

Supporting Information

Conductive Ti_3C_2 and MOF-derived CoS_x boosting the photocatalytic hydrogen production activity of TiO_2

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1. Experimental Section:

1.1 Chemicals: Titanium isopropoxide, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2-Methylimidazole, methanol, ethanol and thioacetamide (TAA) are analytical grade (Shanghai Macklin Biochemical Technology Co., Ltd), and used as received without further purification. Titanium aluminum carbide (Ti_3AlC_2 , $\geq 98\%$) was purchased from Tianmazhahui Technology Company (Beijing, China).

1.2 Sample preparation

1.2.1 Synthesis of amorphous TiO_2

The amorphous TiO_2 was synthesized through a hydrolysis method. Briefly, titanium isopropoxide (10 mL) as the precursor was added to 25 mL methanol. Thereafter, the 5 mL distilled water was slowly added to the above solution dropwise, followed with a series of hydrolysis processes to form the Ti-O complex via magnetic stirring at room temperature for 1 h. After that, the white powders were collected by centrifugation and washed thoroughly with ethanol and distilled water for several times respectively, and then dried at 60 °C for 10 h to obtain the amorphous TiO_2 .

1.2.2 Synthesis of Ti_3C_2

Typically, the Al layer in Ti_3AlC_2 was peeled off with HF (49 wt%), and stirred at room temperature for 4 h. Then the black powders were thoroughly washed with distilled water, and dried at 60 °C for 10 h to obtain the Ti_3C_2 .

1.2.3 Synthesis of TiO_2 - Ti_3C_2 -ZIF-67, TiO_2 -ZIF-67 and ZIF-67

TiO_2 - Ti_3C_2 -ZIF-67 samples were synthesized through a simple mixing process. In the synthesis, the mixture, including 5 mmol of the above prepared amorphous TiO_2 , various amounts of Ti_3C_2 , 0.05 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.4 mmol of 2-methylimidazole, was stirred at room temperature for 24 h. Then, the product was collected by centrifugation, and washed by ethanol for several times. Finally, the powders were obtained by drying at 60 °C for 12 h. The samples procured with various concentration of Ti_3C_2 and 1% ZIF-67 were labeled as TiO_2 -x Ti_3C_2 -ZIF-67

($x = 0.2, 0.5, 1, 2, 5\%$), in which x were the mass ratio of Ti_3C_2 to TiO_2 in the composites. TiO_2 -ZIF-67 samples were also prepared via the similar procedure but without the addition of Ti_3C_2 . The samples prepared with various contents of $Co(NO_3)_2 \cdot 6H_2O$ and 2-methylimidazole (The molar ratio of $Co(NO_3)_2 \cdot 6H_2O$ to 2-methylimidazole kepted 1:8) were marked as TiO_2 - x ZIF-67 ($x = 0.2, 0.5, 1, 2, 5\%$), which x were the molar ratio of ZIF-67 to TiO_2 in the composites. For comparison, pure ZIF-67 was synthesized under the similar conditions but without the addition of TiO_2 and Ti_3C_2 . And the molar ratio of $Co(NO_3)_2 \cdot 6H_2O$ to 2-methylimidazole also was 1:8.

1.2.4 Synthesis of TiO_2 - Ti_3C_2 - CoS_x , TiO_2 - CoS_x , TiO_2 - Ti_3C_2 , CoS_x and CoS

The samples were prepared by the solvothermal method using a typical synthetic procedure. Typically, appropriate amount of TAA (the molar ratio of TAA to ZIF-67 in the samples was 3:1) and 100 mg of the as-prepared TiO_2 - Ti_3C_2 -ZIF67 were dissolved in 30ml of methanol with stirring for 1h, thereafter, the mixture was transferred into a Teflon-lined stainless-steel autoclave and heated at 140 °C for 12 h. Then, the product (TiO_2 - Ti_3C_2 - CoS_x) was collected by centrifugation, and washed with ethanol, and dried at 60 °C for 12 h. According to the different addition amount of Ti_3C_2 in the prepared TiO_2 - Ti_3C_2 -ZIF-67, the samples were labeled as TM_xC_1 ($x = 0.2, 0.5, 1, 2, 5$). TiO_2 - CoS_x was transformed from TiO_2 -ZIF-67 by a similar method. On the basis of the different molar amount of ZIF-67 in the samples, the samples prepared with various contents of CoS_x were marked as TC_x ($x = 0.2, 0.5, 1, 2, 5\%$). Similarly, the TiO_2 - Ti_3C_2 samples were prepared via the above procedure but without the addition of CoS_x . The samples prepared with different qualities Ti_3C_2 were recorded as TM_x ($x = 0.2, 0.5, 1, 2, 5\%$). CoS_x was derived from ZIF-67 under the similar conditions. The CoS prepared with an $Co(NO_3)_2$ precursor was similar to the method of CoS_x without the addition of 2-methylimidazole. For comparison, pure TiO_2 were synthesized under the same situations in the absence of Ti_3C_2 and CoS_x .

2. Characterization

The powder X-ray diffraction (XRD) patterns were recorded on a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite monochromatized $Cu K\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$). Corresponding work voltage and current were 40 kV and 100 mA, respectively. The morphology of samples was researched using a scanning electron microscope (SEM, Zeiss SUPRA 55) with an accelerating voltage of 20 kV, combined with energy dispersive X-ray spectroscopy (EDS) for

determining the distribution of chemical components. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded on JEOL-2100F apparatus at an accelerating voltage of 200 kV. The UV-Vis absorption and diffused reflectance spectra were recorded using a Cary 5000 UV-Vis spectrometer (Varian, USA) with BaSO₄ as a reflectance standard. The X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB 250 Xi (USA)-ray photoelectron spectrometer using Al as the excitation source. Photoluminescence (PL) emission spectra were measured at room temperature by using a Fluorescence spectrophotometer with the excitation wavelength of 350 nm for the oxide. Time-resolved photo-luminescence (TRPL) decay measurements were performed by a photomultiplier (PMTH-S1-CR131) through a lock-in amplifier (SR 830). Electrochemical measurements were performed on a CHI 660E Electrochemical Workstation (CH Instruments, Inc. Shanghai). The electrochemical cell was assembled with a conventional three-electrode system, in which a glassy carbon electrode (3 mm in diameter), (sheet resistance 20–25 Ω/square) with a geometrical area of $1.0 \pm 0.1 \text{ cm}^2$ as the working electrode, a platinum wire as the auxiliary electrode, and a Ag/AgCl electrode as the reference electrode. The sample dropped on the working electrode was prepared as follows: all the samples were dispersed in the mixed solution of deionized water and methanol ($V_d : V_m = 3 : 1$) with a concentration of 1 mg/mL and deposited on the glassy carbon electrode and dried infrared light irradiation. The electrolyte of transient photocurrent responses experiments, Electrochemical impedance spectroscopy (EIS), and Mott-Schottky (MS) was 0.5 M Na₂SO₄ aqueous solution and the the electrolyte of linear sweep voltammetry (LSV) was 0.5 M sulfuric acid. EIS was performed at a impressed voltage of -0.3 eV, for voltage ranging from -2.5 V to 2.5 V. MS was measured for a scan voltage ranging from -1 V to 0.5 V. The transient photocurrent responses measurement was performed under UV-Visible light irradiation. The LSV obtained at a scan rate of 1 mV/s.

3. Photocatalytic Hydrogen Production

The photocatalytic H₂ production experiments were performed in a 100 mL Pyrex flask at ambient temperature and atmospheric pressure, and the openings of the flask were sealed with silicone rubber septum. A 300 W xenon arc lamp positioned 13 cm away from the reaction solution was used as a UV-Visible light source to trigger the photocatalytic reaction. In a typical

photocatalytic H₂-production experiment, 20 mg of the prepared photocatalyst was suspended in 50 mL of mixed aqueous solution containing 40 mL distilled water and 10 mL methanol. Before irradiation, the system was vacuumed for 5 min via the vacuum pump to completely remove the dissolved oxygen and ensure the reactor was in an anaerobic condition. A continuous magnetic stirrer was applied at the bottom of the reactor to keep the photocatalyst particles in suspension during the experiments. H₂ content was analyzed by gas chromatography (GC-7900, CEAULight, China). All glassware was carefully rinsed with deionized water prior to use.

4. Supporting Figures

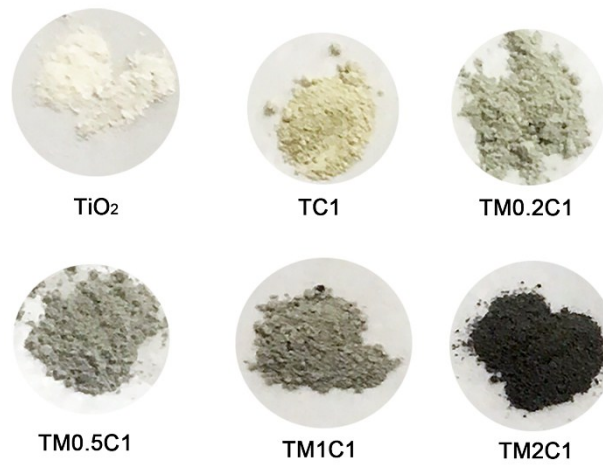


Fig. S1. The photographs of the **TiO₂-CoS_x** heterostructures with different amount of Ti₃C₂.

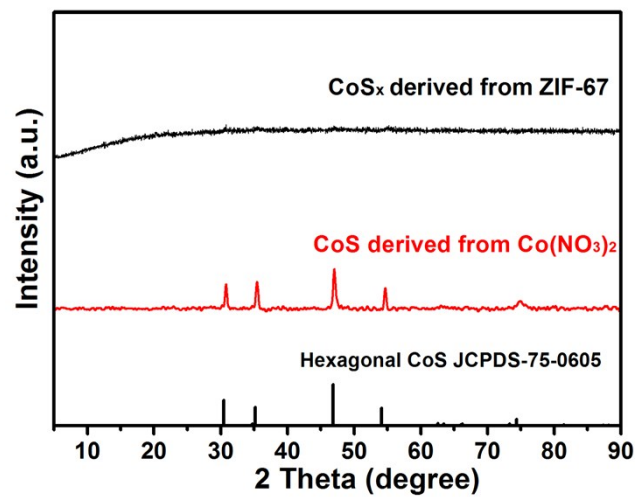


Fig. S2. The XRD pattern of the CoS prepared with Co(NO₃)₂ precursor and CoS_x derived from ZIF-67.

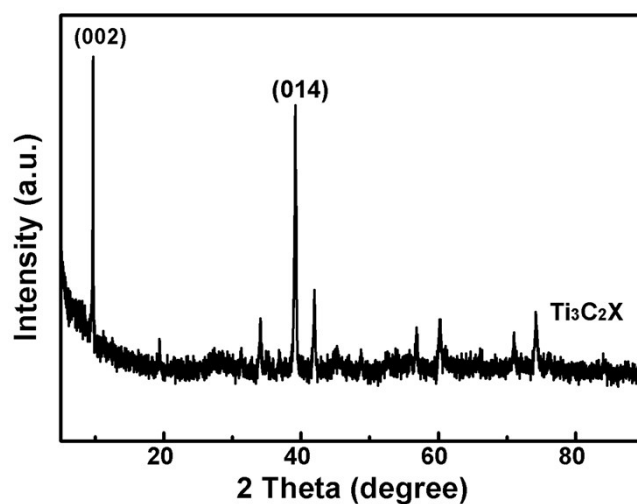


Fig. S3. The X-ray diffraction (XRD) patterns of the Ti_3C_2 derived from the Ti_3AlC_2 .

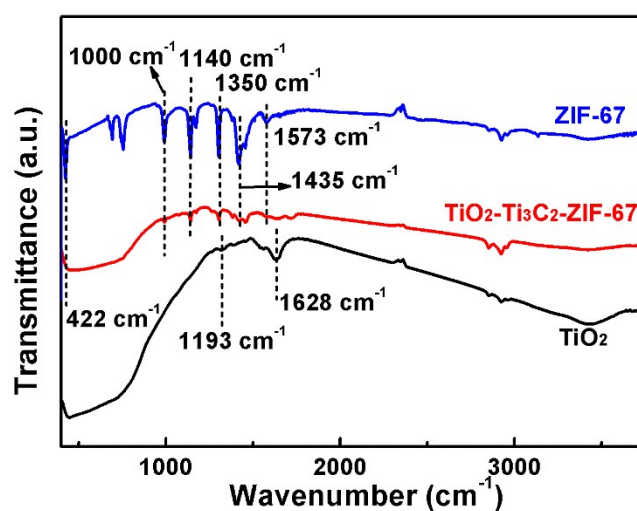


Fig. S4. The FTIR spectra of $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-ZIF-67}$, ZIF-67 and TiO_2 .

Table S1. The composition of the $\text{TiO}_2\text{-0.5 wt\% Ti}_3\text{C}_2\text{-1 at\% CoS}_x$ (TM0.5C1) tested by the mapping of energy dispersive X-ray spectroscopy (EDS).

Elements	Element concentration	Intensity correction	Weight percentage (%)	Atomic percent (%)
C K	12.87	0.8239	12.48	22.36
O K	17.67	0.3298	42.82	57.58
S K	0.24	0.9812	0.19	0.13
Ti K	48.58	0.8858	43.82	19.68
Co K	0.69	0.8110	0.68	0.25
summation			100	100

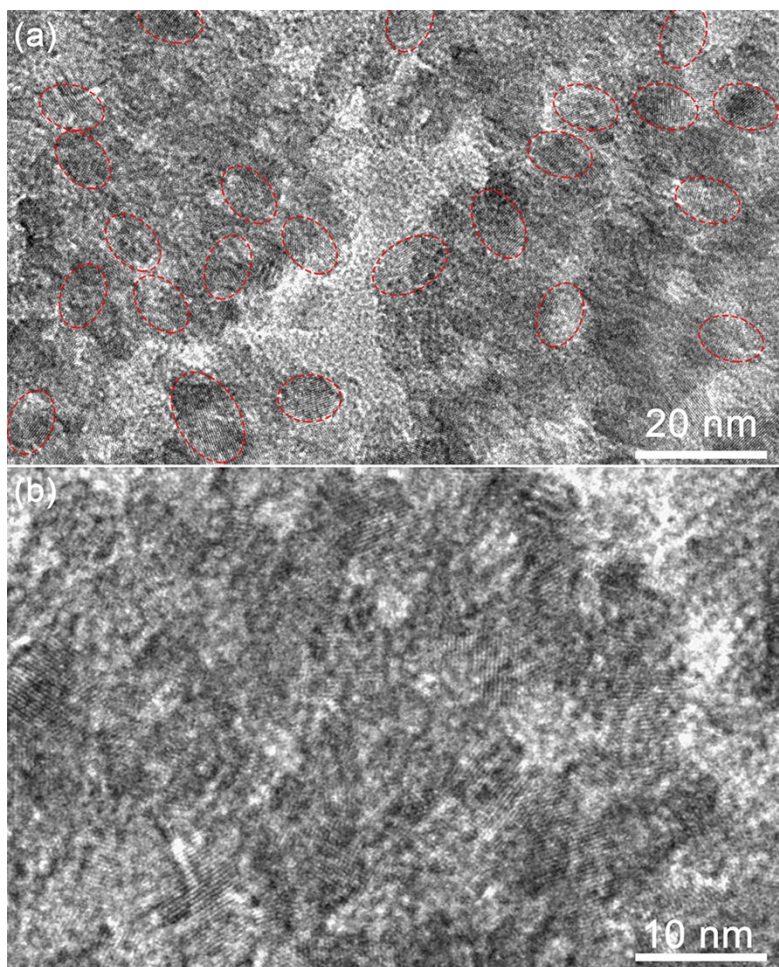


Fig. S5. The HRTEM image of the $\text{TiO}_2\text{-CoS}_x$ heterostructure.

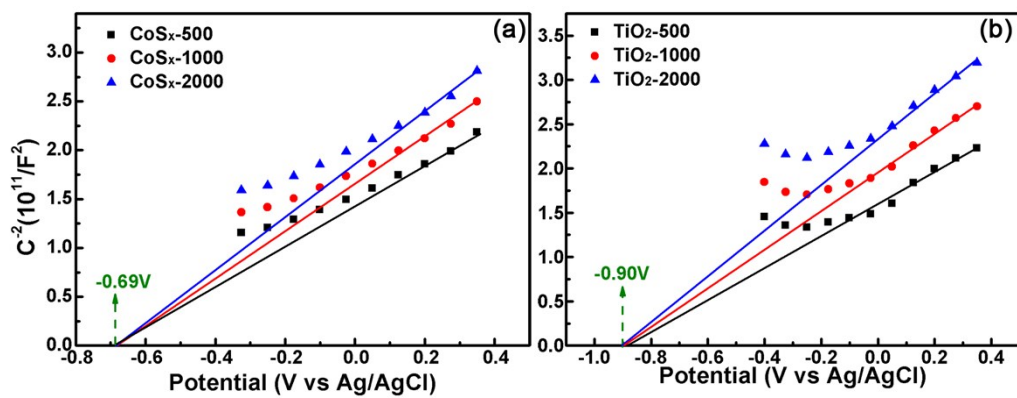


Fig. S6. The Mott-Schottky plots of (a) CoS_x and (b) TiO_2 with different frequency of 500, 1000, and 2000 Hz.

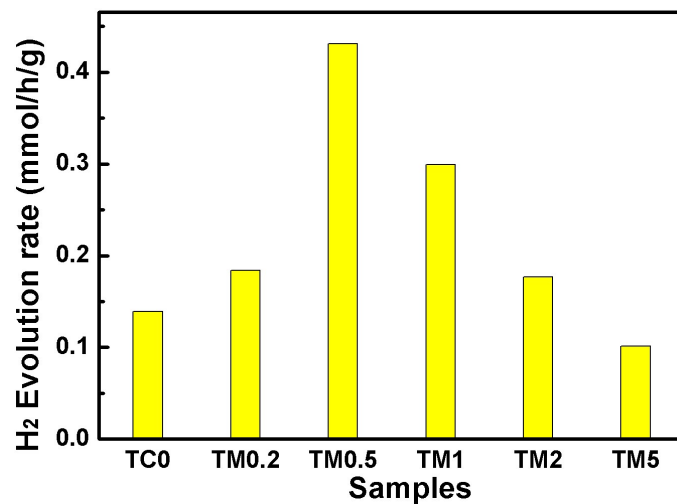


Fig. S7. The photocatalytic H₂-production activities of TiO₂-Ti₃C₂ samples with different content of Ti₃C₂.

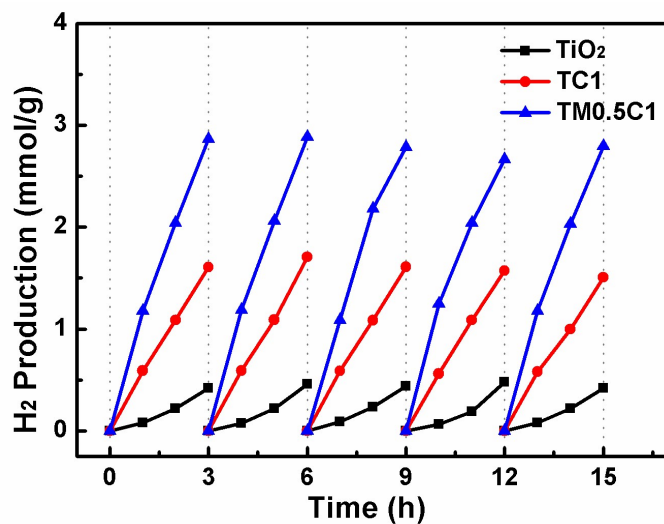


Fig. S8. Time cycles of photocatalytic H₂ evolution for sample TiO₂, TC1 and TM0.5C1.

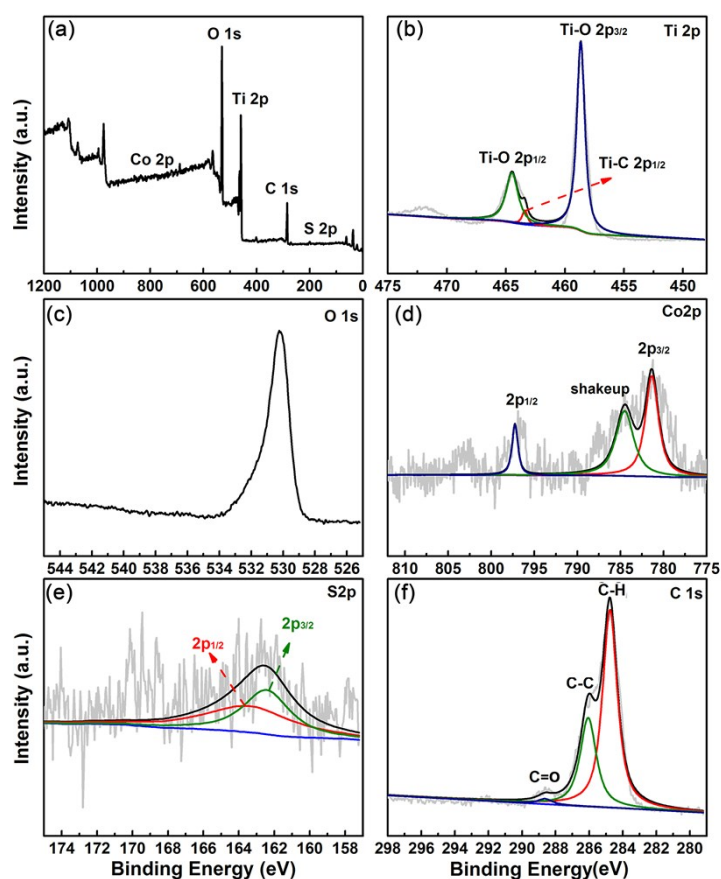


Fig. S9. (a) The XPS survey spectrum of TM0.5C1, the (b) Ti 2p, (c) O 1s, (d) Co 2p, (e) S 2p, and (f) C 1s high-resolution XPS spectra of TM0.5C1 after photocatalytic reaction.

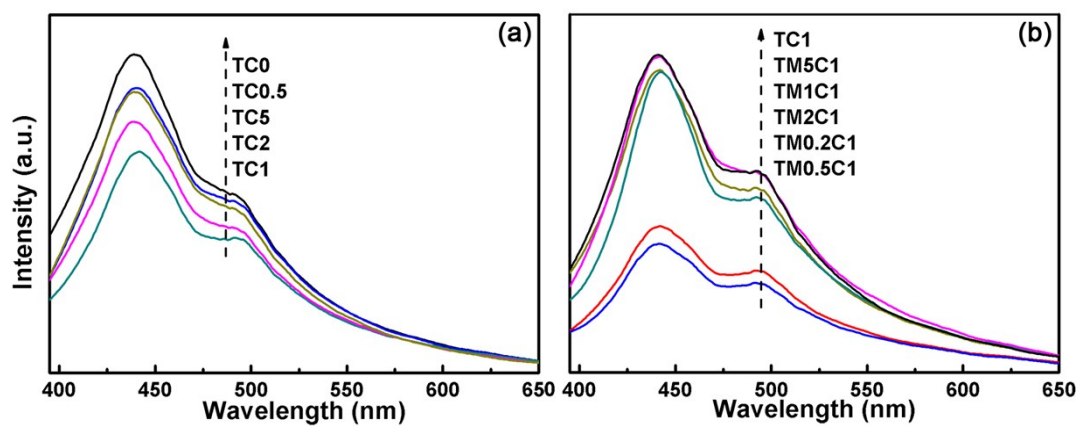


Fig. S10. The PL emission spectra of (a) $\text{TiO}_2\text{-CoS}_x$ and (b) $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-CoS}_x$ samples with different amount of CoS_x and Ti_3C_2 , respectively.

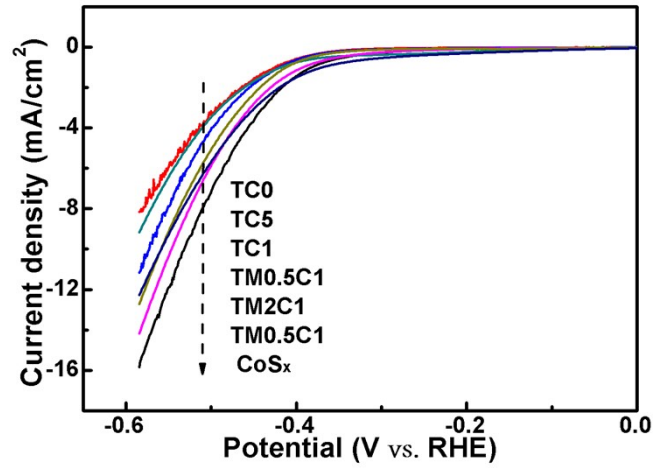


Fig. S11. The comparison of the LSV results of $\text{TiO}_2\text{-CoS}_x$ and $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-CoS}_x$ samples with different amount of CoS_x and Ti_3C_2 , respectively.

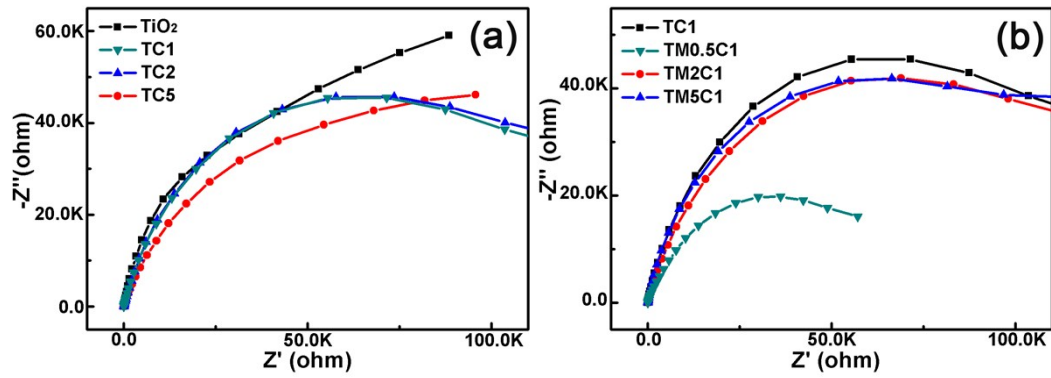


Fig. S12. The EIS spectra of (a) $\text{TiO}_2\text{-CoS}_x$ and (b) $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{-CoS}_x$ samples with different amount of CoS_x and Ti_3C_2 , respectively.