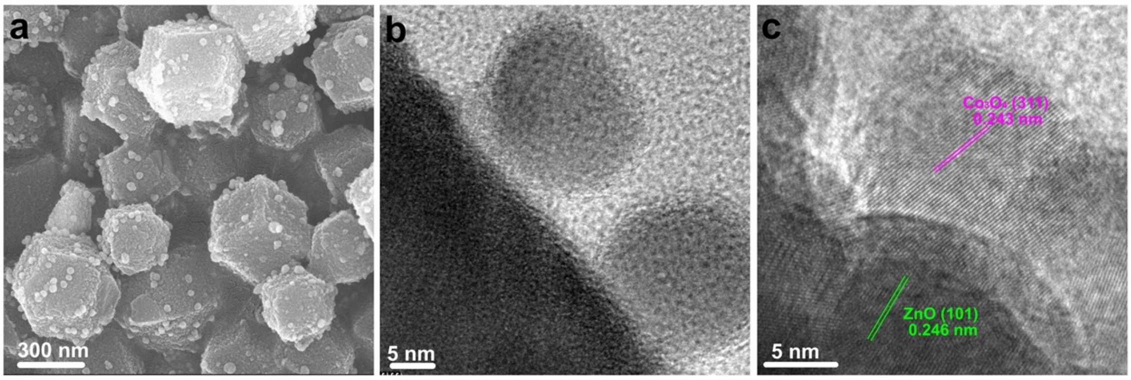

Fig. S5 (a) SEM , (b) TEM and (c) high resolution TEM of ZIF-8@ZIF-67 derived ZnO@Co_3O_4.

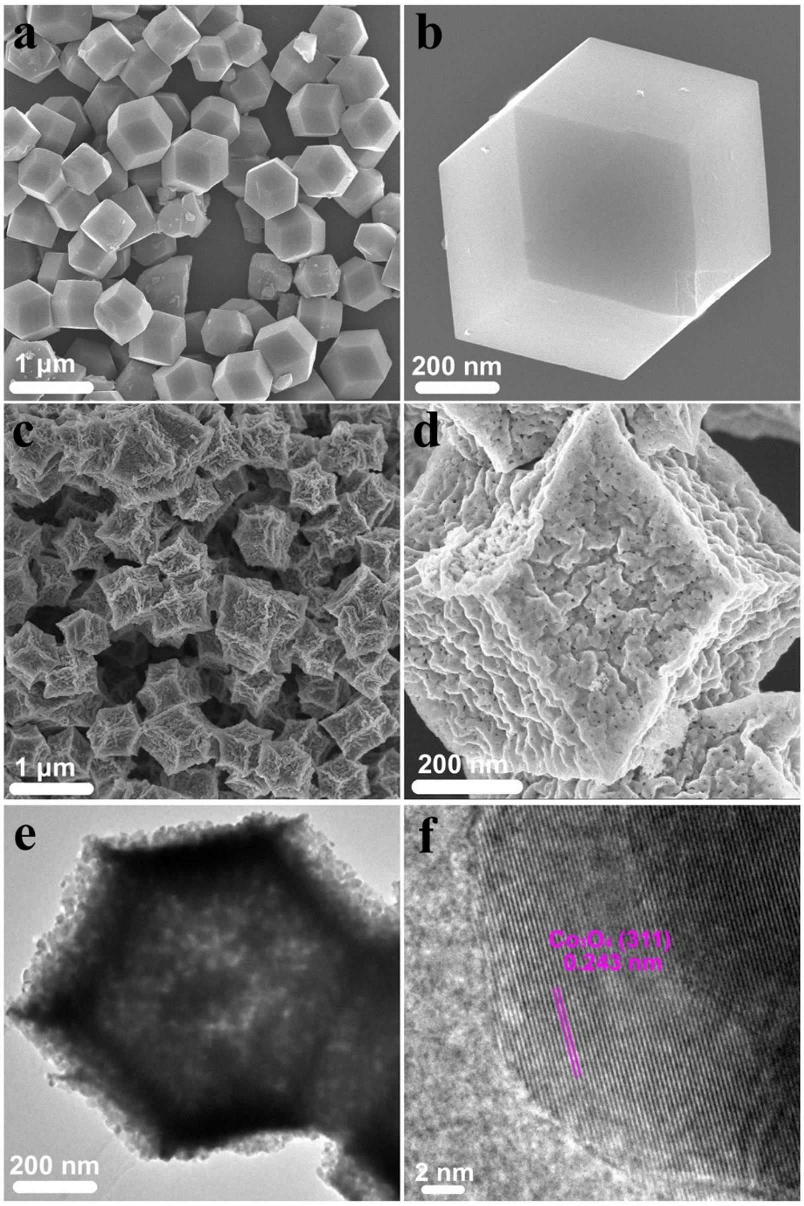

Fig. S6 (a, b) SEM images of ZIF-67, (c, d) SEM, (e) TEM, and (f) high resolution TEM images of ZIF-67 derived Co_3O_4.

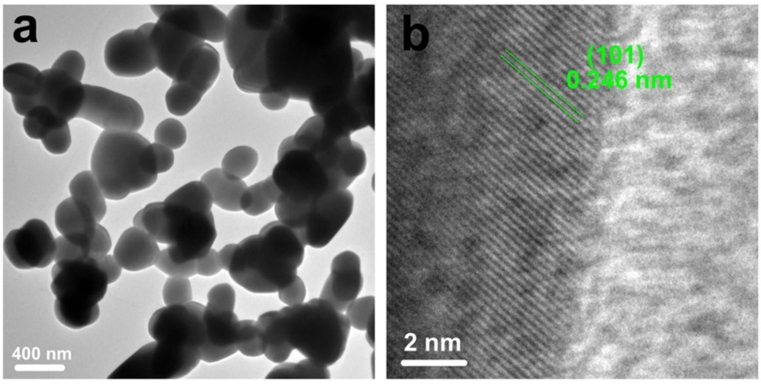

Fig. S7 (a) TEM and (b) high resolution TEM images of the commercial ZnO.

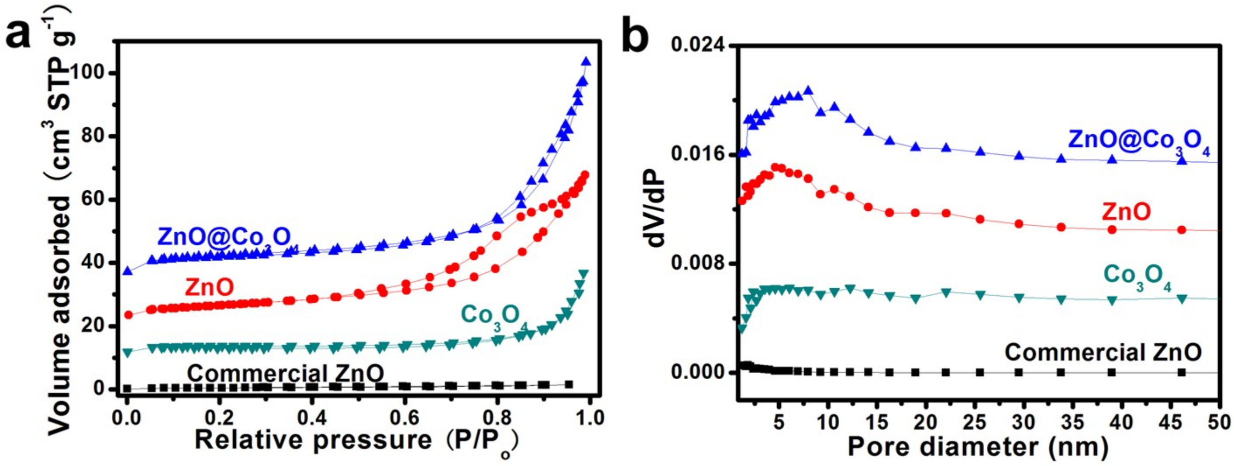

Fig. S8 (a) N_2 adsorption-desorption isotherms and (b) pore size distribution of the ZIFs derived samples and the commecial ZnO.

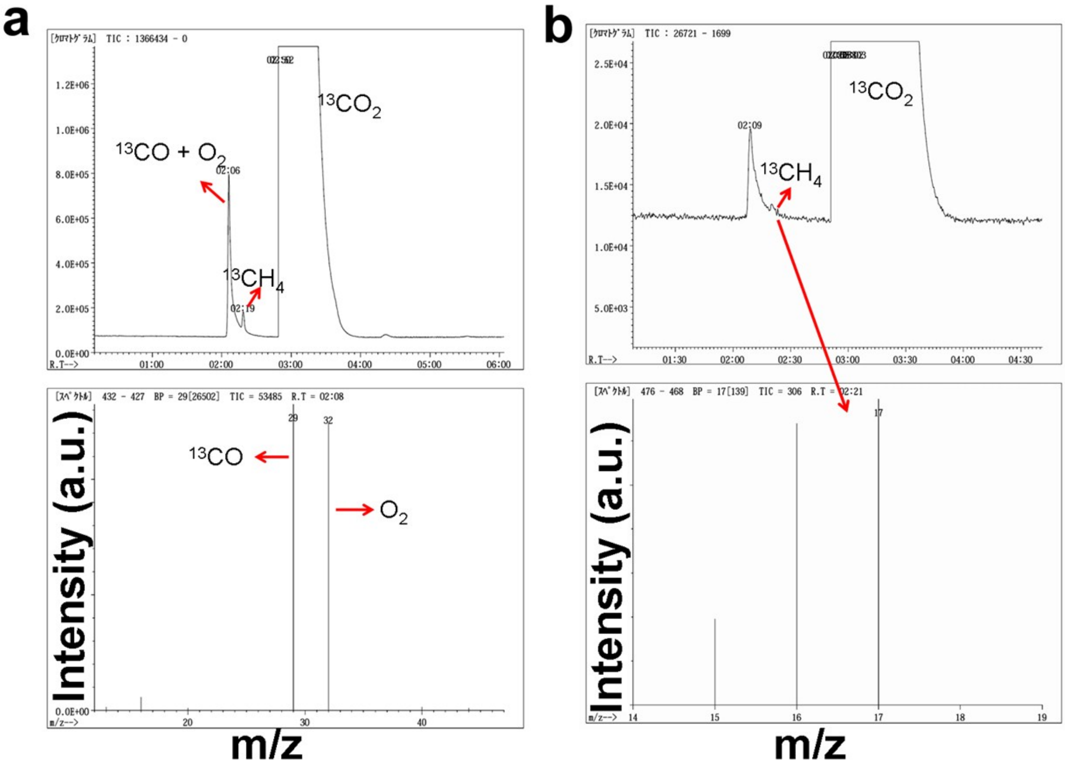

Fig. S9 GC-MS spectra of the products (a) CO and (b) CH_4 of photocatalytic $^{13}CO_2$ reduction over $ZnO@Co_3O_4$ after 12 h irradiation.

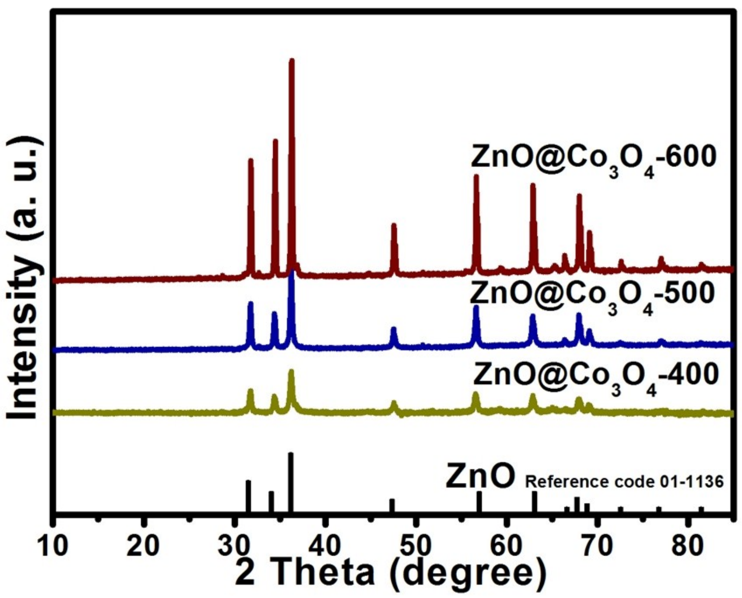

Fig. S10 (a) XRD patterns (λ = 0.15418 nm) of ZnO@Co_3O_4-400, ZnO@Co_3O_4-500 and (c,d) ZnO@Co_3O_4-600.

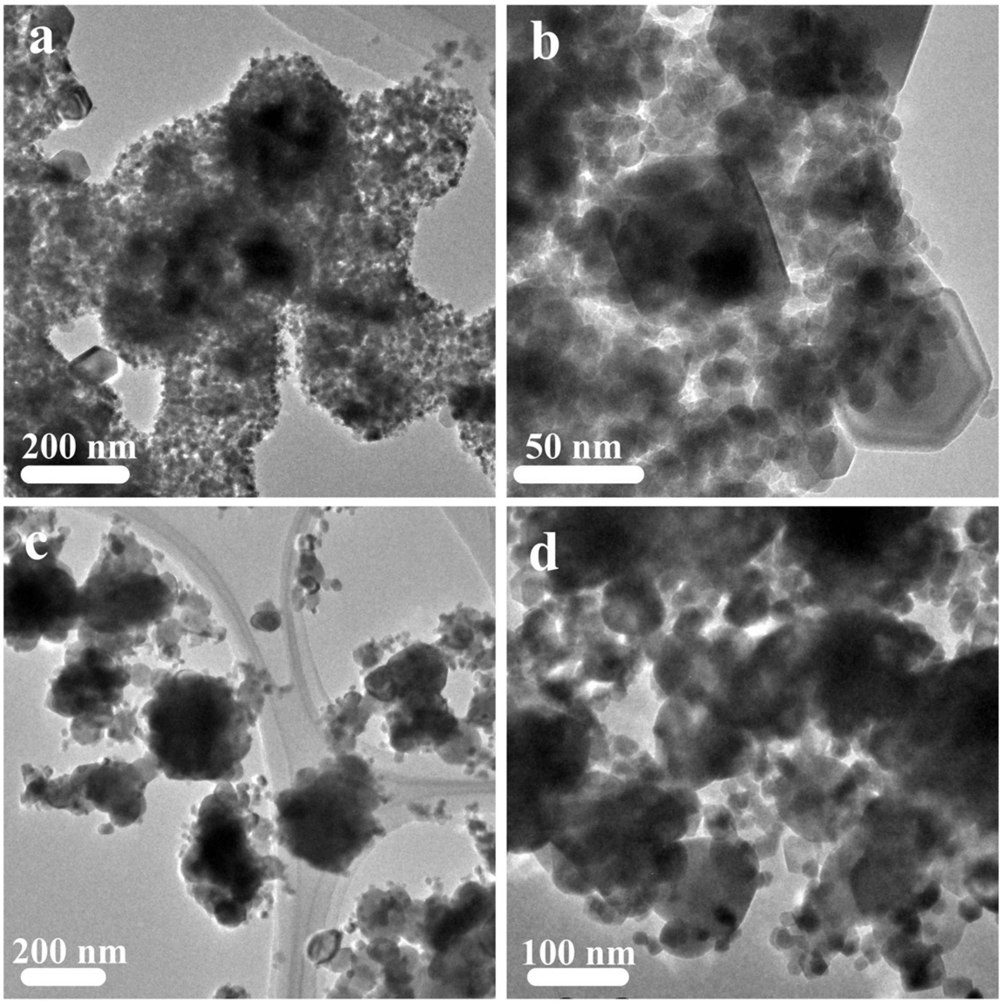

Fig. S11 TEM images of (a,b) ZnO@Co_3O_4-500 and (c,d) ZnO@Co_3O_4-600 prepared from ZIF-8@ZIF-67.

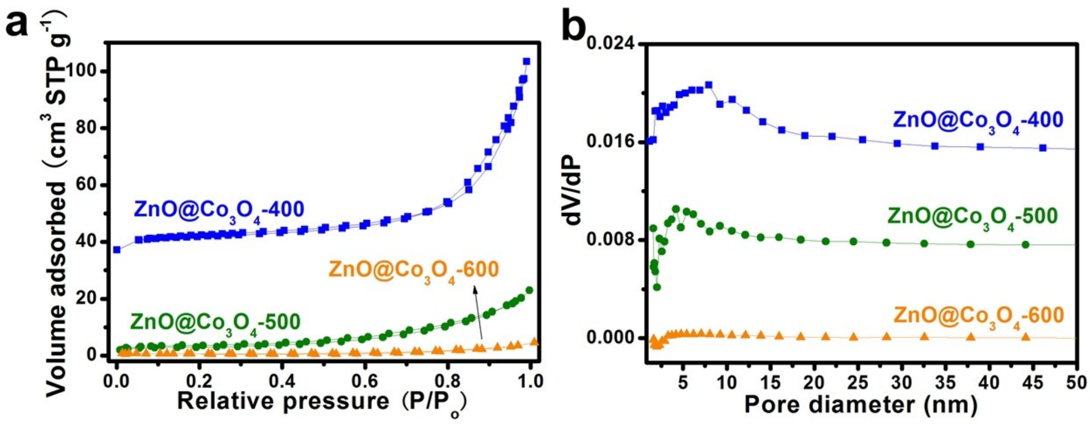

Fig. S12 (a) N_2 adsorption-desorption isotherms and (b) pore size distribution of $ZnO@Co_3O_4$-400, $ZnO@Co_3O_4$-500 and (c,d) $ZnO@Co_3O_4$-600.

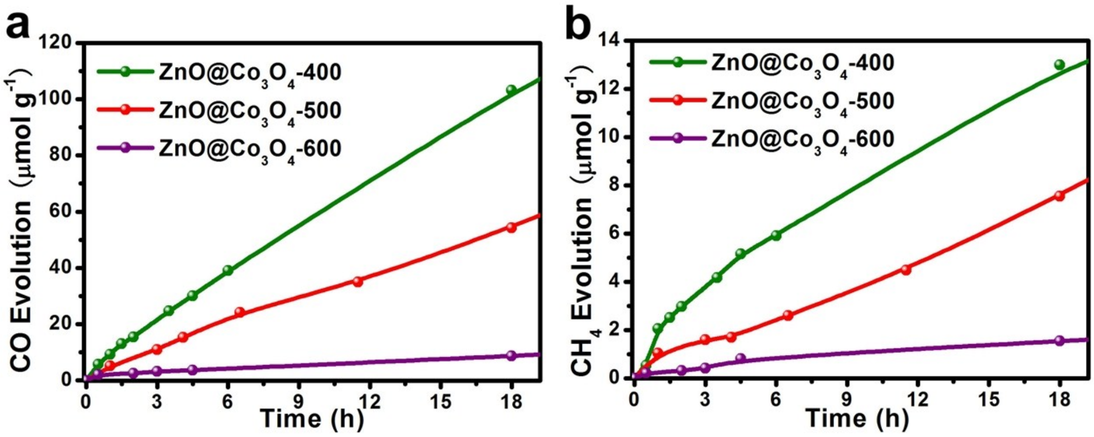

Fig. S13 (a) CO and (b) CH_4 evolution of ZnO@Co_3O_4-400, ZnO@Co_3O_4-500 and ZnO@Co_3O_4-600 under UV-vis irradiation.

(a) ZnO

$$ZnO + 2h^+ + H_2O \longrightarrow ZnO + +1/2O_2 + 2H^+ \quad (1)$$

$$CO_2 + 8e^- + 8H^+ \longrightarrow CH_4 + 2H_2O \quad (2)$$

$$CO_2 + 2e^- + 2H^+ \longrightarrow CO + H_2O \quad (3)$$

$$ZnO + 2h^+ \longrightarrow Zn^{2+} + 1/2O_2 \quad (4)$$

$$2CO_2 + 2e^- + Zn^{2+} \longrightarrow ZnCO_3 + CO \quad (5)$$

(b) $ZnO@Co_3O_4$

$$ZnO + 2h^+ + Co_3O_4 + H_2O \longrightarrow ZnO + Co_3O_4 + 1/2O_2 + 2H^+ \quad (6)$$

$$CO_2 + 8e^- + 8H^+ \longrightarrow CH_4 + 2H_2O \quad (2)$$

$$CO_2 + 2e^- + 2H^+ \longrightarrow CO + H_2O \quad (3)$$

Fig. S14 Proposed reaction equations for the photoreduction of CO_2 with (a) ZnO and (b) $ZnO@Co_3O_4$ under UV-vis irradiation.

Table S1 Structural parameters of the ZIFs derived samples and the commecial ZnO.

Catalyst	S_{BET} (m^2 g^{-1})	V_{total} (cm^3 g^{-1})	Average pore size (nm)
Commercial ZnO	1.65	0.0022	5.4
ZnO	29.3	0.100	13.6
ZnO@Co_3O_4-400	25.0	0.104	16.7
Co_3O_4	11.3	0.041	14.6
ZnO@Co_3O_4-500	11.5	0.034	11.9
ZnO@Co_3O_4-600	1.80	0.0063	14.1

Table S2 Summary of the various photocatalytic systems employed for CO_2 reduction.

Catalyst	Co-catalyst	Light source	Conditions	Major products	Rate (μmol g^{-1} h^{-1})	Ref.
ZIF derived ZnO	Co_3O_4	UV-Vis light: 300 W Xe lamp	CO_2 and H_2O vapor	CH_4 CO	0.99 6.51	This work
Zn_2GeO_4 nanobelt	1 wt % Pt and 1 wt % RuO2	UV-Vis light: 300 W Xe lamp	CO_2 and H_2O vapor	CH_4	0.025	1
Anatase TiO_2 rods with {010} facets	1 wt% Pt	UV-Vis light: 300 W Xe lamp	CO_2 and H_2O vapor	CH_4	0.0057	2
Hollow anatase TiO_2 single crystals with {101} facets	1 wt% RuO2	UV-Vis light: 300 W Xe lamp	CO_2 and H_2O vapor	CH_4	0.0017	3
Leaf-architectured $SrTiO_3$	1 wt % Au	UV-Vis light: 300 W Xe arc lamp	CO_2 and H_2O vapor	CH_4 CO	0.28 0.35	4
$NaTaO_3$	1 wt % Au	UV-Vis light: 200 W Hg-Xe arc lamp	CO_2 and H_2O vapor	CH_4 CO	0.036 0.17	5
$NaNbO_3$ with cubic–orthorhombic surface-junctions	0.5 wt% Pt	UV-Vis light: 300 W Xe lamp	CO_2 and H_2O vapor	CH_4	5.94	6
Cubic $NaNbO_3$	0.5 wt% Pt	UV-Vis light: 300 W Xe lamp	CO2 and H2O vapor	CH_4	5.31	7
Cubic $NaNbO_3$	0.5 wt% Pt	UV-Vis light: 300 W Xe lamp	CO_2 and H_2O vapor	CH_4	4.86	8
TiO_2	3 wt% NaOH	UV-Vis light: 300 W Xe lamp	CO_2 and H_2O vapor	CH_4	8.77	9

TiO_2 Nanosheets Exposed with 95% {100} Facets	1 wt% Pt	UV-Vis light: 300 W Xe lamp	CO_2 and H_2O vapor	CH_4	0.011	10
Micro/mesoporous Zn_2GeO_4	1 wt% Pt	UV-Vis light: 300 W Xe lamp	CO_2 and H_2O vapor	CH_4	0.412	11
Titania Nanosheets and Graphene Nanosheets	-	UV-Vis light: 300 W Xe lamp	CO_2 and H_2O vapor	CH_4 CO	1.14 8.91	12
Mesoporous Zn_2GaO_4	1 wt% RuO2	UV-Vis light: 300 W Xe lamp	CO_2 and H_2O vapor	CH_4	2.59	13
Ordered mesoporous TiO_2	-	UV-Vis light: 300 W Xe arc lamp	CO_2 and H_2O vapor	CH_4 CO	0.15 0.19	14

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