# Supplementary Information

## Chemicals and materials

$Ti_3AlC_2$ powders (400 mesh) were purchased from 11 Technology Co., Ltd. Ammonium molybdate ($H_{32}Mo_7N_6O_{28}$, Alfa Aesar, 99%), thiourea ($CH_4N_2S$, Sigma-Aldrich, ⩾99.0%), glucose ($C_6H_{12}O_6$, Aladdin, 99.5%), absolute ethanol ($C_2H_5OH$, ⩾99.7%), acetone ($CH_3COCH_3$, ⩾99.5%), tetramethylammonium hydroxide ($C_4H_{13}NO$, TMAOH, Aladdin, 25%), sulfuric acid ($H_2SO_4$, 95% ~ 98%), hydrochloric acid (HCl, 36% ~ 38%), sodium hydroxide (NaOH, Aladdin, 96%), potassium hydroxide (KOH, Aladdin, 90%), phosphate buffer (pH=7.0, Macklin), Ar gas (99.99%) were obtained from Sinopharm Chemical Reagent Co., Ltd. Reagent 5% Nafion solution was purchased from DuPont. Deionized water was used throughout the whole experiment. All chemicals were used as received without further purification.

## Preparation of fluorine-free $Ti_3C_2T_X$

The fluorine-free $Ti_3C_2T_X$ (Na-$Ti_3C_2T_X$) was prepared by a NaOH etching method as previously reported.[47] In short, 80 mg of $Ti_3AlC_2$ powders were immersed in a 27.5 M NaOH solution under argon (Ar) atmosphere. The mixture was then hydrothermally treated at 270 °C for 12 hours. Finally, the result suspension was filtered with deionized water washing for three times. The obtained powder was dried at 60°C for 12 hours.

## Preparation of D-Na-$Ti_3C_2T_X$

A 50 mg portion of Na-$Ti_3C_2T_X$ was dispersed into 10 mL of TMAOH. The solution was stirred at room temperature for 24 hours and then sonicated for D (D=0, 2, 5, 10 and 15) hours (5-Na-$Ti_3C_2T_X$ and I-Na-$Ti_3C_2T_X$ are the same). Finally, the obtained suspension was centrifugated at 6000 rpm for 30 minutes and dried in a freeze-drying vacuum.

## Preparation of D-Na-$Ti_3C_2T_X$/$MoS_2$

38.3 mg of ammonium molybdate, 500 mg of thiourea, 50 mg of glucose and 20 mg D-Na-$Ti_3C_2T_X$ were dissolved in 30 mL hydrochloric acid solution. Then, the mixed solution was transferred into an 50 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 12 hours. The black powders were collected by centrifugation, washed 3 times with deionized water and acetone and dried under vacuum at 60 °C.

## Characterizations

X-ray diffraction (XRD) patterns of the as-prepared powders were obtained with a Rigaku Ultima IV Powder Diffractometer (Cu Kα radiation, $\lambda = 0.15406$ nm, sweeping speed: 5° $min^{-1}$). Raman spectra were recorded on a Renishaw inVia reflex spectrometer using laser excitation of 532 nm. XPS spectra were used to analyze the valence states of Mo, S, Ti and other elements with Kratos Axis Ultra$^{DLD}$ spectrometer. The morphologies and microstructures of the as-prepared samples were characterized by scanning electron microscopy (SEM, 5 kV for morphology observation, Tescan, Czech) and transmission electron microscopy (TEM, 200 kV, FEI, America).

## Electrode preparation

The catalyst powders (4 mg) were dispersed in a mixture of 10 μL Nafion solution and 1 mL water-ethanol solution (3:1 by volume) to form a suspension. Then the suspension was sonicated at room temperature for 30 minutes to form a uniform catalyst electrode slurry. After that, 10 μL slurry was dropped on a glassy carbon electrode (GC) with a diameter of 5 mm, followed by natural drying (10 hours) at room temperature to obtain a HER electrode. The loading of the catalyst on the surface of the glassy carbon electrode was about 0.2 mg $cm^{-2}$.

## Electrochemical measurement

All electrochemical measurements were performed on an electrochemical workstation (Biologic VMP3) at room temperature and atmospheric conditions. Under acidic conditions, 0.5 M $H_2SO_4$ solution was used as the electrolyte solution, graphite rods (99.9995%, Alfa Aesar) were used as the counter electrodes, and Ag/AgCl electrodes were employed as reference electrodes, based on the Nernst equation $E$ (RHE) = $E$ (Ag/AgCl) + 0.059 pH + 0.198 V. Under neutral conditions, phosphate buffer solution (PBS) was the electrolyte solution, graphite rods (99.9995%, Alfa Aesar) were the counter electrodes, and Saturated Calomel Electrode (SCE) were the reference electrodes, based on the Nernst equation $E$ (RHE) = $E$ (SCE) + 0.059 pH + 0.241 V. Under alkaline conditions, the electrolyte was 1M KOH solution, graphite rods (99.9995%, Alfa Aesar) were the counter electrodes, and Hg/HgO were the reference electrodes, based on the Nernst equation $E$ (RHE) = $E$ (Hg/HgO) + 0.059 pH + 0.098 V. All potentials were referenced to the reversible hydrogen electrode potential in this work.

The polarization curves of HER were obtained by linear sweep voltammetry (LSV) with a scan rate of 2 mV $s^{-1}$ and a scan-interval of 0.2 to -0.6 V. Electrochemical impedance spectroscopy (EIS) measurements were carried out at an overpotential of 0.3 V and 0 V from $10^5$ to $10^{-1}$ Hz with an amplitude of 10 mV AC impedance. To measure the double-layer capacitance ($C_{dl}$), the cyclic voltammetry (CV) were recorded from 0.2 to 0.4 V at scan rates of 2, 5, 10, 20 and 40 mV $s^{-1}$. The HER stability of the catalyst was investigated with CV cycle method and chronopotentiometry experiment. The CV cycle tests range were 0.2 to -0.6 V and the sweep speed was 100 mV $s^{-1}$. The current density during the chronopotentiometry experiments was -100 mA $cm^{-2}$ and the test time were 20 hours.

Table S1

| Catalyst | Electrolyte | Overpotential | Tafel slope | References |
|---|---|---|---|---|
| **Few-layer fluorine-free $Ti_3C_2T_X/MoS_2$** | 0.5 M $H_2SO_4$<br>0.5 M PBS<br>1 M KOH | -139 mV<br>-299 mV<br>-217 mV | 78 mV $dec^{-1}$<br>178 mV $dec^{-1}$<br>107 mV $dec^{-1}$ | **This work** |
| **$MoS_2$** | 0.5 M $H_2SO_4$ | -269 mV | 66.7 mV $dec^{-1}$ | 21 |
| **Lamellar $MoS_2$** | 0.5 M $H_2SO_4$ | -461 mV | 142.6 mV $dec^{-1}$ | 33 |
| **Oxygen-functionalized $Ti_3C_2T_X$** | 0.5 M $H_2SO_4$ | -217 mV | 88.5 mV $dec^{-1}$ | 37 |
| **$Ti_3C_2T_X/MoS_2$** | 0.5 M $H_2SO_4$ | -280 mV | 68 mV $dec^{-1}$ | 22 |
| **“Nanoroll” like $Ti_3C_2T_X/MoS_2$** | 0.5 M $H_2SO_4$ | -152 mV | 70 mV $dec^{-1}$ | 23 |
| **$MoS_2$-12h/CB-12h** | 0.1 M $HClO_4$ | ~-260 mV | 79.6 mV $dec^{-1}$ | 27 |
| **$MoS_2$/C** | 0.5 M PBS | -310 mV | 94.4 mV $dec^{-1}$ | 24 |
| **amorphous $MoS_2$/FTO** | alkaline solution | -540 mV | / | 25 |

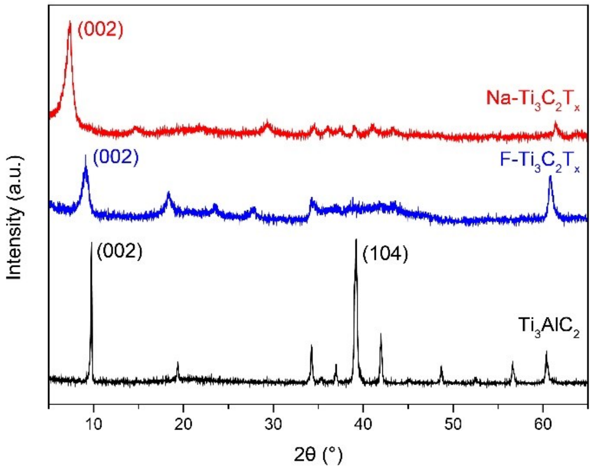

Fig. S1 XRD patterns of MAX, F-$Ti_3C_2T_X$ and Na-$Ti_3C_2T_X$.

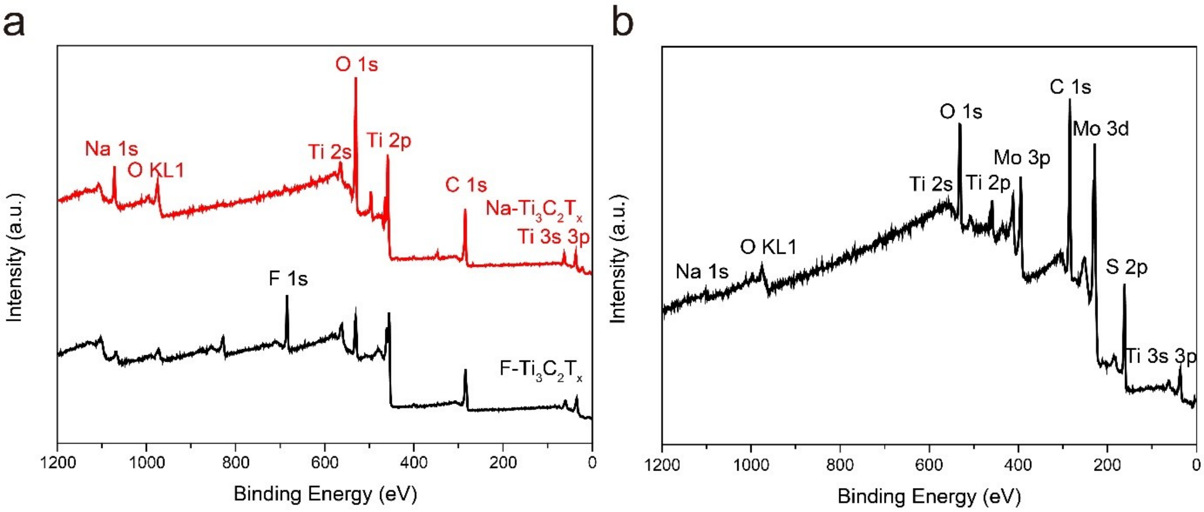

Fig. S2 XPS spectra of (a) F-$Ti_3C_2T_X$ and Na-$Ti_3C_2T_X$, (b) I-Na-$Ti_3C_2T_X$/$MoS_2$ hybrid.

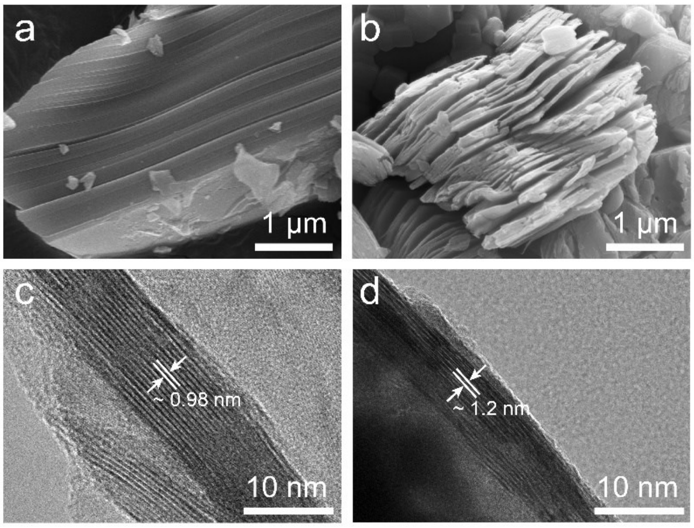

Fig. S3 (a) SEM image of MAX, (b-c) SEM and TEM images of F-$Ti_3C_2T_X$, (d) TEM image of Na-$Ti_3C_2T_X$.

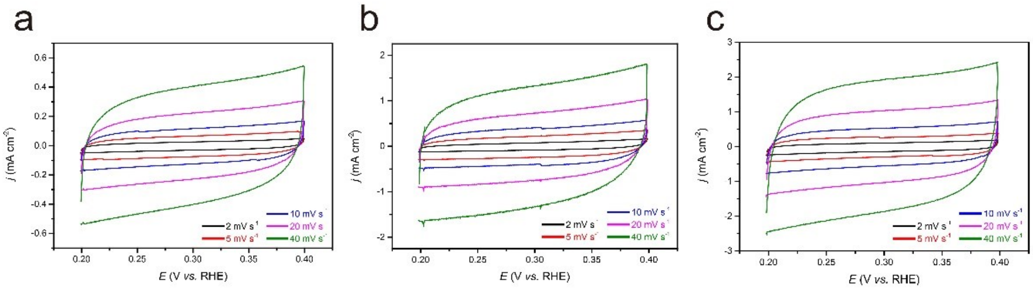

Fig. S4 CV curves of (a) $MoS_2$, (b) F-$Ti_3C_2T_X$/$MoS_2$, (c) I-Na-$Ti_3C_2T_X$/$MoS_2$.

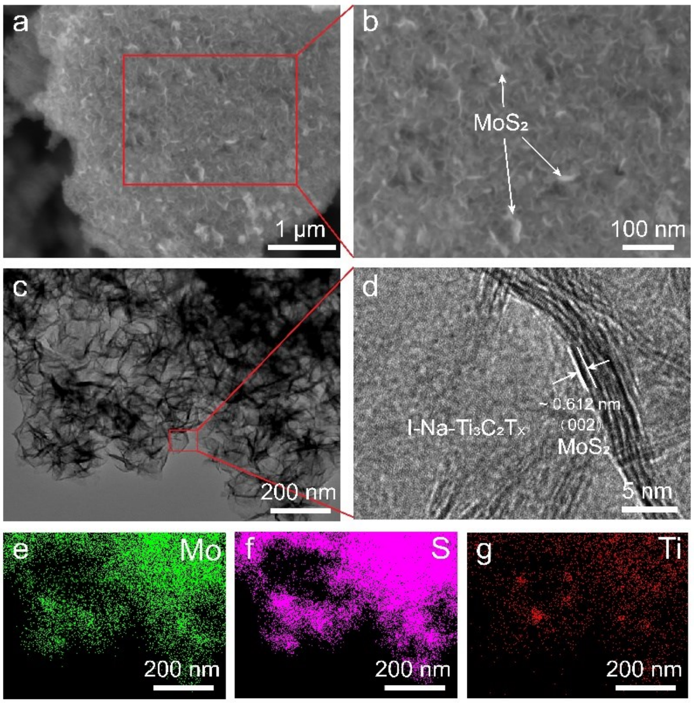

Fig. S5 (a-b) SEM and (c-d) TEM images of 5-Na-$Ti_3C_2T_X$/$MoS_2$ after the reaction for 20 hours, (e-g) corresponding elemental mappings of Mo, S and Ti of (c).

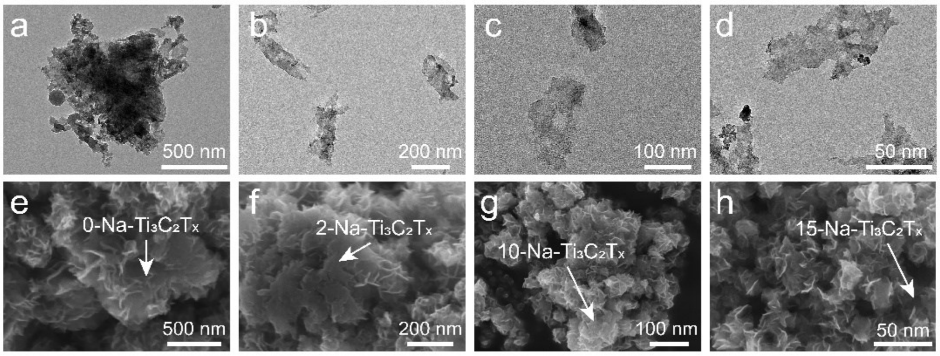

Fig. S6 SEM and TEM images of (a, e) 0-Na-$Ti_3C_2T_X$/$MoS_2$, (b, f) 2-Na-$Ti_3C_2T_X$/$MoS_2$, (c, g) 10-Na-$Ti_3C_2T_X$/$MoS_2$, and (d, h) 15-Na-$Ti_3C_2T_X$/$MoS_2$ with different lateral sizes.

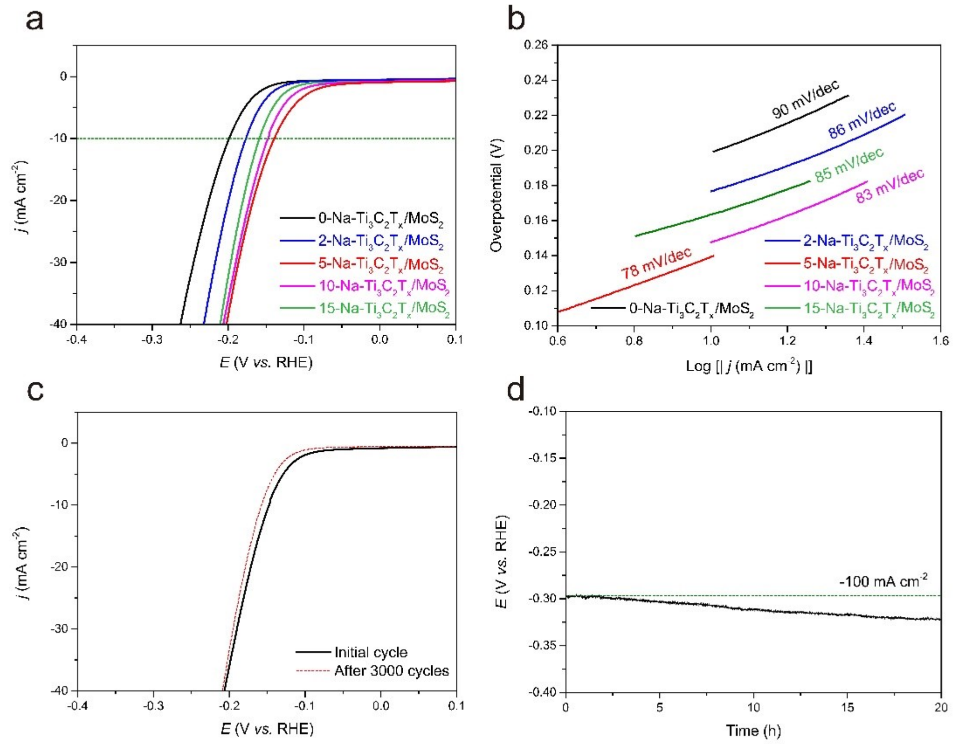

Fig. S7 (a) Polarization curves and (b) Tafel plots of 0-Na-$Ti_3C_2T_X/MoS_2$, 2-Na-$Ti_3C_2T_X/MoS_2$, 5-Na-$Ti_3C_2T_X/MoS_2$, 10-Na-$Ti_3C_2T_X/MoS_2$ and 15-Na-$Ti_3C_2T_X/MoS_2$, (c) Polarization curves were recorded for 10-Na-$Ti_3C_2T_X/MoS_2$ before and after 3000 potential cycles, (d) Time-dependent current density curve of 10-Na-$Ti_3C_2T_X/MoS_2$ under a static current density of -100 mA cm$^{-2}$ for 20h. All tests were performed in 0.5 M $H_2SO_4$ solution.