Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Supporting information

Metal-Organic Framework Immobilized Cobalt Oxide Nanoparticles for Efficient Photocatalytic Water Oxidation

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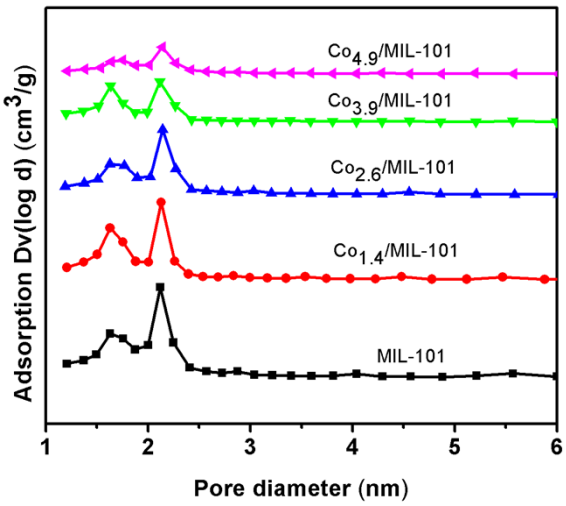

Fig. S1 N_2 adsorption isotherm of activated MIL-101, $Co_{1.4}$/MIL-101, $Co_{2.6}$/MIL-101, $Co_{3.9}$/MIL-101 (**1**) and $Co_{4.9}$/MIL-101.

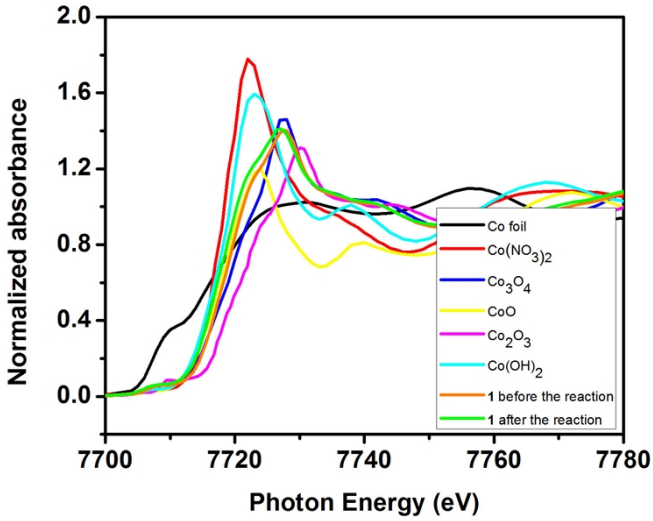

Fig. S2 XANES spectra of Co foil, $Co(NO_3)_2$, Co_3O_4, CoO, Co_2O_3, $Co(OH)_2$, **1** and **1** after the photocatalytic reaction.

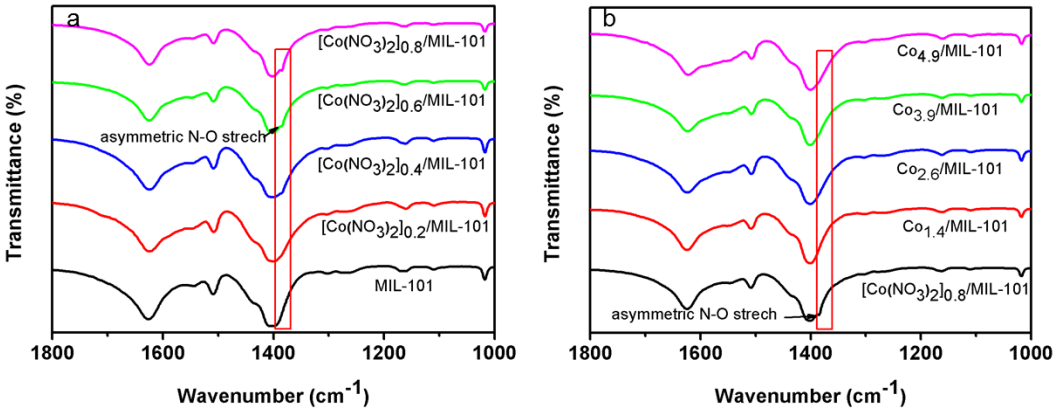

Fig. S3 FTIR spectra of (a) MIL-101, $[Co(NO_3)_2]_a$/MIL-101 and (b) $[Co(NO_3)_2]_{0.8}$/MIL-101, Co_x/MIL-101.

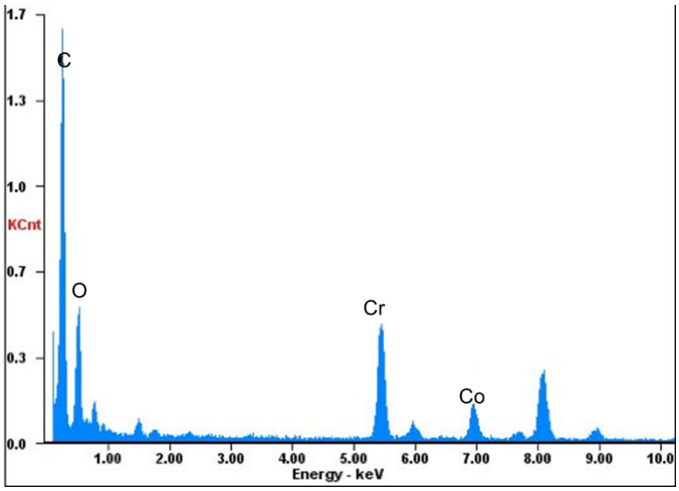

Fig. S4 EDX analysis result of **1** ($Co_{3.9}$/MIL-101).

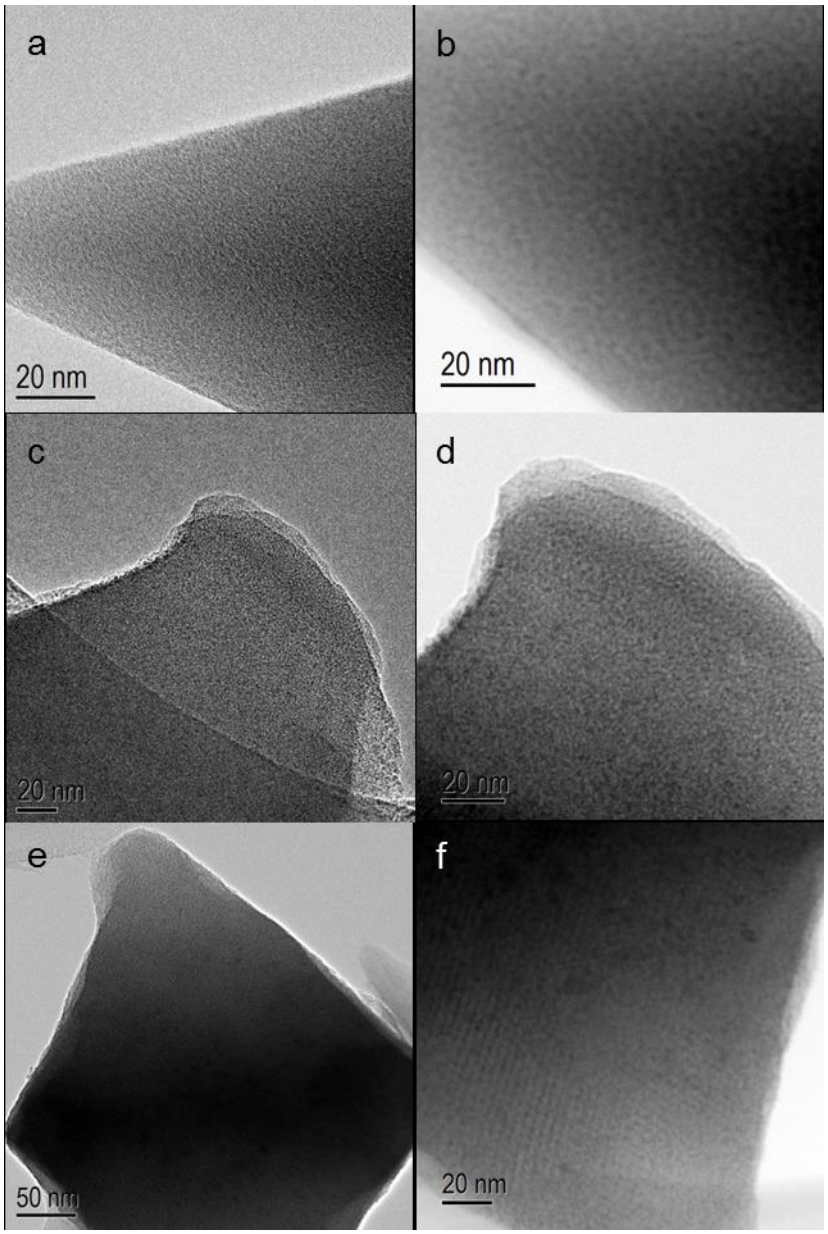

Fig. S5 TEM images of $Co_{1.4}$/MIL-101 (a), $Co_{2.6}$/MIL-101 (c) and $Co_{4.9}$/MIL-101 (e). Bright field TEM images of $Co_{1.4}$/MIL-101 (b), $Co_{2.6}$/MIL-101 (d) and $Co_{4.9}$/MIL-101 (f).

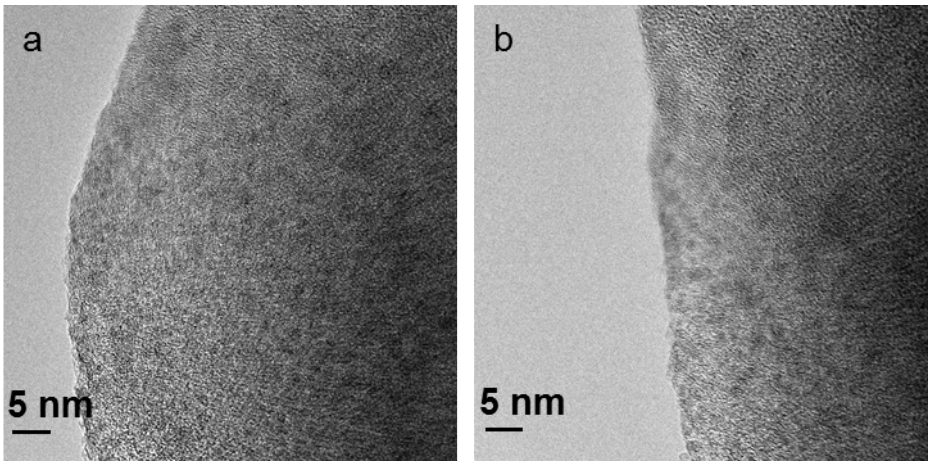

Fig. S6 High-resolution TEM images of **1**.

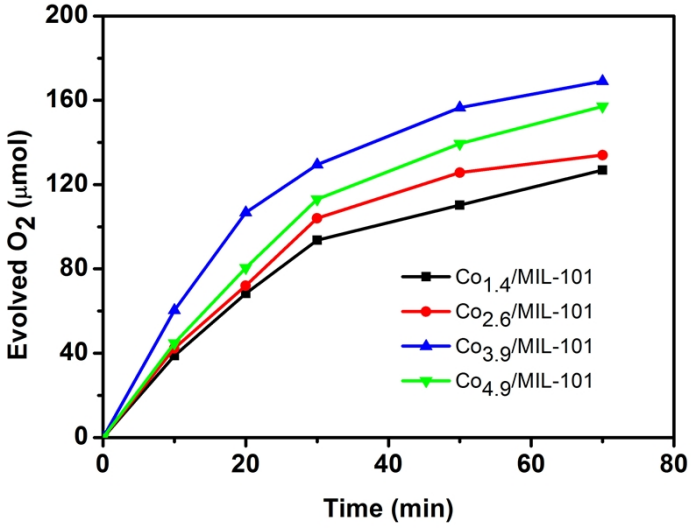

Fig. S7 Time course of O_2 evolution over $Co_{1.4}$/MIL-101, $Co_{2.6}$/MIL-101, $Co_{3.9}$/MIL-101 and $Co_{4.9}$/MIL-101 as the catalysts. Reaction condition: 12.5 mg of catalyst, 7.5 mM of $Na_2S_2O_8$, 1.0 mM of [$Ru(bpy)_3]Cl_2$ in 50 mL of 10 mM borate buffer, pH = 9, 300 W Xenon lamp, $\lambda > 420$ nm.

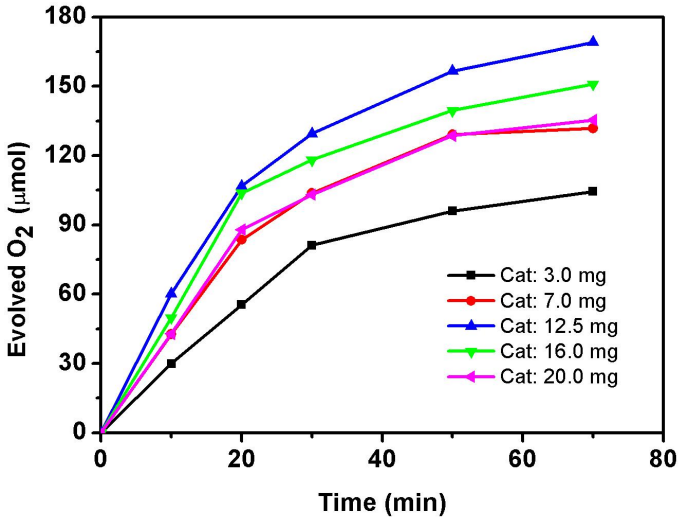

Fig. S8 Time course of O_2 evolution over different amount of **1** as the catalysts. Reaction condition: 7.5 mM of $Na_2S_2O_8$, 1.0 mM of [$Ru(bpy)_3]Cl_2$ in 50 mL of 10 mM borate buffer, pH = 300 W Xenon lamp, $\lambda > 420$ nm.

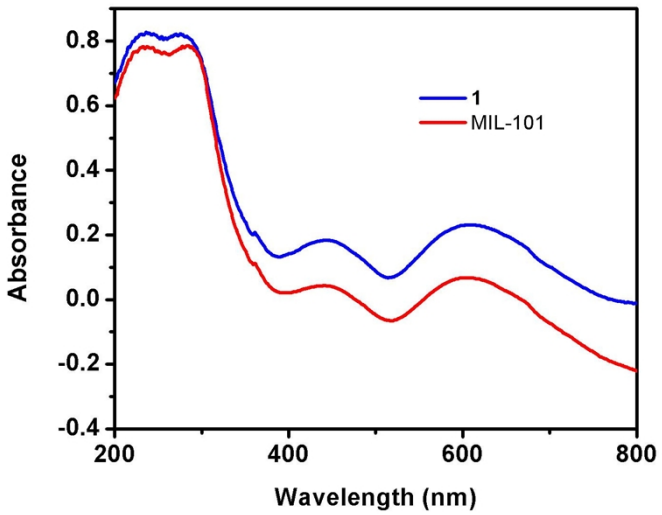

Fig. S9 UV-vis diffuse reflectance spectroscopy of MIL-101 and **1**.

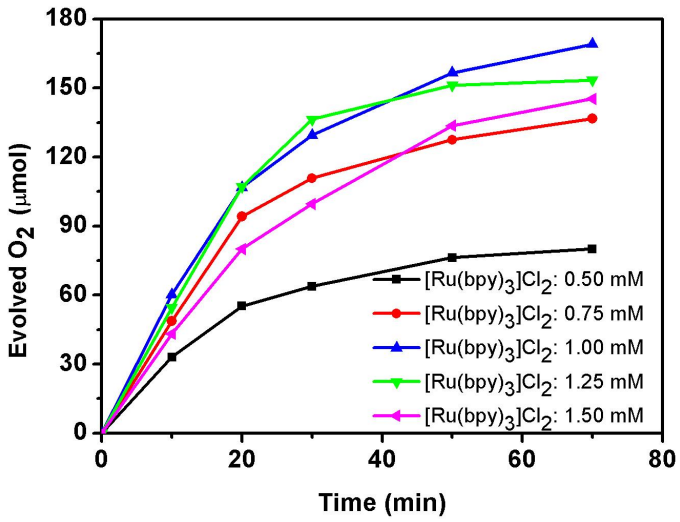

Fig. S10 Time course of O_2 evolution at different concentration of $[Ru(bpy)_3]Cl_2$. Reaction condition: 12.5 mg of **1**, 7.5 mM of $Na_2S_2O_8$, in 50 mL of 10 mM borate buffer, pH = 9, 300 W Xenon lamp, $\lambda > 420$ nm.

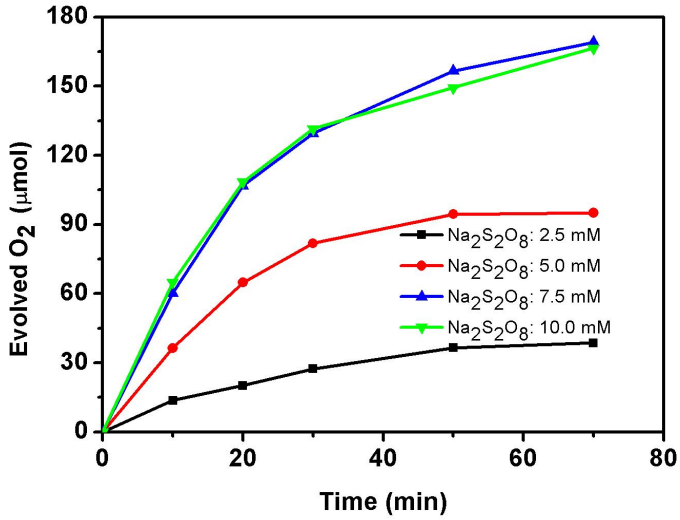

Fig. S11 Time course of O_2 evolution at different concentration of $Na_2S_2O_8$. Reaction condition: 12.5 mg of **1**, 1mM of $[Ru(bpy)_3]Cl_2$, in 50 mL of 10 mM borate buffer, pH = 9, 300 W Xenon lamp, $\lambda > 420$ nm.

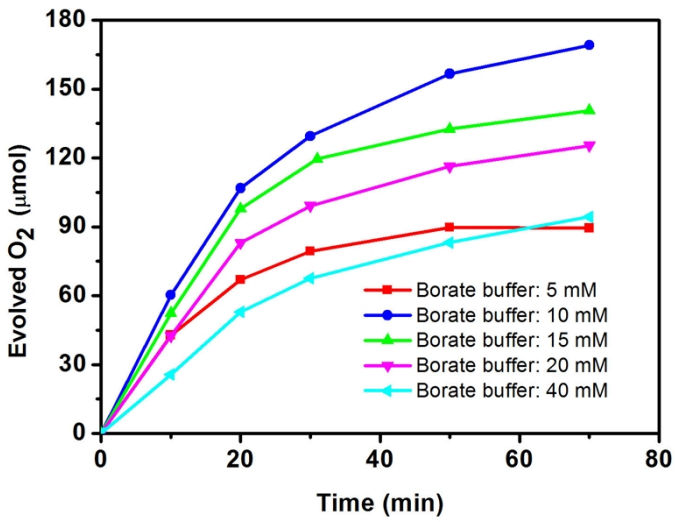

Fig. S12 Time course of O_2 evolution at different concentration of borate buffer. Reaction condition: 12.5 mg of **1**, 7.5 mM of $Na_2S_2O_8$, 1mM of $[Ru(bpy)_3]Cl_2$, in 50 mL borate buffer, pH = 9, 300 W Xenon lamp, $\lambda > 420$nm.

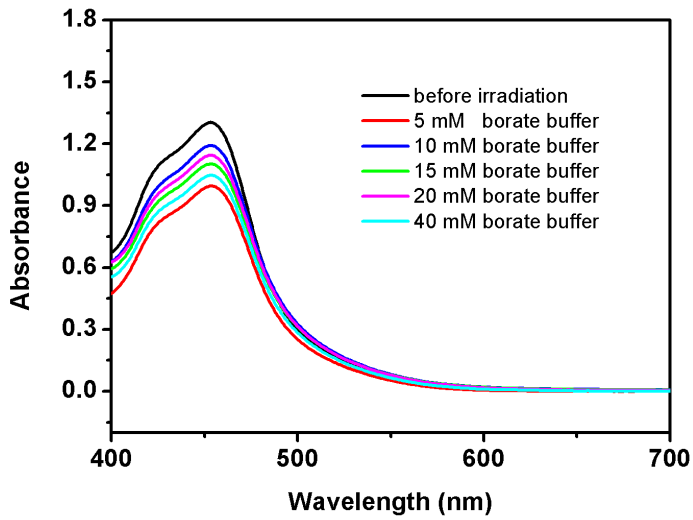

Fig. S13 UV-vis spectra of supernatant solutions after the reaction for 70 min at different buffer concentration. The solutions were diluted to one tenth for analysis.

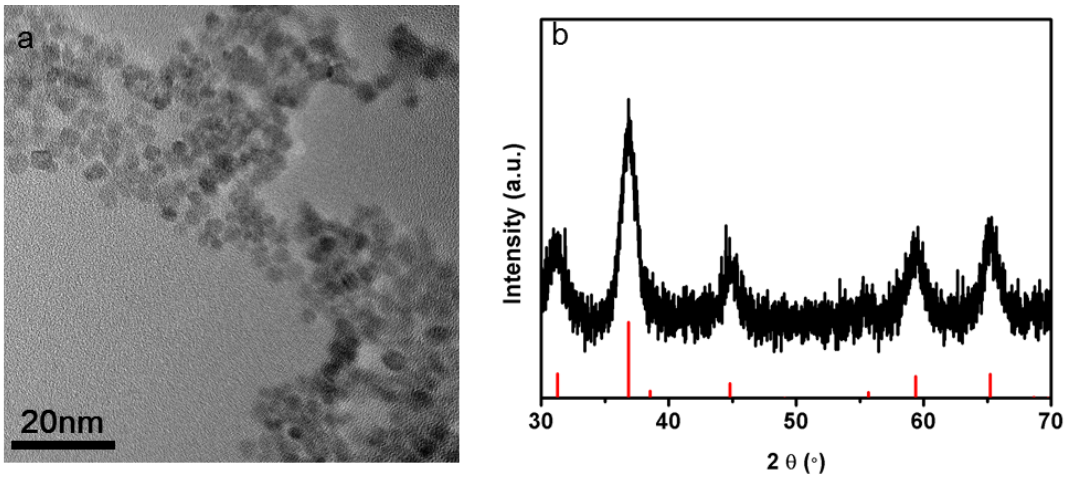

Fig. S14 (a) TEM image and (b) powder XRD pattern of as-prepared Co_3O_4 and standard line pattern of Co_3O_4 (JCPDS card No. 10-73-1701).

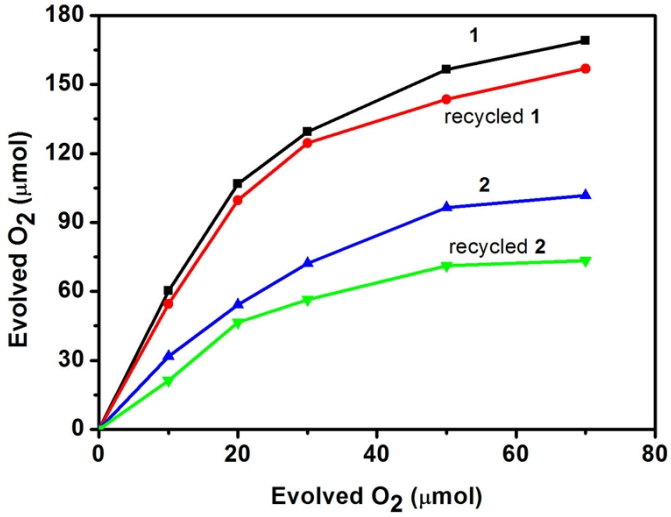

Fig. S15 Time course of O_2 evolution over **1**, recycled **1**, **2** ($[Co(NO_3)_2]_{0.6}$/MIL-101), and recycled **2**. Reaction condition: 12.5 mg of catalysts, 7.5 mM of $Na_2S_2O_8$, 1.0 mM of $[Ru(bpy)_3]Cl_2$ in 50 mL of 10.0 mM borate buffer, pH = 9, 300 W Xenon lamp, $\lambda > 420$ nm.

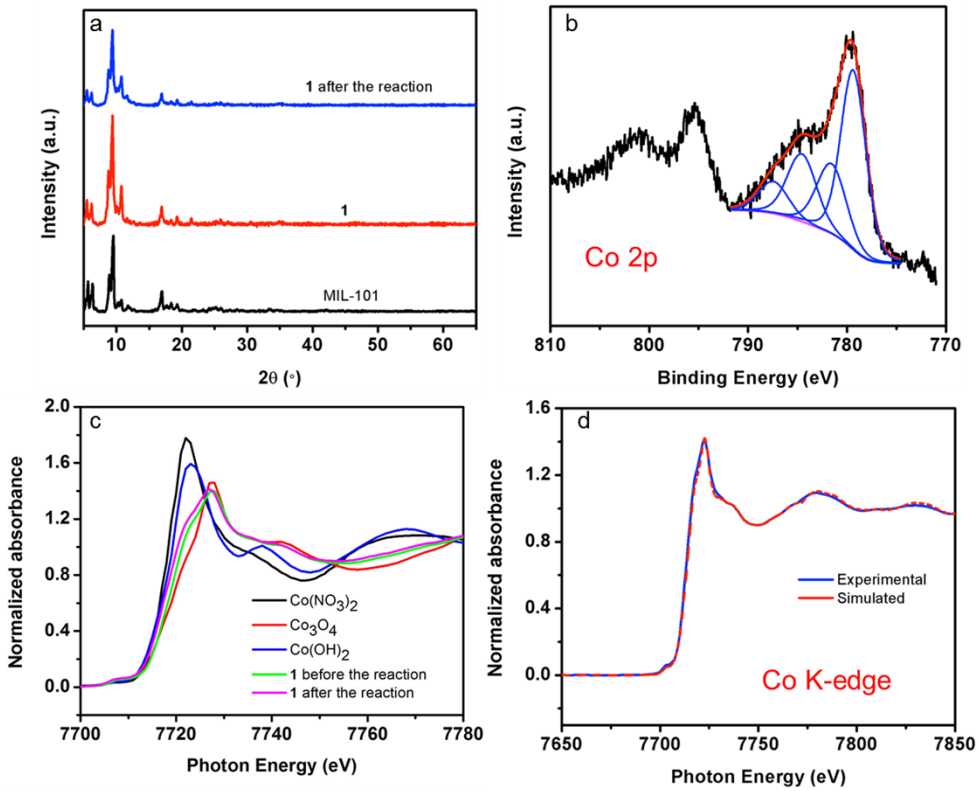

Fig. S16 (a) Powder XRD patterns of bare MIL-101, **1** and **1** after the photocatalytic reaction, (b) Co 2p XPS spectrum of **1** after the photocatalytic reaction, (c) XANES spectra **1** after the reaction and reference $Co(OH)_2$, Co_3O_4 and $Co(NO_3)_2$, and (d) the experimental and simulated XANES spectra of **1** after photocatalytic reaction.

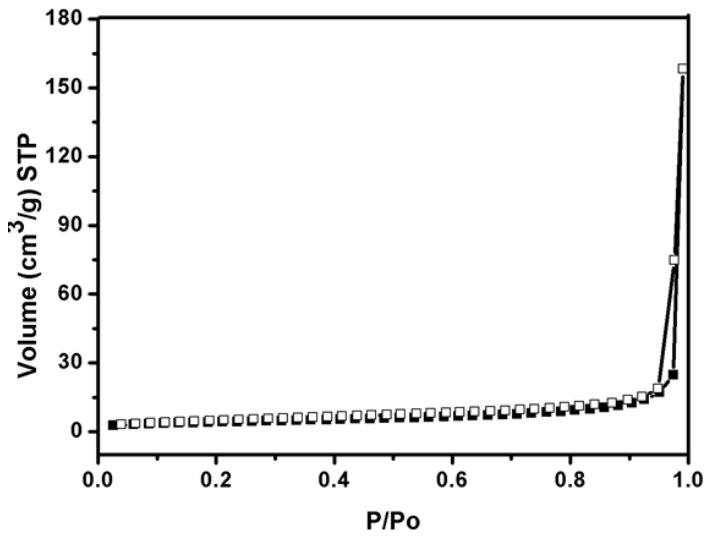

Fig. S17 N_2 adsorption isotherm of SiO_2 nanosphere. The BET surface area of SiO_2 nanosphere was determined to be 14.2 m^2/g.

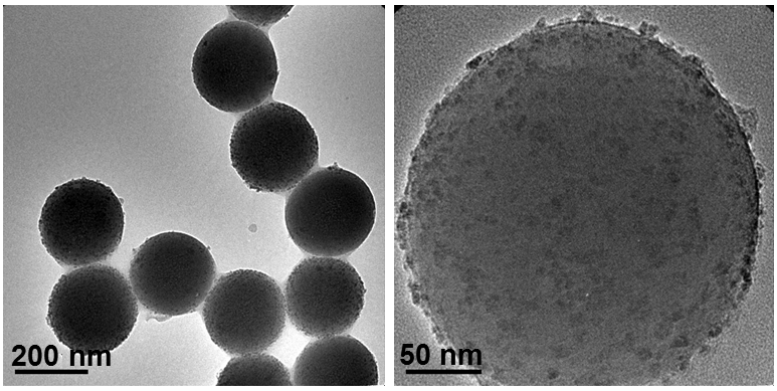

Fig. S18 TEM images of $Co_{3.7}/SiO_2$.

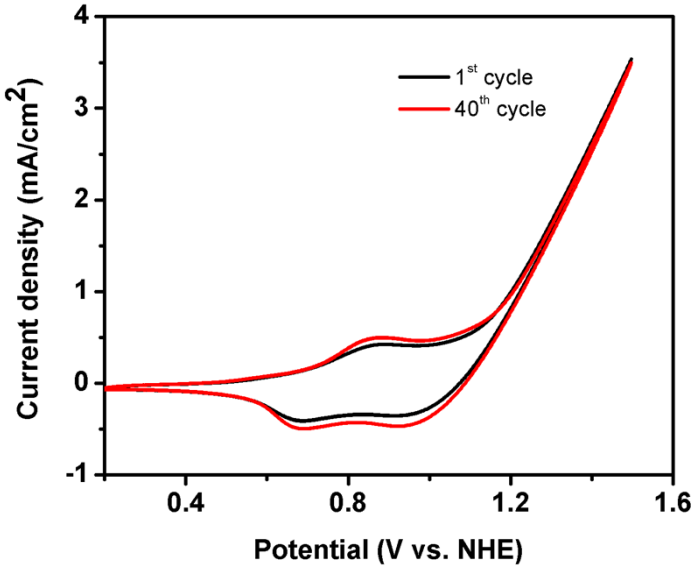

Fig. S19 CV curves of **1** at the 1st cycle and 40th cycle at a scan rate of 100 mV/s.

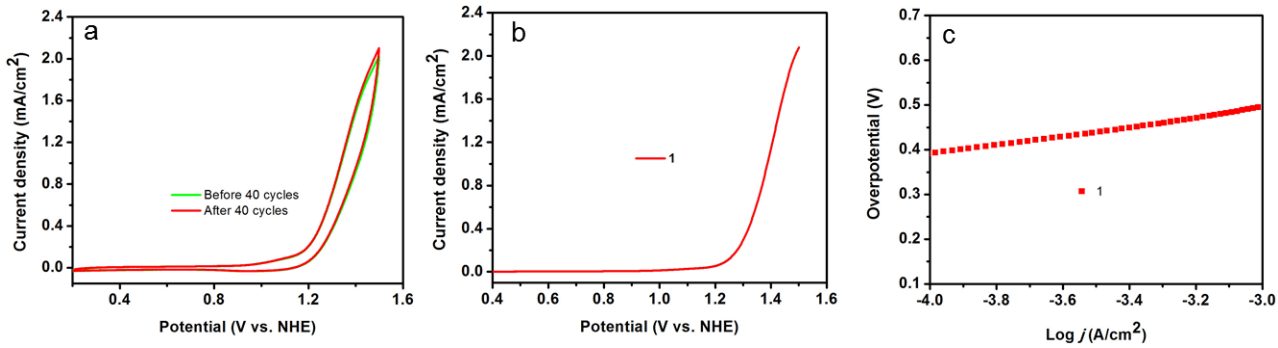

Fig. S20 (a) CV curves of **1** at a scan rate of 20 mV/s before and after 40 continuous cycles, (b) LSV curve of **1** at a scan rate of 2 mV/s, (c) Tafel plot of **1** obtained from LSV curve. All the results are obtained in 0.1 M phosphate buffer, pH = 7.

Table S1. Percentages of cobalt loaded on MIL-101.

Sample	Precursor concentration (mol/L)	Theoretical percentage (wt%)	Determined percentage (wt%)
$Co_{1.4}$/MIL-101	0.2	1.5	1.4
$Co_{2.6}$/MIL-101	0.4	2.8	2.6
$Co_{3.9}$/MIL-101	0.6	4.1	3.9
$Co_{4.9}$/MIL-101	0.8	5.2	4.9

Table S2. BET surface area and pore volume of Co_x/MIL-101 samples.

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)
MIL-101	4199	2.39
$Co_{1.4}$/MIL-101	3821	2.08
$Co_{2.6}$/MIL-101	3105	1.63
$Co_{3.9}$/MIL-101	2411	1.26
$Co_{4.9}$/MIL-101	1459	0.83

Table S3. Summary of the photocatalytic oxygen evolution performances of catalysts investigated in this work and literature.

Sample	Reaction condition	Initial rate (μmol/min)	TOF(s^{-1} per Co atom)×10^3	O_2 yield (%)	Reference
$Co_{1.4}$/MIL-101	a	3.24	18.2±0.6	68±2	This work
$Co_{2.6}$/MIL-101	a	4.33	13.1±0.9	71±3	This work
1	a	6.05	12.2±0.6	88±2	This work
$Co_{4.9}$/MIL-101	a	4.05	6.5±0.5	82±4	This work
$Co_{3.7}/SiO_2$	a	3.48	7.4±0.4	53±2	This work
Co_3O_4 (6 nm)	b	0.64	1.3±0.4	12±1	This work
2	a	3.17	6.4±0.6	54±2	This work
Co_3O_4/KIT-6 (3.8%)	c	-	0.41	71	1
Co_3O_4/SBA-15 (4.0%)	c	-	0.34	63	1
Co_3O_4/Al_2O_3 (4.0%)	c	-	0.46	84	1
Co_3O_4 (6 nm)	c	-	0.25	47	1
Co_3O_4	d	-	0.24	-	2
Co_3O_4/SBA-15 (4.0%)	e	-	0.64	-	3

[a]12.5 mg of catalysts, 7.5 mM of $Na_2S_2O_8$, 1.0 mM of $[Ru(bpy)_3]Cl_2$ in 50 mL of 10.0 mM borate

buffer, pH = 9, 300 W Xenon lamp, $\lambda > 420$ nm.

[b]0.66 mg of catalysts, 7.5 mM of $Na_2S_2O_8$, 1.0 mM of $[Ru(bpy)_3]Cl_2$ in 50 mL of 10.0 mM borate buffer, pH = 9, 300 W Xenon lamp, $\lambda > 420$ nm.

[c]75 mg catalyst, 1.67 mM $[Ru(bpy)_3]Cl_2$, 13.5 mM $Na_2S_2O_8$, 68.5 mM Na_2SO_4, Na_2SiF^{6-}, $NaHCO_3$ buffer, pH = 5.8, 300 W Xe lamp,λ>400 nm.

[d]10 mg catalyst, 1.5 mM $[Ru(bpy)_3]Cl_2$, 13.5 mM $Na_2S_2O_8$, 68.5 mM Na_2SO_4, Na_2SiF_6–$NaHCO_3$ buffer, pH = 5.8, 300 W Xe lamp, λ>400 nm.

[e]200 mg catalyst, 1.5 mM $[Ru(bpy)_3]Cl_2$, 13.5 mM $Na_2S_2O_8$, 68.5 mM Na_2SO_4, Na_2SiF_6–$NaHCO_3$ buffer, pH = 5.8, 240 mW emission line (476nm) of an Ar ion laser.

Reference

1 Yusuf, S.; Jiao, F. *ACS catal.* **2012**, *2*, 2753-2760.

2 Rosen, J.; Hutchings, G. S.; Jiao, F. *J. Am. Chem. Soc.* **2013**, *135*, 4516-4521.

3 Jiao, F.; Frei, H. *Angew. Chem. Int. Ed.* **2009**, *48*, 1841-1844.