Supporting information for

A facile method for the synthesis of a porous cobalt oxide-carbon hybrid as a highly efficient water oxidation catalyst

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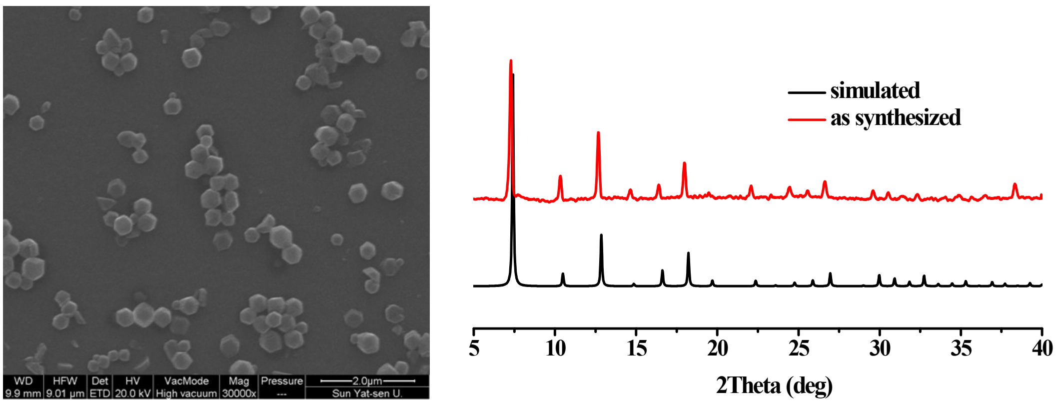

Figure S1. The SEM image (left) and PXRD pattern (right) for the synthesized nanocrystals of ZIF-67.

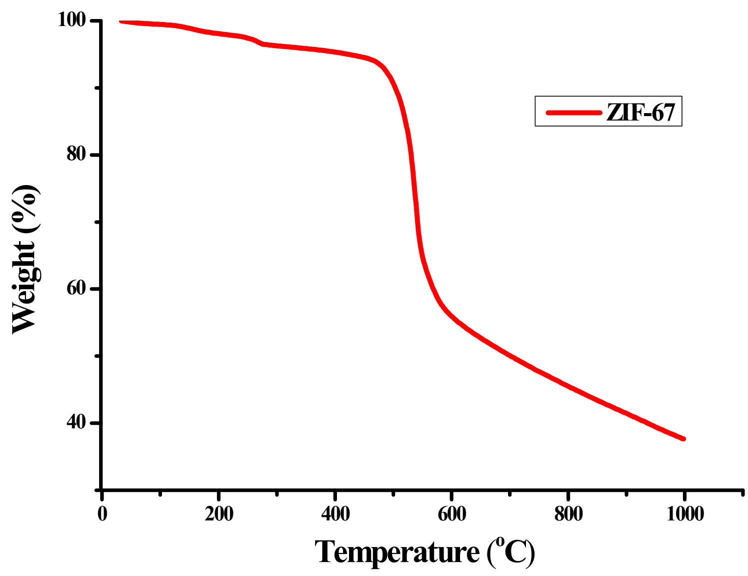

Figure S2. TGA curve for ZIF-67 under a nitrogen atmosphere. The sample was dried at 80 °C for 2 h before measurement.

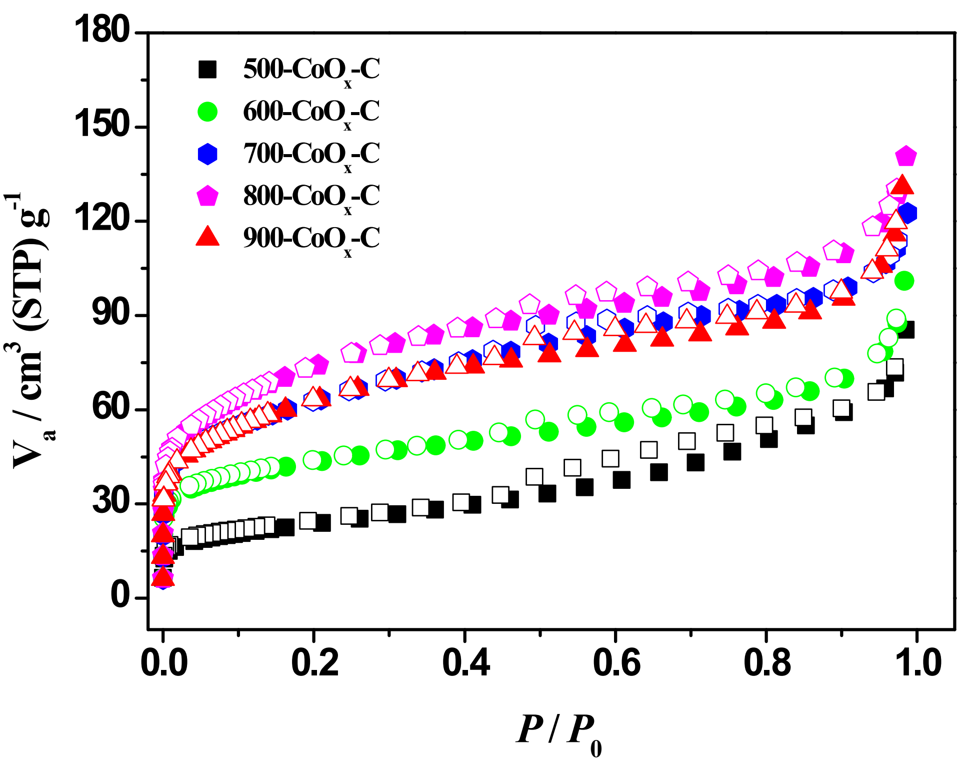

Figure S3. N_2 adsorption isotherms for T-CoO_x-C at 77 K.

Table S1. The results of N_2 adsorption-desorption analysis for T-CoO_x-C

	Volume adsorbed ($cm^3 \cdot g^{-1}$)	Average pore size (nm)	specific surface area ($m^2 \cdot g^{-1}$)
500-CoO_x-C	85	6.3	84
600-CoO_x-C	101	4.0	157
700-CoO_x-C	123	3.4	223
800-CoO_x-C	141	3.3	262
900-CoO_x-C	131	3.6	225

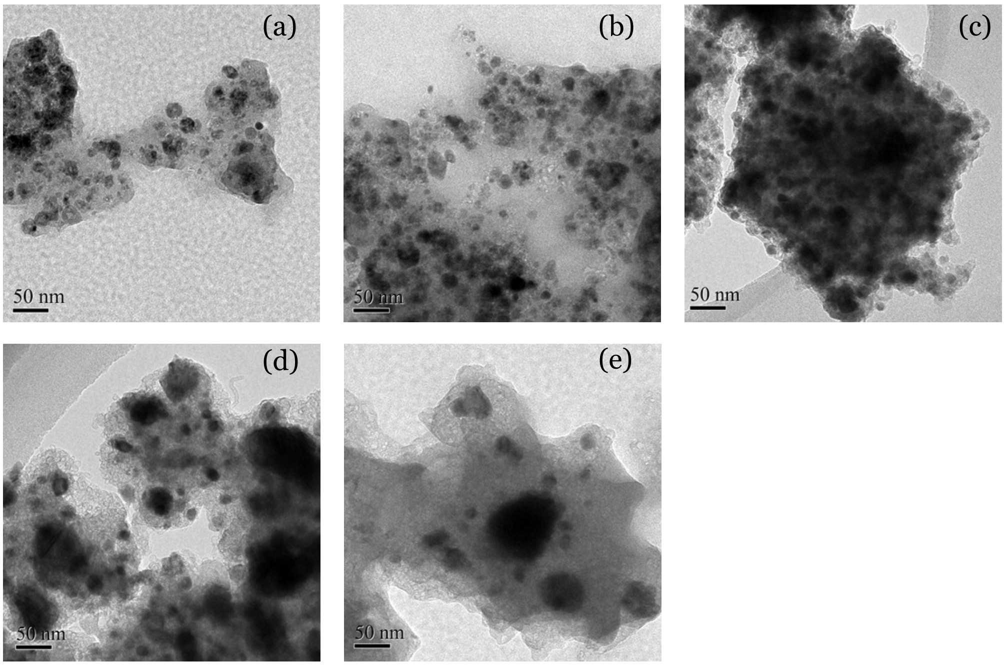

Figure S4. TEM images for (a) 500-CoO_x-C, (b) 600-CoO_x-C, (c) 700-CoO_x-C, (d) 800-CoO_x-C and (e) 900-CoO_x-C.

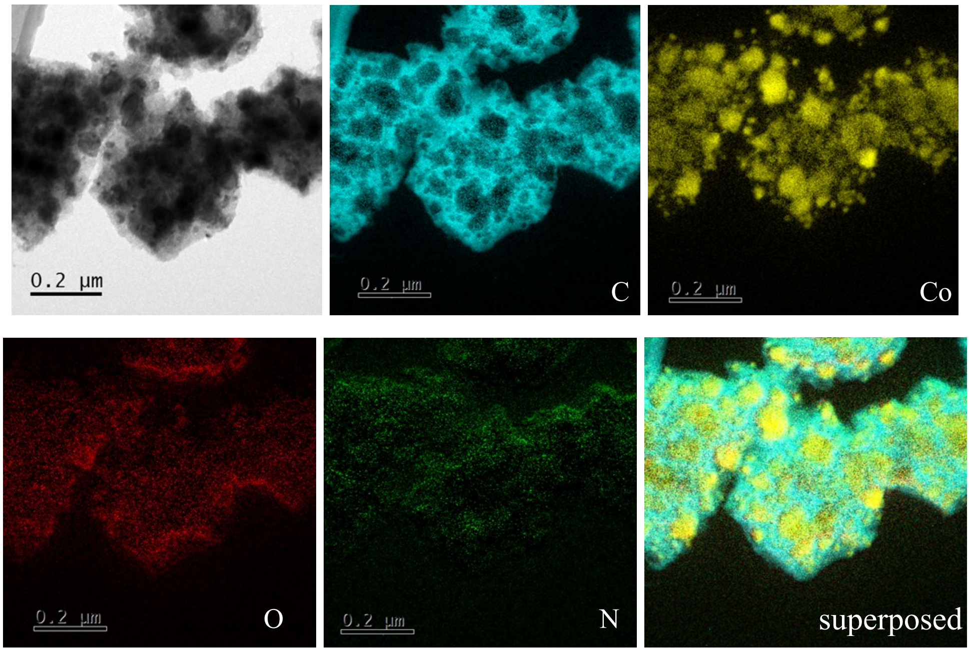

Figure S5. TEM image (top left), and EDS elemental mapping images for 800-CoO_x-C.

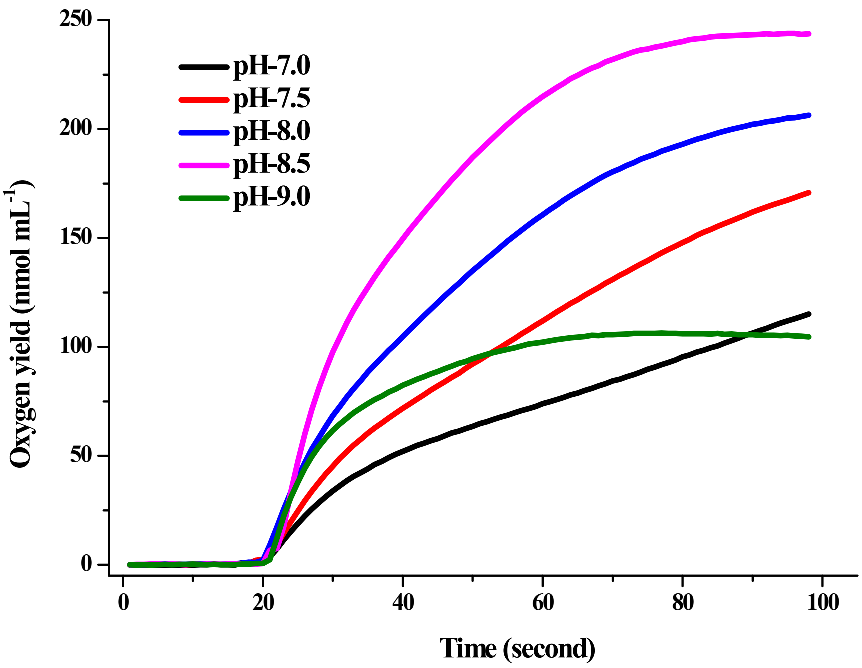

Figure S6. Oxygen yields from chemical water oxidation under different pH values, using $Ru(bpy)_3(PF_6)_3$ (4.5 mM) as an oxidant. Experimental conditions: 1 μg catalyst (3 μM for Co), 0.1M NaB_i buffer.

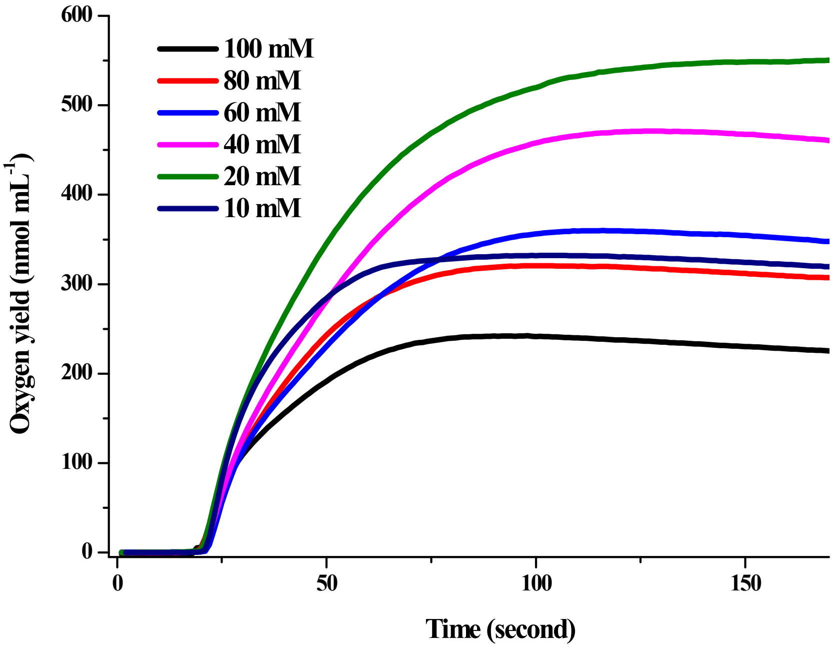

Figure S7. Oxygen yields from chemical water oxidation under different concentrations of NaB_i buffer using 9 mg of $Ru(bpy)_3(PF_6)_3$ (4.5 mM) as an oxidant. Experimental condition: 1 μg catalyst (3 μM for Co), pH 8.5.

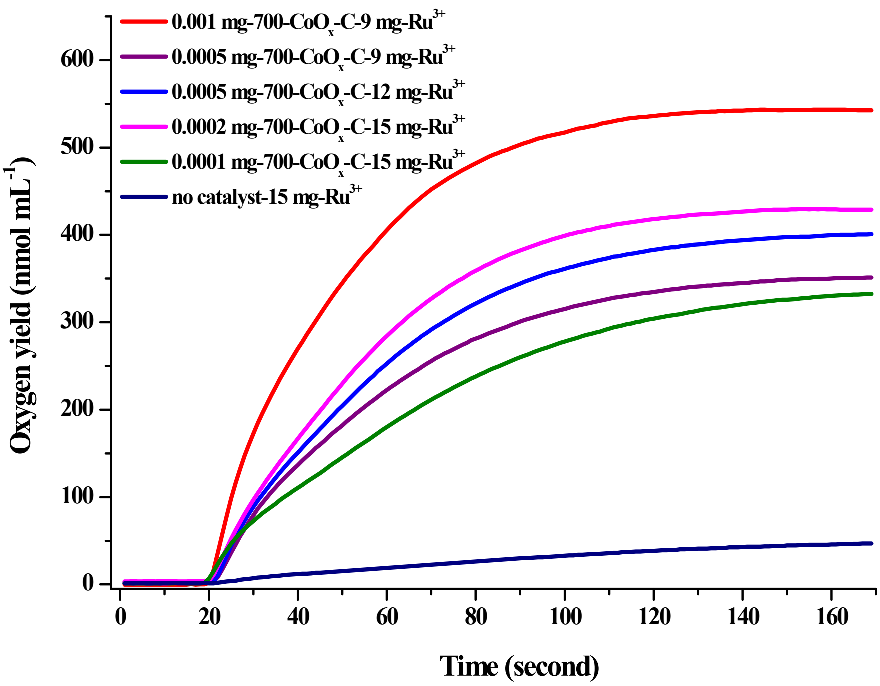

Figure S8. Oxygen yields from chemical water oxidation using different amounts of catalyst, using $Ru(bpy)_3(PF_6)_3$ as an oxidant. Experimental condition: 20 mM NaB_i, pH 8.5.

Table S2. The results of chemical water oxidation under different conditions

700-CoO_x-C (μM for Co)	$Ru(bpy)_3(PF_6)_3$ (mM)	TON	TOF (in initial 20 s)
3	4.5	160 ± 8	4.0 ± 0.1
1.5	4.5	191 ± 7	4.1 ± 0.2
1.5	6	225 ± 11	4.5 ± 0.2
0.6	6	598 ± 20	12.0 ± 0.5
0.3	7.5	910 ± 21	14.6 ± 0.4

Measurement condition: 20 mM NaB_i, pH 8.5.

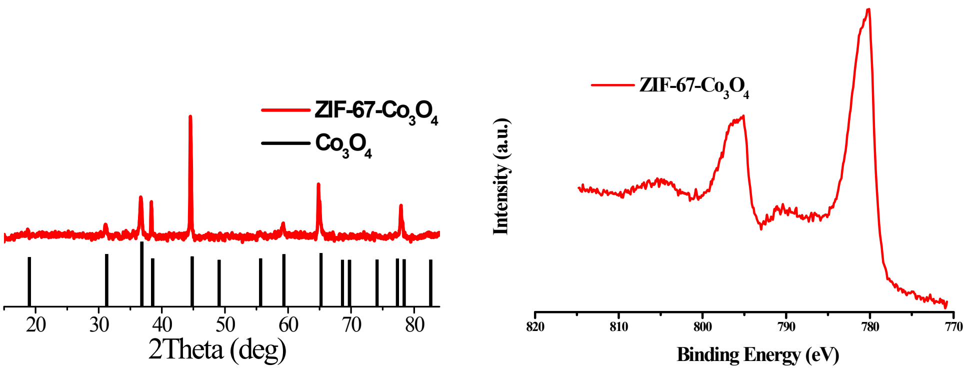

Figure S9. The PXRD pattern (left) and XPS pattern (right) for ZIF-67-Co_3O_4.

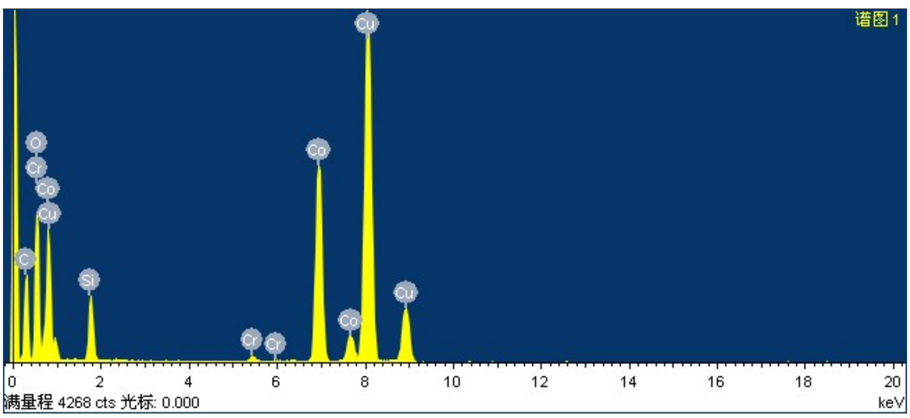

Figure S10. The EDS pattern of ZIF-67-Co_3O_4. (Co and O from ZIF-67-Co_3O_4，Cu from copper net, Cr and Si from the barrel and probe of the instrument)

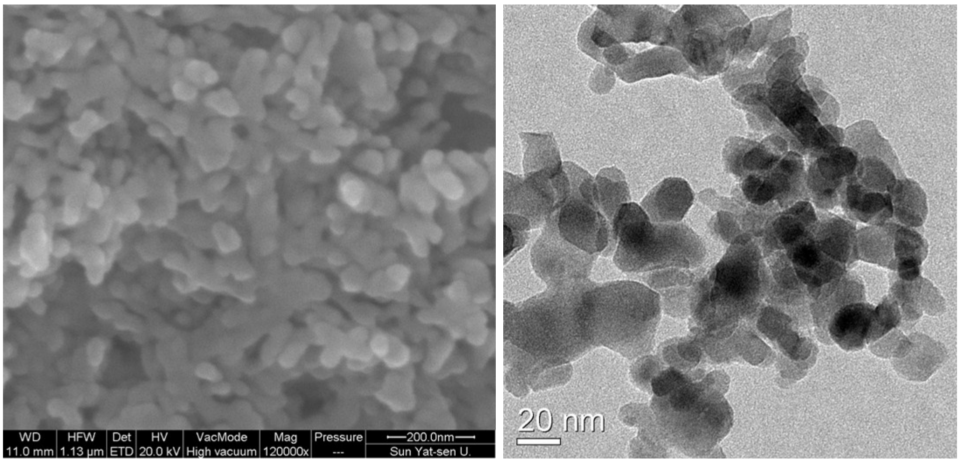

Figure S11. SEM (left) and TEM (right) images for ZIF-67-Co_3O_4.

Table S3. TONs and TOFs for different catalysts from chemical water oxidation

Catalyst	TON	TOF (in initial 20 s)
700-CoO_x-C	910 ± 21	14.6 ± 0.4
mixed ZIF-67-Co_3O_4 + carbon	503 ± 16	7.2 ± 0.2
ZIF-67-Co_3O_4	225 ± 13	2.6 ± 0.1
IrO_2	303 ± 17	3.4 ± 0.1
RuO_2	102 ± 7	1.0 ± 0.04

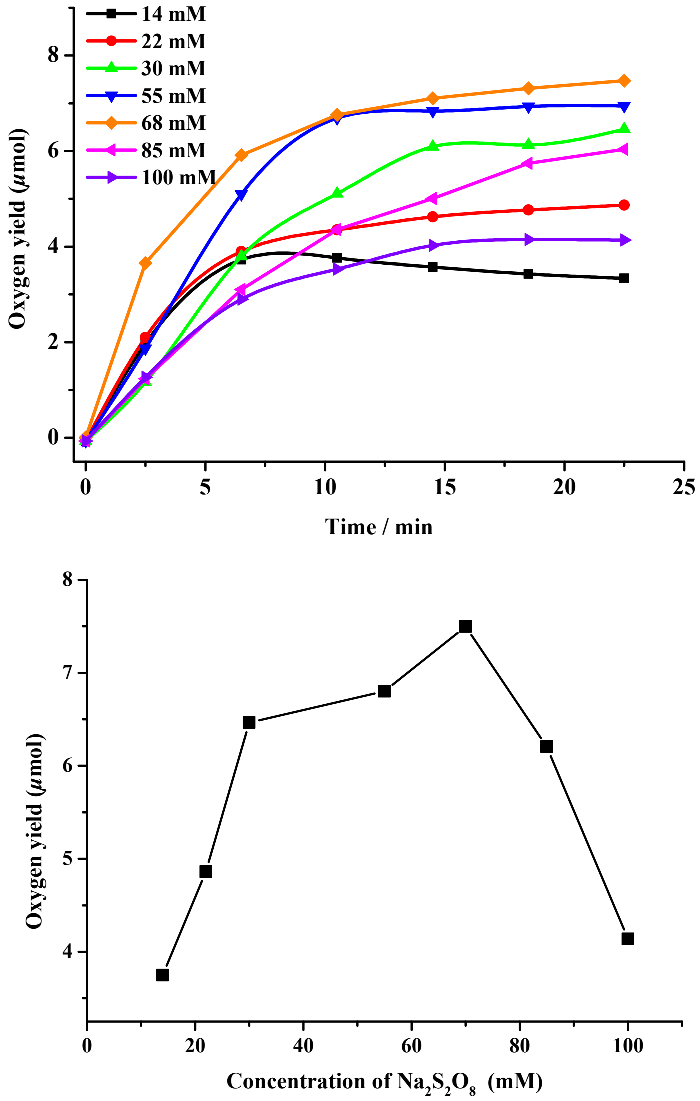

Figure S12. Oxygen yields from photochemical oxidation under different concentrations of $Na_2S_2O_8$. Experimental conditions: 100 W xenon lamp ($\lambda \geq 420$ nm), 0.1 mg 700-CoO_x-C (3 μM for Co), $[Ru(bpy)_3](ClO_4)_2$ (4.2 mM), 0.1 M sodium phosphate buffer pH 8.5, total volume of solution 3.1 mL.

Table S4. TONs and TOFs for recently reported Co-based WOCs under photo-chemical water odixation

catalyst	oxidant	TON (per Co atom)	TOF (s^{-1})	pH	*ref*
700-CoO_x-C	$[Ru(bpy)_3]^{2+}$-$Na_2S_2O_8$	12	3.9×10^{-2}	8.5	*This work*
Cobalt Oxide Nanocubanes	$[Ru(bpy)_3]^{2+}$-$Na_2S_2O_8$	1.35	2.3×10^{-2}	5.8	*J. Am. Chem. Soc.* **2015**, *137*, 4223−4229
Co_3O_4/porous SiO_2 core/shell	$[Ru(bpy)_3]^{2+}$-$Na_2S_2O_8$	2.12		5.8	*ACS Catal.* **2015**, *5*, 1037−1044
Mesoporous Co_3O_4	Ce^{4+}	0.25	2.2×10^{-3}	1 ~ 2	*J. Am. Chem. Soc.* **2013**, *135*, 4516-4521
Co_3O_4 in mesoporous silica support	$[Ru(bpy)_3]^{2+}$-$Na_2S_2O_8$		2.12×10^{-4} ~ 4.05×10^{-4}	5.8	*ACS Catal.* **2012**, *2*, 2753−2760
$Li_2Co_2O_4$	$[Ru(bpy)_3]^{2+}$-$Na_2S_2O_8$	0.2	1.0×10^{-3}	5.8	*Angew. Chem. Int. Ed.* **2012**, *51*, 1616-1619
Co_3O_4 in mesoporous silica SBA-15 support	$[Ru(bpy)_3]^{2+}$-$Na_2S_2O_8$	1.34		5.8	*Angew. Chem. Int. Ed.* **2009**, *48*, 1841-1844
6 nm Mn doped Co_3O_4 nanoparticles	$[Ru(bpy)_3]^{2+}$-$Na_2S_2O_8$	1.5	1.8×10^{-3}	5.8	*Catal. Today* **2014**, *225*, 171-176.
Hollow Co_3O_4 microsphere	$[Ru(bpy)_3]^{2+}$-$Na_2S_2O_8$		2.7×10^{-4}	5.8	*Nanoscale* **2014**, *6*, 7255-7262.
Co-SBA (single site)	$[Ru(bpy)_3]^{2+}$-$Na_2S_2O_8$		1.4×10^{-2}	5.6	*Energy Environ. Sci.* **2013**, *6*, 3080-3087.
Co-APO-5	$[Ru(bpy)_3]^{2+}$-$Na_2S_2O_8$		2.3×10^{-3}	6.0	*ACS Catal.* **2013**, *3*, 1272-1278
3 nm Co_3O_4 nanoparticles /SBA-15	$[Ru(bpy)_3]^{2+}$-$Na_2S_2O_8$		1.9×10^{-3}	5.8	*ACS Catal.* **2013**, *3*, 383-388

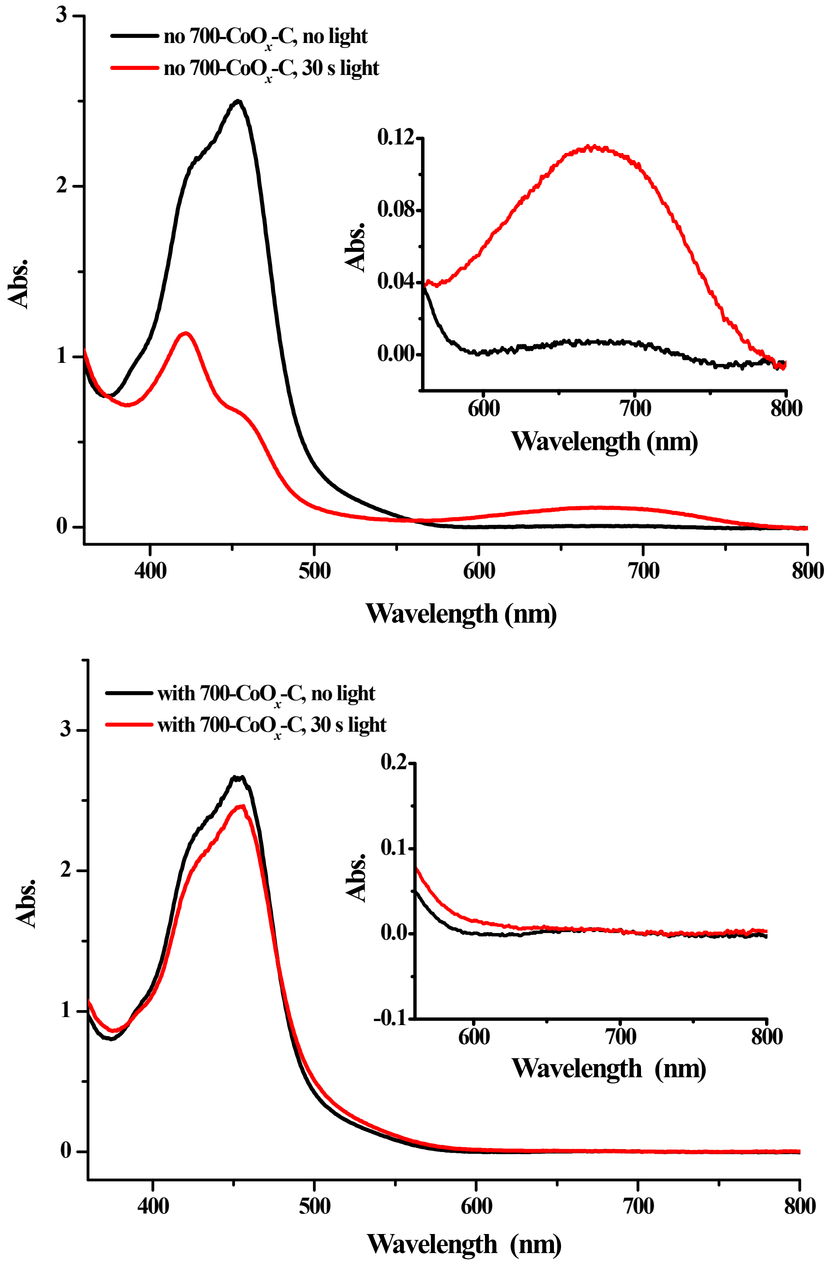

Figure S13. The UV-vis spectra of $[Ru(bpy)_3](ClO_4)_2$-$Na_2S_2O_8$ solution in the light-driven reaction (Above: no catalyst; Bottom: with 0.21 mM 700-CoO$_x$-C catalyst). Experimental conditions: 4.2 mM $[Ru(bpy)_3](ClO_4)_2$ and 68 mM $Na_2S_2O_8$; 100 W xenon lamp ($\lambda \geq 420$ nm), 0.1 M sodium phosphate buffer (pH 8.5), total solution volume 5 mL; The solution for UV-Vis test was diluted 10 times with NaPi buffer before measurement.

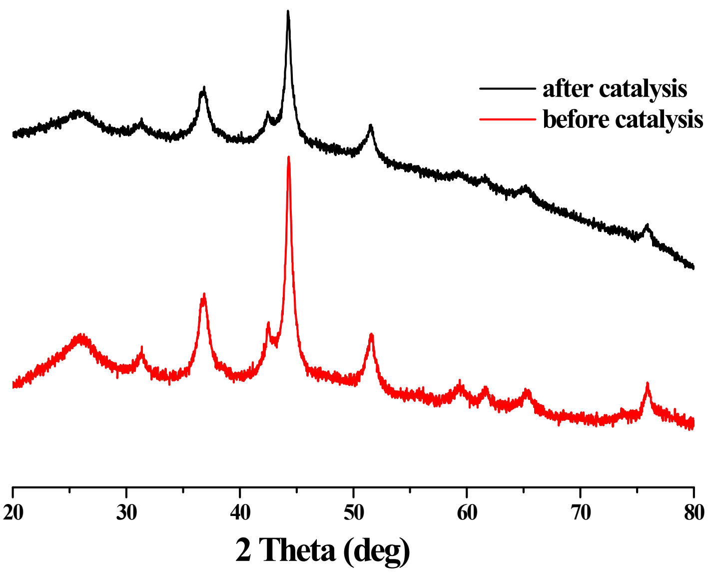

Figure S14. The PXRD patterns for 700-CoO_x-C catalyst before (red) and after (black) catalytic reaction.

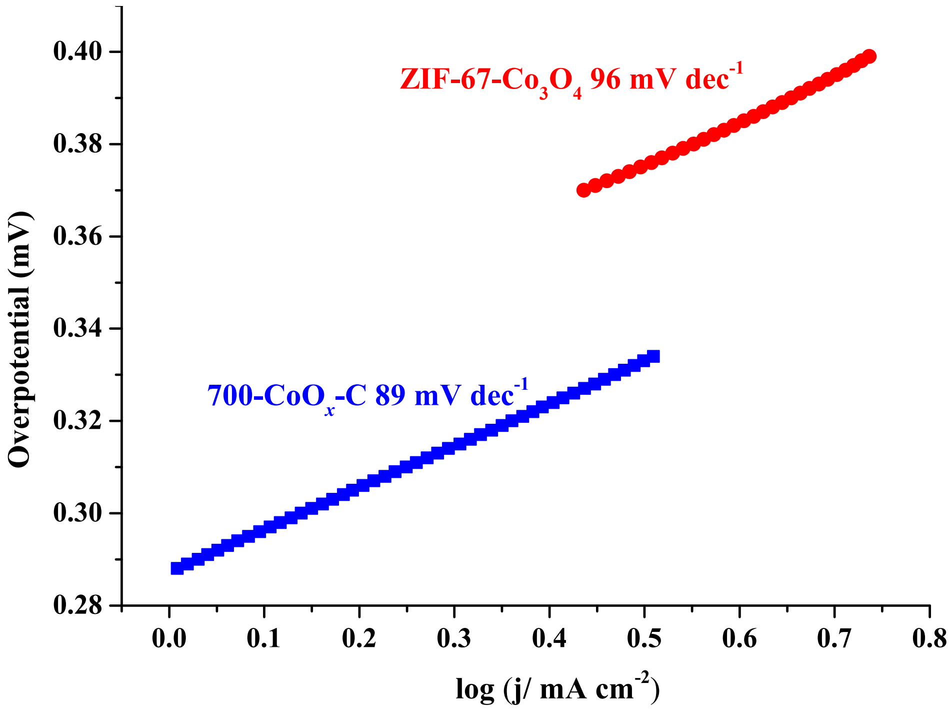

Figure S15. Tafel plot of 700-CoO_x-C in 0.1 M KOH solution (scan rate: 5 mV s^{-1}).

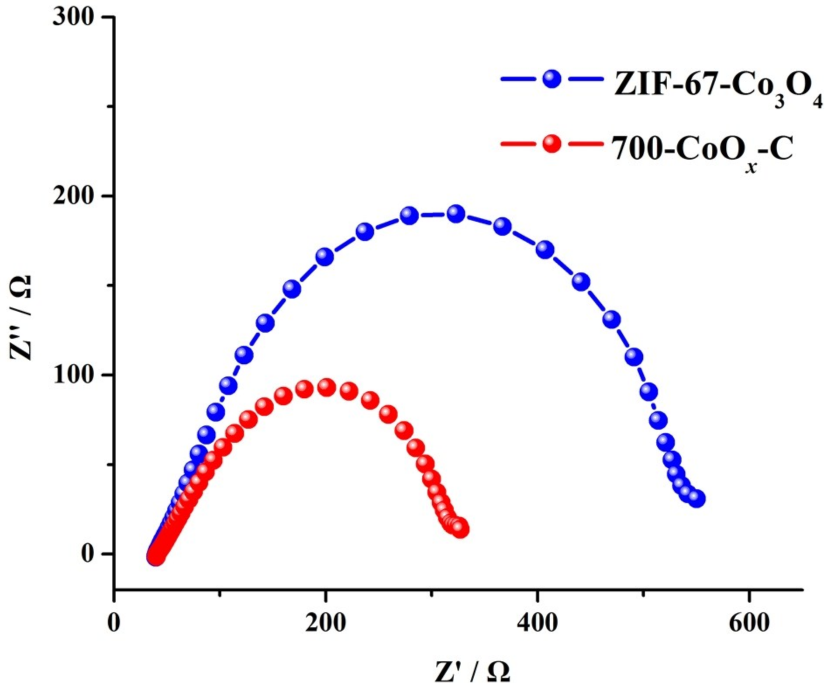

Figure S16. Electrochemical impedance spectrum of 700-CoO_x-C and ZIF-67-Co_3O_4 recorded at 1.63 V vs. RHE in 0.1 M KOH.

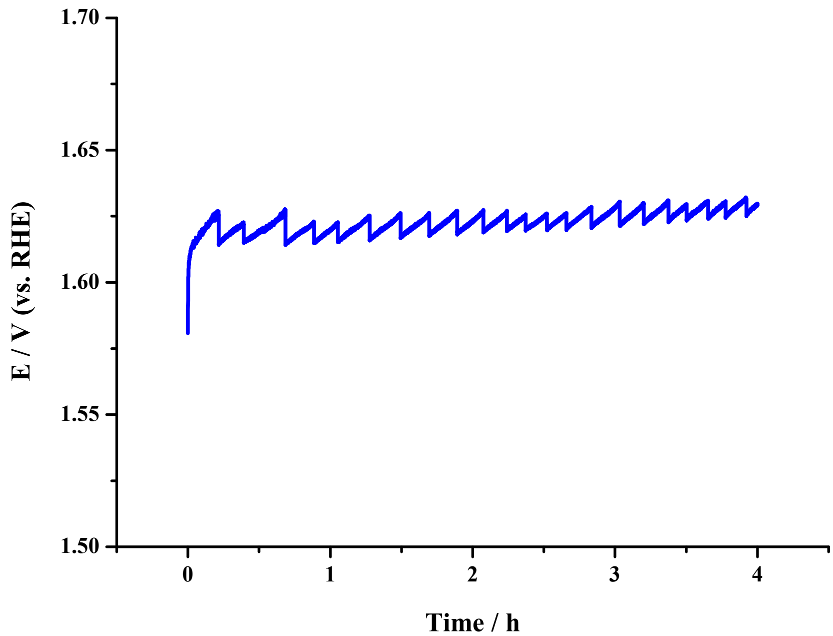

Figure S17. The curve of chronopotentiometry for 700-CoO_x-C (~ 0.2 mg cm^{-2}) on RDE (1500 rpm) at a constant current density of 10 mA cm^{-2} in 0.1 M KOH solution (The indented shape of the curve is due to the formation and release of oxygen bubbles at the surface of Nafion-catalyst film).