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Supporting Information

In situ synthesis of ordered mesoporous Co-doped TiO_2 and their enhanced photocatalytic activities and selectivities in reduction of CO_2

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Additional experimental section:

1 Synthesis of reference samples

For purposes of comparison in the same reactor system, we synthesize or buy some typical semiconductors or composites, including Degussa P-25, N-doped TiO_2, Au/TiO_2, C_3N_4, WO_3). The performance and characteristics of these materials are shown in Fig. S8 and Table S2. Degussa P-25(TiO_2) was bought from Evonik-Degussa; ST-01(TiO_2) and WO_3 were bought from Wako pure chemical industries.

Synthesis of N-doped TiO_2: in a typical preparation, a certain amount of ST-01 was annealed in a tubular furnace at 550 ^oC for 2 h under NH_3 atmosphere. The sample was named as N-TiO_2.

Synthesis of Au/TiO_2: in a typical preparation, ordered mesoporous TiO_2 (OMT) powder was immersed into a certain amount of $HAuCl_4$ aqueous solution. Then, a small amount of ascorbic acid aqueous solution was added to reduce Au. The theoretical weight percentage of Au is about 7%. The sample was named as Au-OMT.

Synthesis of bulk g-C_3N_4: in a typical preparation,[R1] a certain amount of dicyandiamide was annealed in a tubular furnace at 550 ^oC for 4 h under air atmosphere.

2 Calculation of the quantum efficiency

On the basis of the assumption that a photon must be effectively absorbed, the photocatalytic quantum efficiency (QE) is typically defined as the ratio of the rate of photocatalytic events to the absorbed photons. [R2,R3]

$$\mathrm{QE} = \frac{N_{\text{photocat. events}}}{N_{\text{absorbed photons}}}$$

The photocatalytic events have to be summed over the (molar) amounts of all the products, $N_{photocat.events} = \sum_i n_i M_i$, Where n_i is the number of electrons required to obtain one molecule of product M_i.

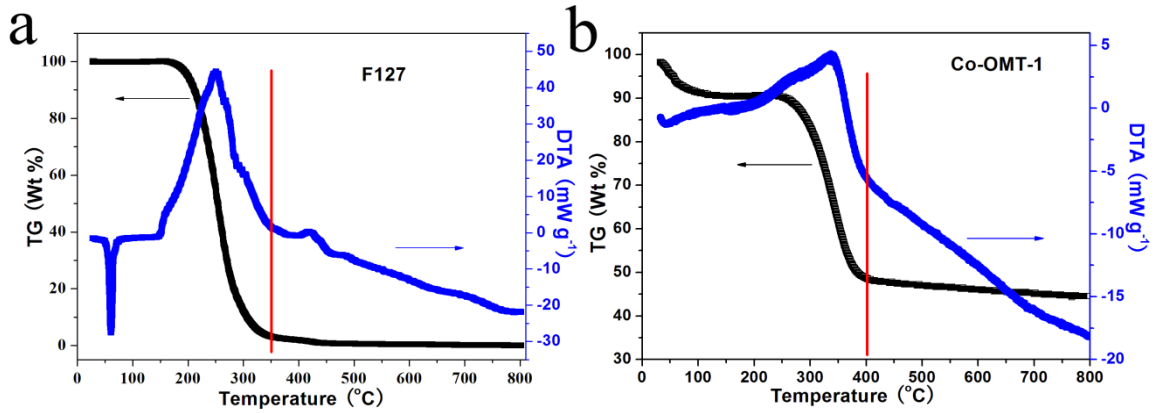

Fig. S1 TG/DTA curves of F127 (a) recorded in N_2 and Co-OMT-1 (b) recorded in air

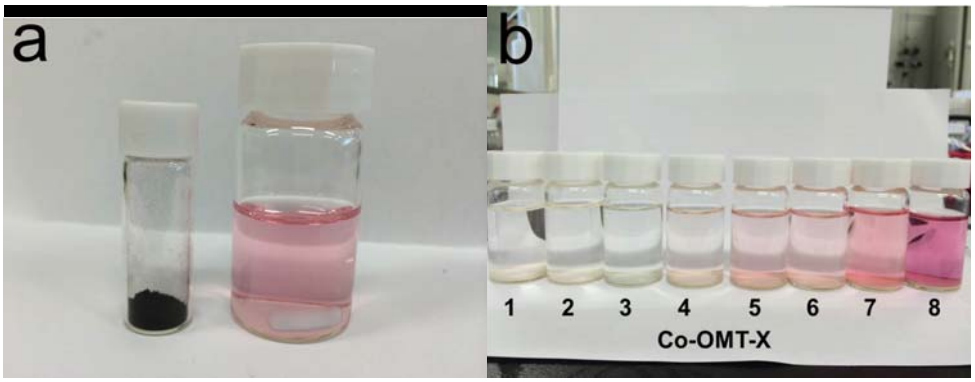

Fig. S2 (a) The photo of of Co_3O_4 before and after dissolving by HCl. (b) The photos of Co-doped TiO_2 dissolving by HCl to remove the Co_3O_4.

Table S1 The molar ratio of samples before and after removing the Co_3O_4**.**

Sample	Theoretical molar ratio (Co: Ti) [a]	Practical molar ratio (Co: Ti) [b]	Doping levels of Co^{2+} (Co: Ti) [c]
OMT	0	0	0
Co-OMT-1	0.002	0.0023	0.0020
Co-OMT-2	0.005	0.0049	0.0021
Co-OMT-3	0.01	0.013	0.0040
Co-OMT-4	0.025	0.026	0.0041
Co-OMT-5	0.05	0.053	0.0049
Co-OMT-6	0.1	0.12	0.0063
Co-OMT-7	0.15	0.15	0.0064
Co-OMT-8	0.2	0.25	0.0045
Co_3O_4	-	-	-

[a] The value is calculated according to the additive amount in the synthetic process.

[b] The value is calculated according to the EDX analysis before removing the Co_3O_4.

[c] The value is calculated according to the EDX analysis after removing the Co_3O_4.

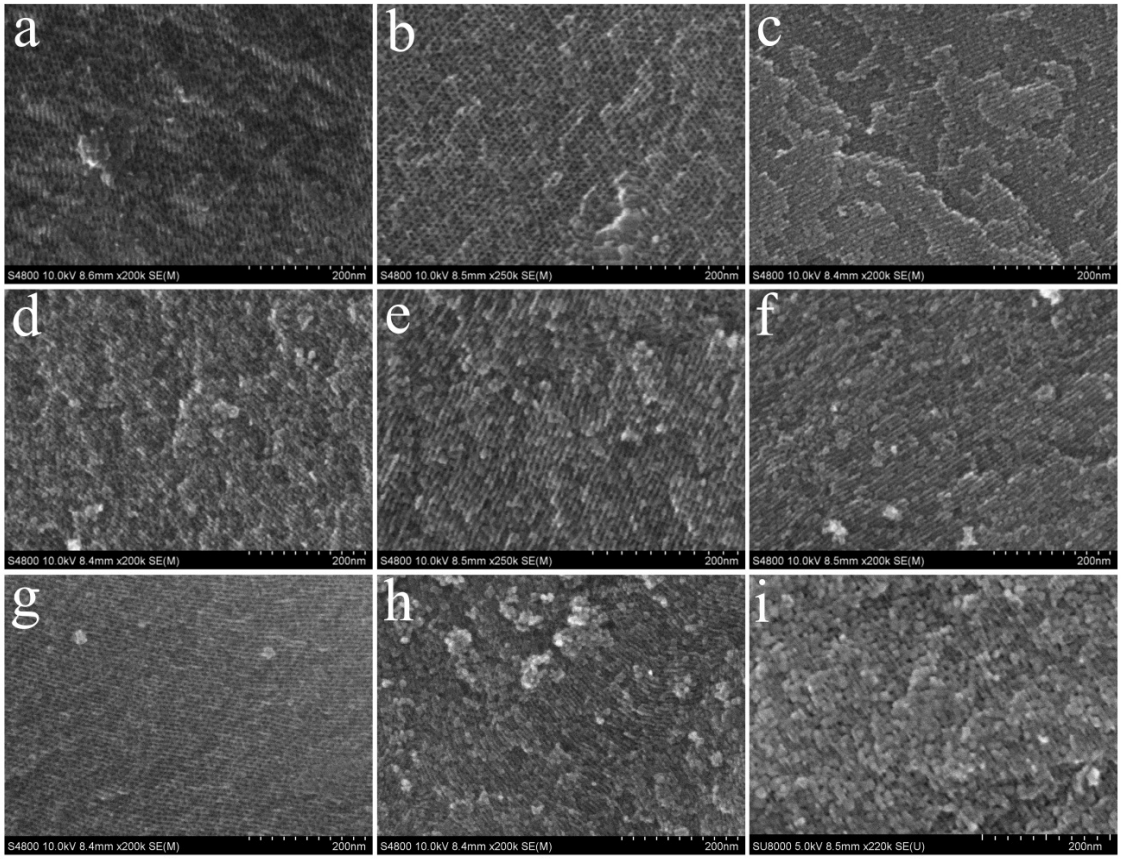

Fig. S3 FE-SEM images of samples: (a) OMT, (b) Co-OMT-1, (c) Co-OMT-2, (d) Co-OMT-3, (e) Co-OMT-4, (f) Co-OMT-5, (g) Co-OMT-6, (h) Co-OMT-7, (i) Co-OMT-8.

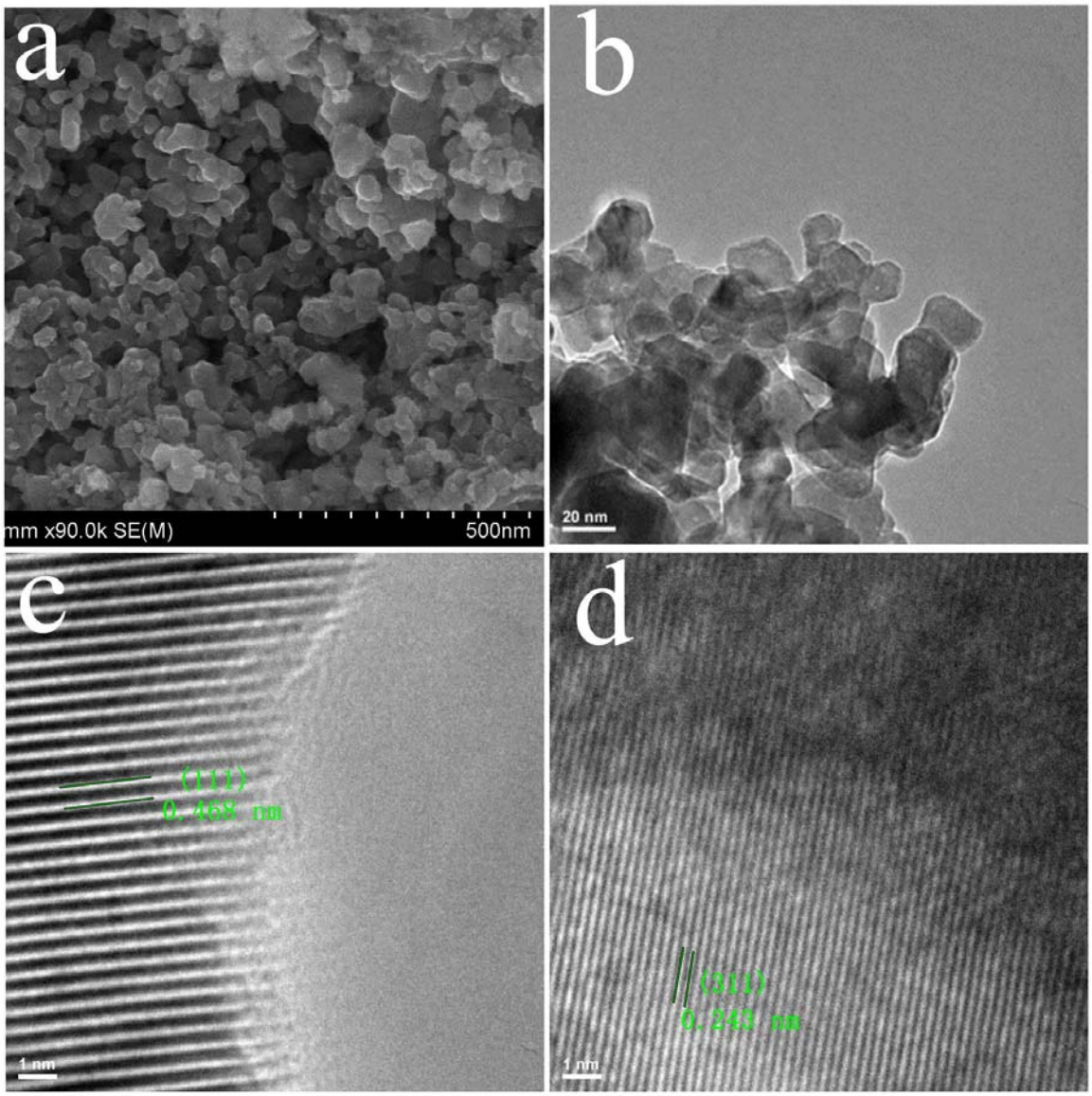

Fig. S4 (a) FE-SEM and (b,c,d) TEM images of Co_3O_4.

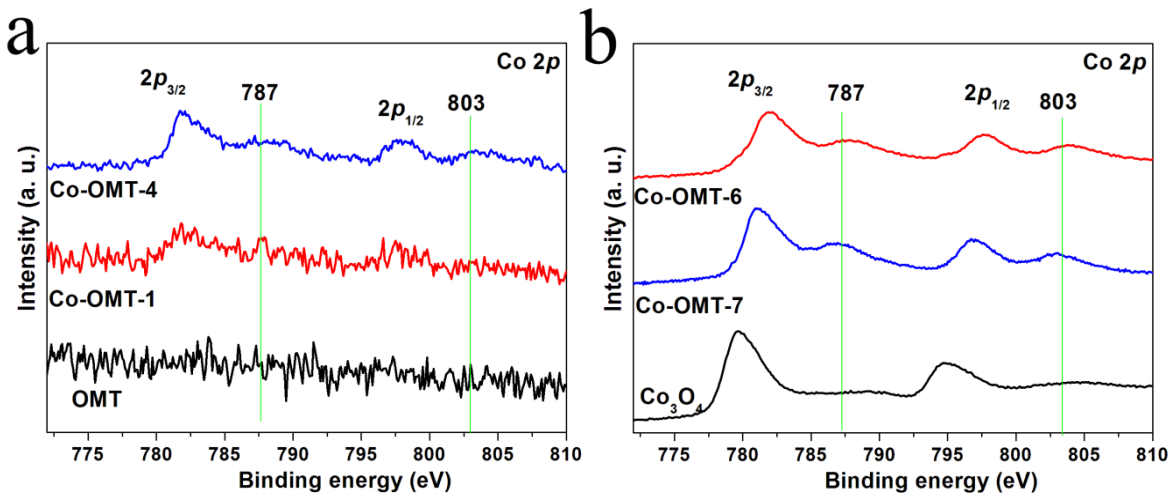

Fig. S5 X-ray photoelectron spectroscopy of samples.

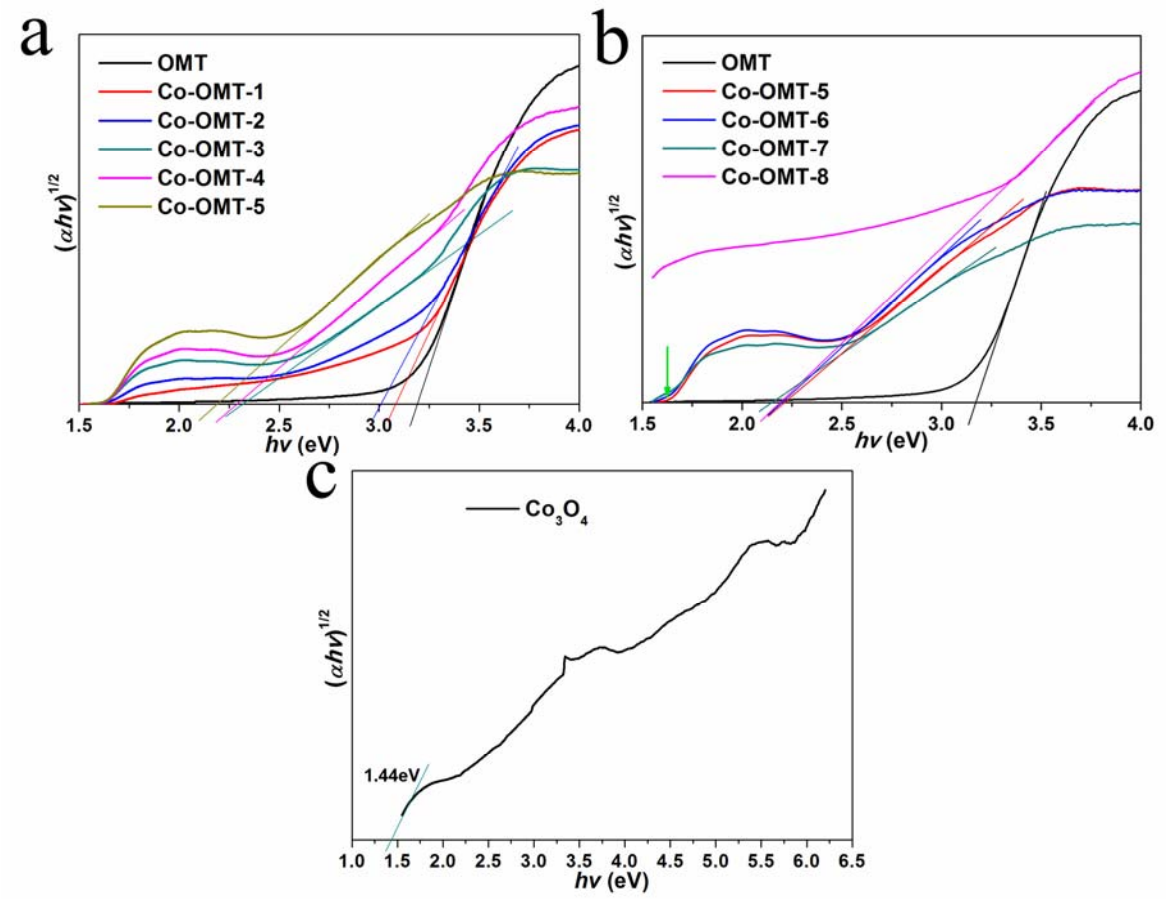

Fig. S6 The Tauc plots of samples.

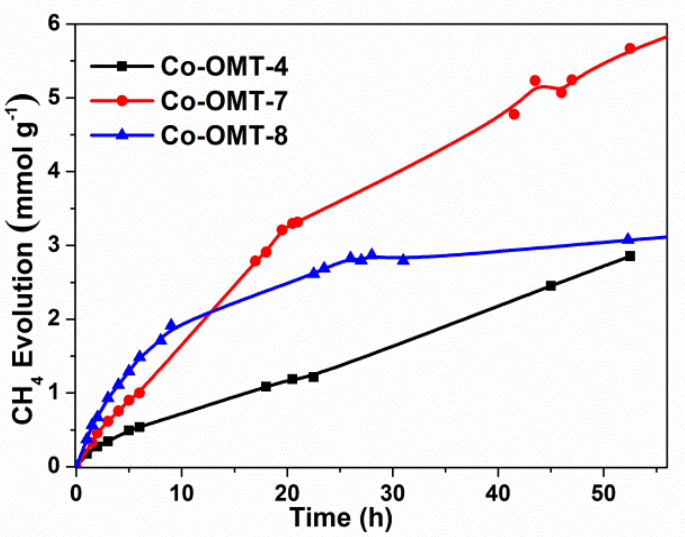

Fig. S7 CH_4 evolution over Co-OMT-4, Co-OMT-7 and Co-OMT-8 under visible light.

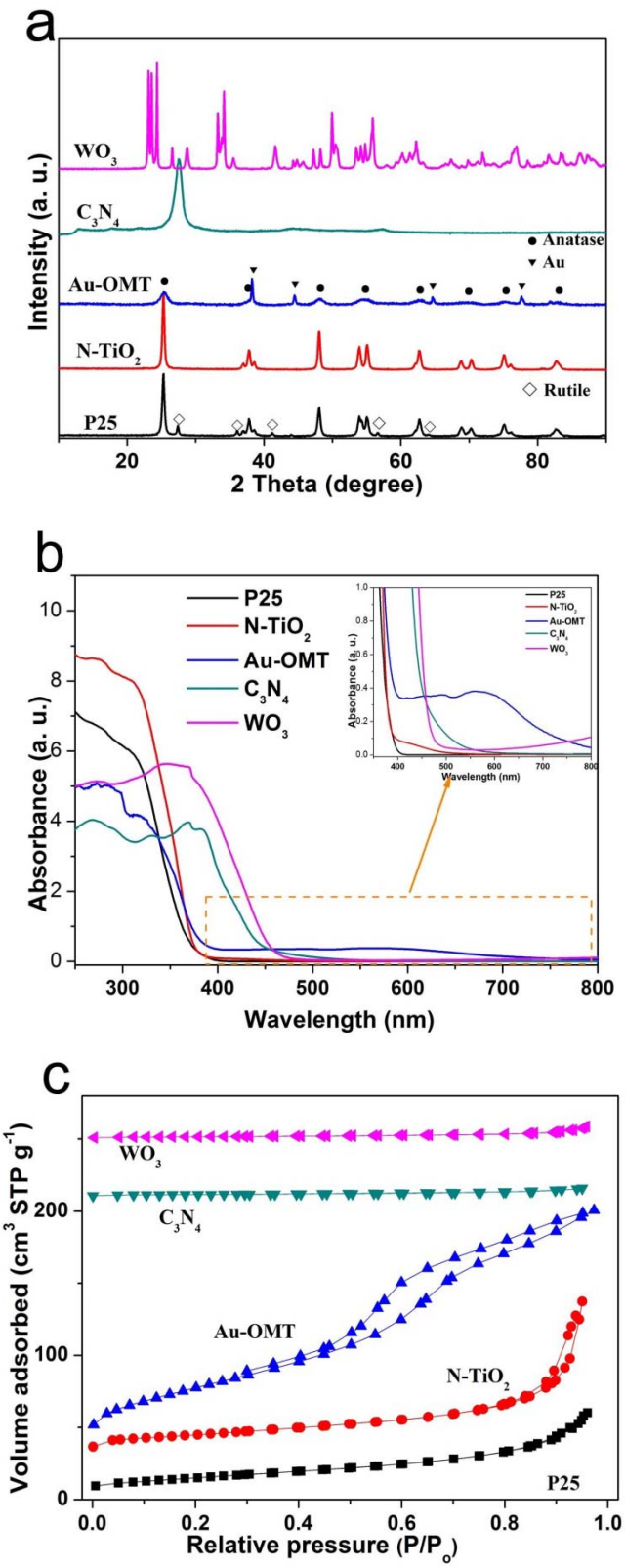

Fig. S8 (a) Wide-angle XRD patterns, (b) UV-vis absorption spectra and (c) N_2 adsorption-desorption isotherms of samples.

The wide-angle XRD patterns of samples were shown in Fig. S8a. We can see that P25 presents a mixture of anatase and rutile; N-TiO_2 presents anatase; Au-OMT

presents a mixture of anatase and gold. The characteristic peaks of C_3N_4 are same as the previous reports.[R1] UV-visible absorption spectra (Fig. S8b) show that all samples except P25, possess the optical absorption capability in the visible light region. The specific surface areas of P25, N-TiO_2, Au-OMT, C_3N_4, WO_3 were 54.4, 53.6, 181.0, 5.2, 5.4 m^2 g^{-1}, respectively (calculated by the BET method from N_2 adsorption-desorption isotherms in Figure S8c).

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

Catalyst	Co-catalyst	Light source	Conditions	Major products	R_{max}[a]	Ref.
Co-OMT-4	-	**Visible light**: 300 W Xe lamp with a cut-off filter (**λ>420 nm**)	CO_2 and H_2O vapor	CH_4 CO	0.09 1.94	This study
		UV-Vis light: 300 W Xe lamp	CO_2 and H_2O vapor	CH_4 CO	0.33 2.09	This study
P25	-	**Visible light**: 300 W Xe lamp with a cut-off filter (**λ>420 nm**)	CO_2 and H_2O vapor	None	0	This study
N-TiO_2	-	**Visible light**: 300 W Xe lamp with a cut-off filter (**λ>420 nm**)	CO_2 and H_2O vapor	CH_4 CO	0.015 0.153	This study
Au-OMT	-	**Visible light**: 300 W Xe lamp with a cut-off filter (**λ>420 nm**)	CO_2 and H_2O vapor	CH_4 CO	0.018 0.056	This study
C_3N_4	-	**Visible light**: 300 W Xe lamp with a cut-off filter (**λ>420 nm**)	CO_2 and H_2O vapor	CH_4 CO	0.031 0.135	This study
WO_3	-	**Visible light**: 300 W Xe lamp with a cut-off filter (**λ>420 nm**)	CO_2 and H_2O vapor	CH_4 CO	0.005 0.017	This study
$ZnAl_2O_4$-modified mesoporous ZnGaNO	0.5 wt% Pt	**Visible light**: 300 W Xe lamp with a cut-off filter (**λ>420 nm**)	CO_2 and H_2O vapor	CH_4	0.0092	R4
RGO–CdS nanorod composite	-	**Visible light**: 300 W Xe arc lamp with a cut-offlter (**λ>420 nm**)	CO_2 and H_2O vapor	CH_4	2.51	R5
P25	-	**UV-Vis light**: 300 W Xe lamp	CO_2 and H_2O vapor	CH_4	0.0027	R6
Ordered	-	**UV-Vis light**: 300 W	CO_2 and H_2O	CH_4	0.19	R6

mesoporous TiO_2		Xe lamp	vapor	CO	0.15	
Zn_2GeO_4 nanobelt	1 wt % Pt and 1 wt % RuO_2	**UV-Vis light**: 300 W Xe lamp	CO_2 and H_2O vapor	CH_4	0.025	R7
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	R8
Hollow anatase TiO_2 single crystals with {101} facets	1 wt% RuO_2	**UV-Vis light**: 300 W Xe lamp	CO_2 and H_2O vapor	CH_4	0.0017	R9
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	R10
$NaTaO_3$	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	R11
TiO_2 nanorod	Ag	**UV light**: four 8 W UVA lamps with a wavelength of 365 nm	CO_2 and H_2O vapor	CH_4	2.64	R12
Brookite TiO_2 nanorods	0.05 wt% Au	**UV light**: a light-emitting diode (Nichia, NCCU033), which emitted light at a wavelength of ca. 365 nm	5 mL of 0.2 mol L^{-1} $KHCO_3$ aqueous solution saturated with CO_2	CH_3OH	0.11	R13
In-doped TiO_2	-	**UV-vis light**: 500W mercury (Hg) flash lamp	CO_2 and H_2O vapor, 0.20 bars reactor pressure, 373K reaction temperature	CH_4 CO	243.75 81.25	R14
MgO/TiO_2 nanotube film	Pt	**UV-vis light**: 300W high pressure Hg lamp	0.1 mol L^{-1} $KHCO_3$ solution	CH_4	100.22[b]	R15

[a] Maximum formation rate reported for the major product(s), in μmol $g^{-1}h^{-1}$.

[b] In ppm h^{-1} cm^{-1}.

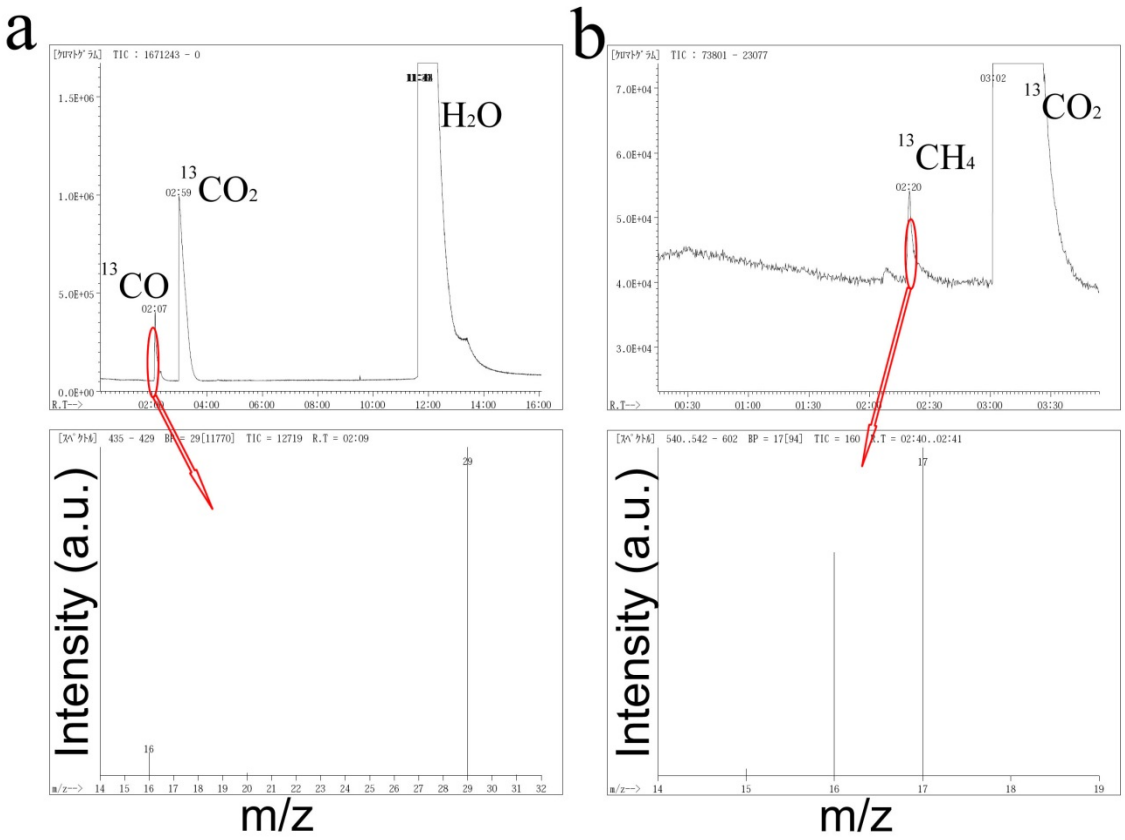

Fig. S9 GC-MS spectra of the products of photocatalytic $^{13}CO_2$ reduction over (a) Co-OMT-4 and (b) Co-OMT-7 after 12 h irradiation.

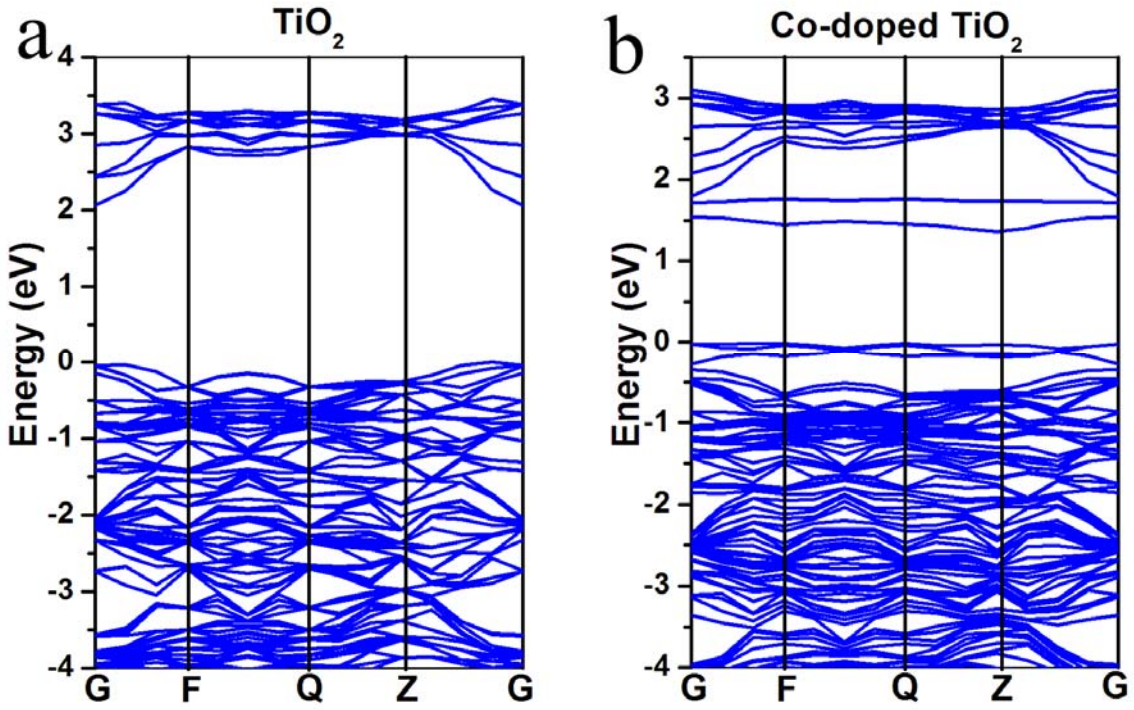

Fig. S10 Electronic structures of (a) anatase TiO_2 and (b) $Co_xTi_{1-x}O_2$ (x=0.0625).

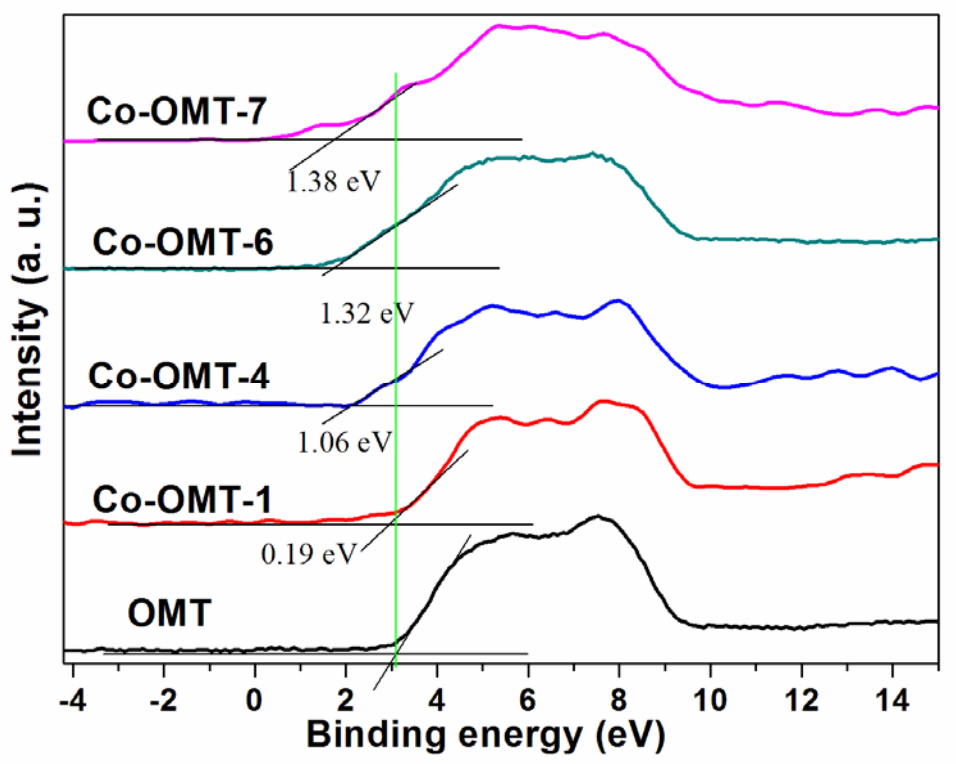

Fig. S11 Valence band XPS spectra of samples. The values in Fig. are the relative difference between the Co-OMT-x and OMT.

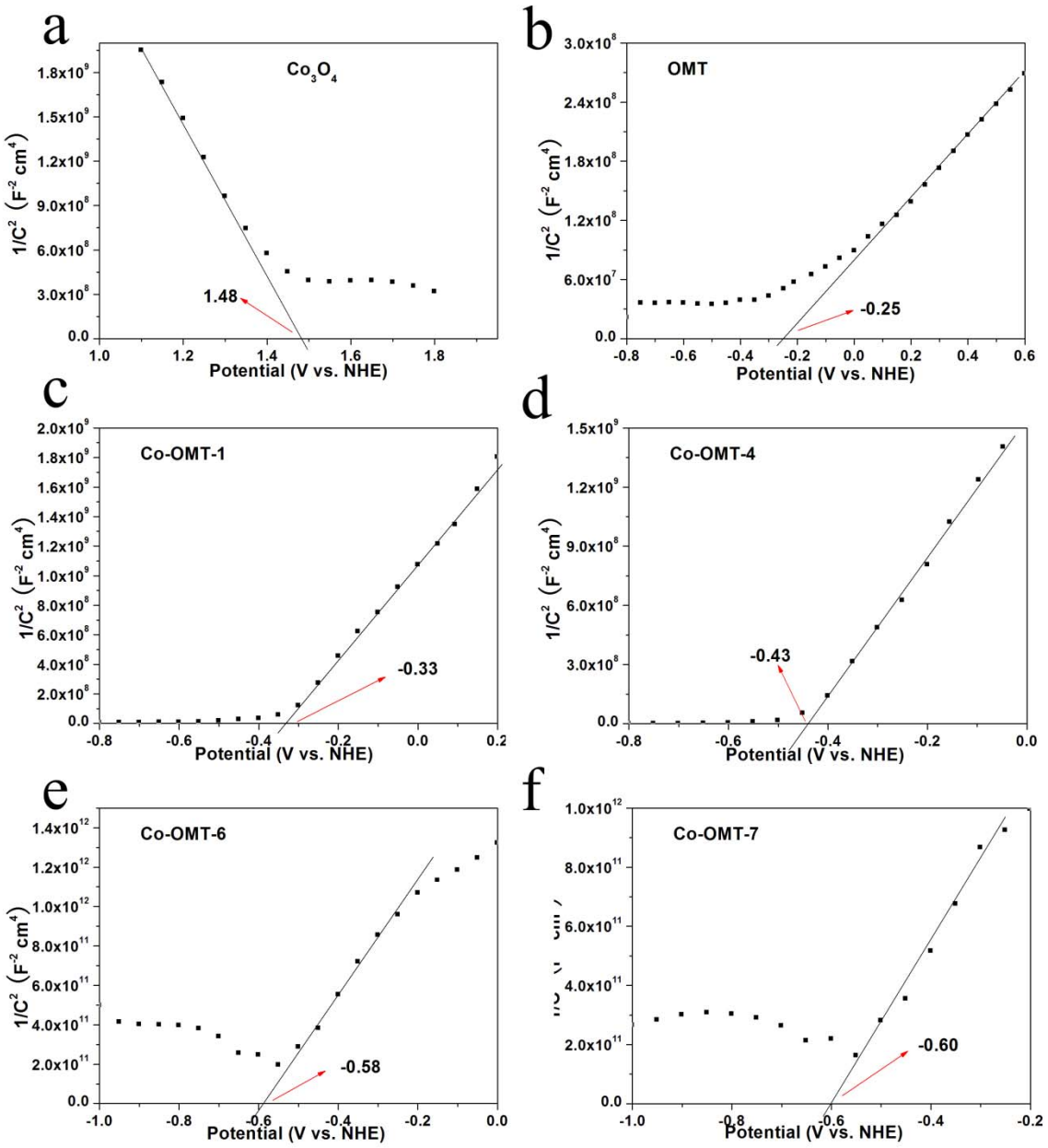

Fig. S12 Mott-Schottky plots of samples: (a) OMT, (b) OMT, (c) Co-OMT-1, (d) Co-OMT-4, (e) Co-OMT-6, (f) Co-OMT-7.

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