Supporting Information

High-performance TiO_2 photocatalyst caused by the versatile functions of the tiny bimetallic MOF-derived NiCoS-porous carbon cocatalyst

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1. Supporting Figures

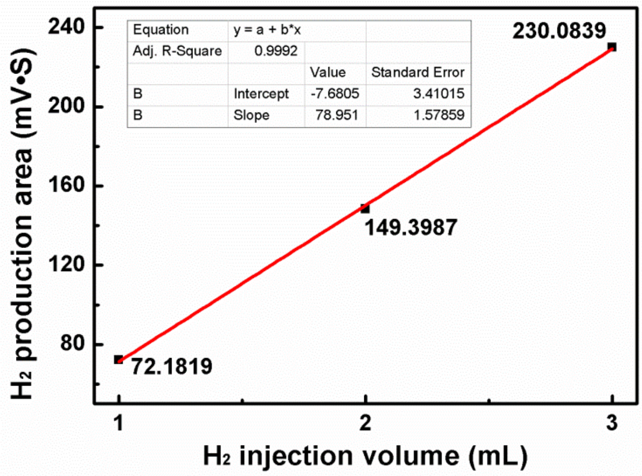


Fig. S1. The fitting straight line of the hydrogen injection volume and the hydrogen production area, and inset showing the corresponding fitting information.

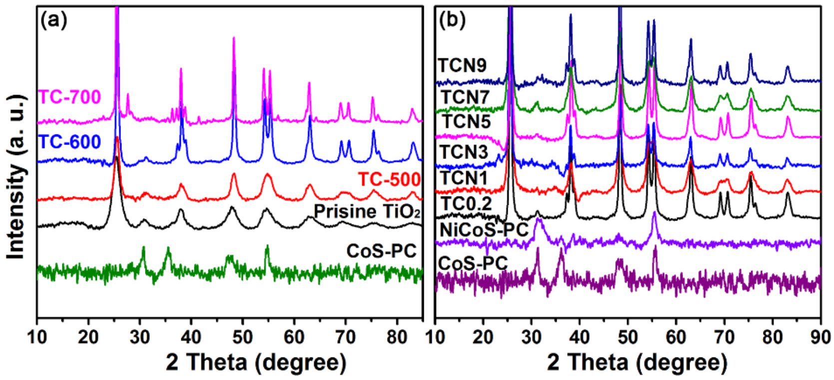


Fig. S2. The X-ray diffraction patterns of the TiO_2@0.2at% ZIF-67 post-annealed at different temperature, and (b) TCNy samples with different molar ratio of Co/Ni.

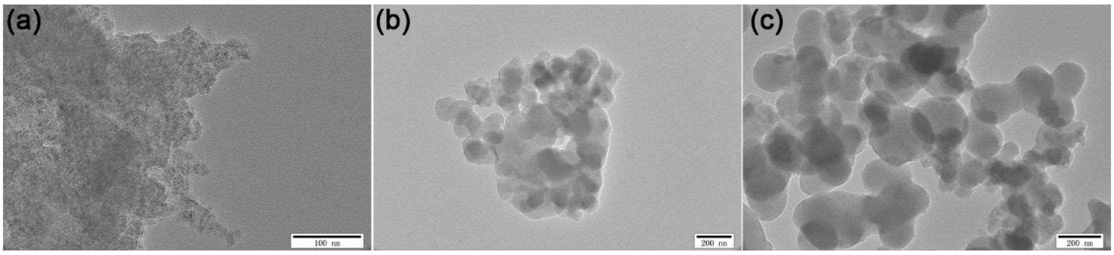


Fig. S3. The TEM images of the (a) pristine TiO_2, and the TiO_2 loaded with (b) 0.2 at% and (c) 0.5 at% ZIF-67.

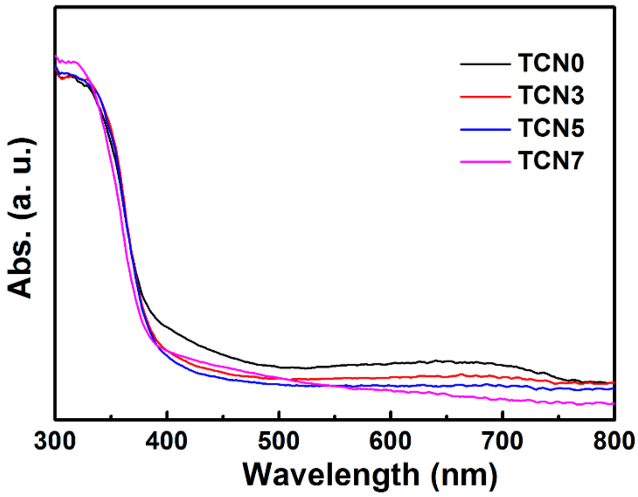


Fig. S4. The UV−visible diffuse reflection spectra of the TCNy samples with different molar ratio of Co/Ni with the total Ni+Co ratio to that of TiO_2 is 0.2 at%. It could be observed that the absorption in the visible region decreased a little bit with the increasing Ni concentration.

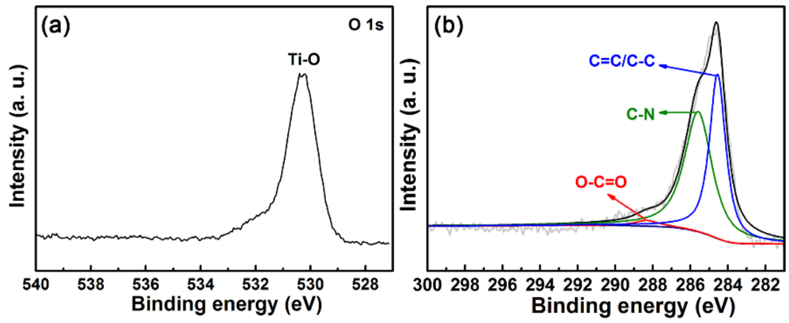
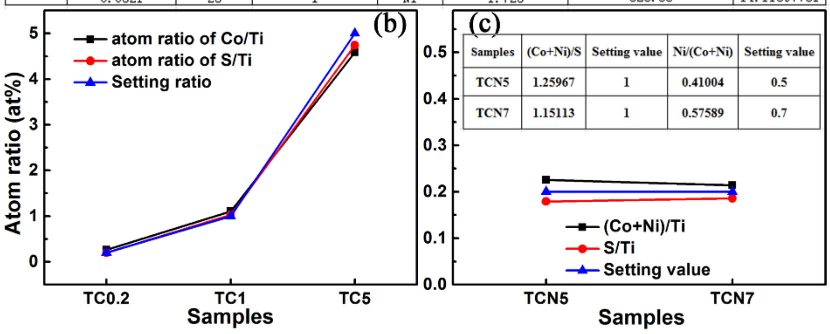


Fig. S5. The comparison of the XPS results of TiO2@Co0.5Ni0.5S-PC (TCN5) and Co0.5Ni0.5S-PC.

(a)

Samples	Sample mass/g	Volume/ml	Dilution factor	Element	Resulsts (mg/L)	Element mass (mg/kg)	Atom ratio
TC0.2	0.0511	25	50	Ti	23.586	576954.50	12052.5277
	0.0511	25	50	Co	3.7801	1849.37	31.38255179
	0.0511	25	50	S	1.5680	767.14	23.92819603
TC1	0.0693	25	50	Ti	31.596	569904.40	11905.25175
	0.0693	25	50	Co	0.429	7733.027	131.224
	0.0693	25	1	S	10.907	3934.81	122.7327639
TC5	0.0673	25	50	Ti	29.636	550436.48	11498.56859
	0.0673	25	50	Co	1.6735	31083.40	527.4630111
	0.0673	25	50	S	47.041	17474.33	545.0508843
TCN5	0.0516	25	50	Ti	23.223	562582.36	11752.29506
	0.0516	25	1	Co	0.0381	921.85	15.64314908
	0.0516	25	1	S	1.393	674.86	21.05004183
	0.0516	25	1	Ni	1.317	638.11	10.87247606
TCN7	0.0521	25	1	Ti	22.830	547744.72	11442.33803
	0.0521	25	1	Co	0.0255	612.53	10.39413527
	0.0521	25	1	S	1.422	682.57	21.29030501
	0.0521	25	1	Ni	1.726	828.35	14.11397731



Samples	(Co+Ni)/S	Setting value	Ni/(Co+Ni)	Setting value
TCN5	1.25967	1	0.41004	0.5
TCN7	1.15113	1	0.57589	0.7

Fig. S6. (a) Inductive coupled plasma (ICP) results, (b) the Co/Ti and S/Ti ratio in TCx samples and the (c) (Co+Ni)/Ti, S/Ti, (Co+Ni)/S, and Ni/(Co+Ni) ratio in the TCNy samples.

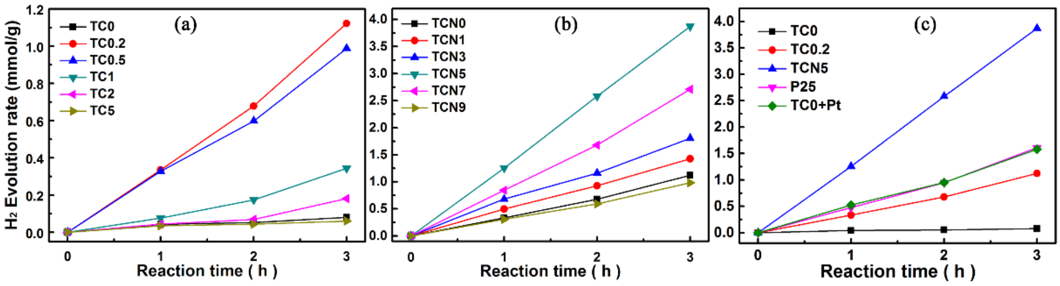


Fig. S7. Comparison of the action spectra of H_2-evolution for the (a) TCx, (b) TCNy samples and (c) commercial P25.

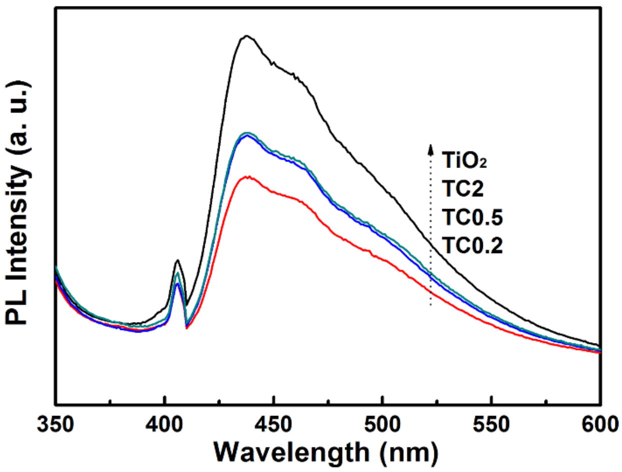


Fig. S8. Room temperature photoluminescence (PL) excitation spectra of the TCx samples.

2. Supporting Tables

Table S1 The synthetic conditions of TiO_2-ZIF-67

Samples	TiO_2 (mmol)	$Co(NO_3)_2 \cdot 6H_2O$ (μmol)	MIM (μmol)	Methanol (mL)	Stirring time (h)	Drying temperature (°C)
TiO_2	3.755	0	0	30	24	60
TC0.2	3.755	7.51	60.08	30	24	60
TC0.5	3.755	18.775	150.2	30	24	60
TC1	3.755	37.55	300.4	30	24	60
TC2	3.755	75.1	600.8	30	24	60

Table S2 The synthetic conditions of TiO_2-NiCo-ZIF

Samples	TiO_2 (mmol)	$Ni(NO_3)_2 \cdot 6H_2O$ (μmol)	$Co(NO_3)_2 \cdot 6H_2O$ (μmol)	MIM (μmol)
TC0.2	3.755	0	7.51	60.08
TCN1	3.755	0.751	6.759	60.08
TCN3	3.755	2.253	5.257	60.08
TCN5	3.755	3.755	3.755	60.08
TCN7	3.755	5.257	2.253	60.08
TCN9	3.755	6.759	0.751	60.08

Table S3 Hydrogen production area in dependence of injected H_2 volume

H_2 injection volume (mL)	H_2 peak area (mV·S)
1	72.1819
2	148.3987
3	230.0839

Table S4. The composition of the TiO_2@$Co_{0.5}Ni_{0.5}S$-PC (TCN5) tested by the X-ray photoelectron spectroscopy (XPS).

Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Atomic %
Ti2p	468.65	459.01	450.15	24286.53	2.32	94972.98	25.94
O1s	534.65	530.24	525.15	30345.53	2.52	90343.54	57.28
S2p	177.1	169.01	159.2	176.97	0.59	661.5	2.05
Co2p	814.1	786.77	773.2	281.07	0.09	3155.74	1.22
Ni2p	886.1	858.46	846.2	368.89	0.07	3050	1.08