

## Electronic Supplementary Information

### Experimental Section

**Materials:** Ti Mesh (TiM) was obtained from Suzhou Taili New Energy Co., Ltd.  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_4\text{F}$ , urea and hydrazine hydrate (80%) were purchased from Tianjin Fuchen Chemical Reagent Factory. S powder was purchased from Sigma Aldrich Chemical Reagent Co., Ltd. All reagents were used as received. The water used throughout all experiments was purified through a Millipore system.

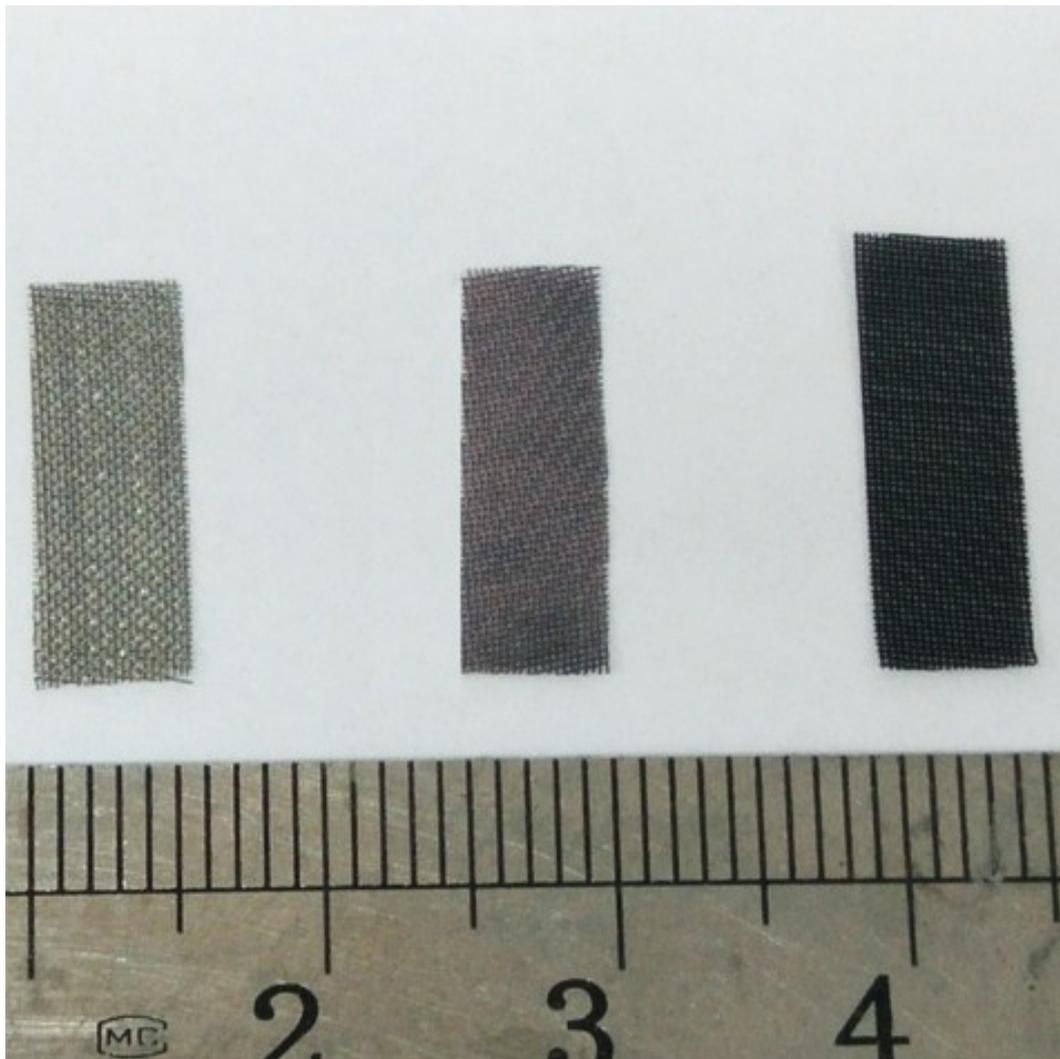
**Preparation of  $\text{CoS}_2/\text{TiM}$ :** A piece of TiM (2 cm  $\times$  3 cm) was carefully pre-treated with concentrated HCl for 15 minutes to remove impurity of surface, and then deionized water and ethanol were used for several times to ensure the surface of the TiM was well cleaned and dried. To prepare  $\text{Co}(\text{OH})\text{F}/\text{TiM}$ , a solution was first prepared the mixture of 2 mmol  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 4 mmol  $\text{NH}_4\text{F}$ , and 10 mmol urea in 50 mL water by magnetic stirring to form a uniform solution. Then the solution was transferred to a 50 mL teflon-lined stainless-steel autoclave, into which a pre-treated TiM was immersed. The autoclave was sealed and maintained at 120°C for 6 h. After the autoclave was cooled down to room temperature, the resulting  $\text{Co}(\text{OH})\text{F}/\text{TiM}$  was taken out with ultrasonic cleaning for several times, followed by drying at 60 °C for 12 h. To prepare  $\text{CoS}_2/\text{TiM}$ ,  $\text{Co}(\text{OH})\text{F}/\text{TiM}$  was placed in the hot center of a tube furnace and a porcelain boat containing approximately 2 g of S powder was placed at the upstream position. Subsequently, the porcelain boat was heated at 400 °C for 1 h with a heating speed of 5 °C  $\text{min}^{-1}$  in Ar atmosphere, then naturally cooled down to ambient temperature.

**Characterizations:** Powder X-ray powder diffraction (XRD) data were collected on Bruker D8 ADVANCE Diffractometer ( $\lambda = 1.5418 \text{ \AA}$ ). Scanning electron microscopy (SEM) measurements were performed on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) measurements were performed on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) data were acquired on a Thermal ESCALAB 250 spectrometer using an Al K $\alpha$  X-ray source (1486.6 eV photons).

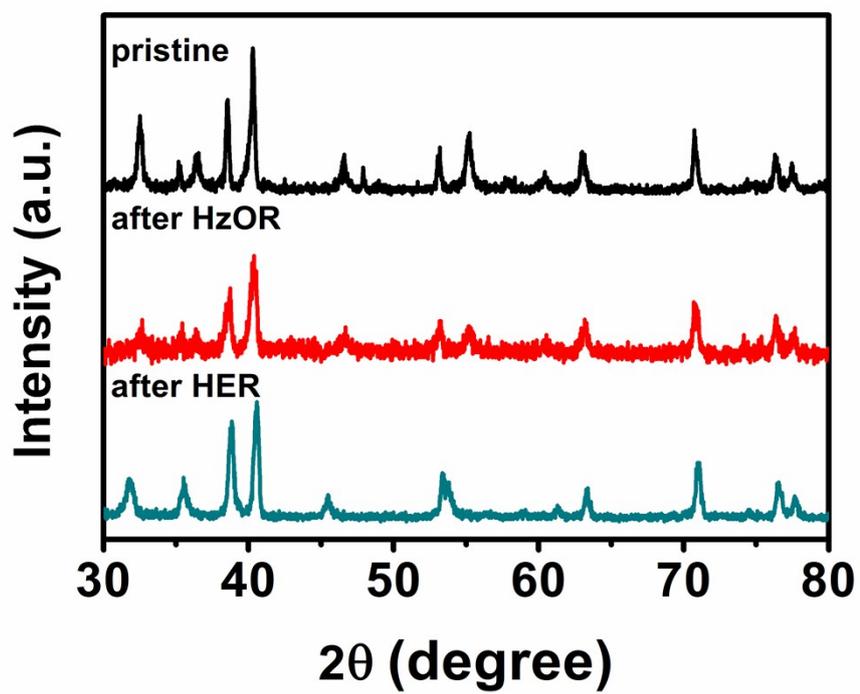
**Electrochemical measurements:** A three-electrode system was used throughout the electrochemical experiment with a CHI-760D electrochemical workstation (CHI Instruments, Shanghai, China) at room temperature. The as-prepared TiM-based electrodes were used as the working electrodes. A graphite plate and a saturated calomel electrode (SCE) were used as the auxiliary and reference electrodes, respectively. In all measurements, the SCE reference electrode was calibrated with respect to reversible hydrogen electrode (RHE) in 1.0 M KOH:  $E(\text{RHE}) = E(\text{SCE}) + 1.068 \text{ V}$ . Linear sweep voltammetry (LSV) measurements were conducted in 1.0 M KOH with a scan rate of  $5 \text{ mV s}^{-1}$ .

**Determination of Faradic efficiency:** The generated gas was confirmed by gas chromatography analysis and measured quantitatively using a calibrated pressure sensor to monitor the pressure change in the cathode compartment of an H-type electrolytic cell. The Faradic efficiency was calculated by comparing the amount of

measured hydrogen generated by galvanostatic electrolysis with calculated hydrogen based on passed charge.



**Fig. S1.** Optical photograph of bare TiM, Co(OH)F/TiM and CoS<sub>2</sub>/TiM (from left to right).



**Fig. S2.** XRD of pristine CoS<sub>2</sub>/TiM and corresponding patterns after HzOR and HER.

**Table S1.** Comparison of HzOR performance in alkaline electrolytes for CoS<sub>2</sub>/TiM and some previously reported electrocatalysts.

Catalyst	Electrolyte	$\eta_{100 \text{ mA cm}^{-2}}$ (mV)	Ref.
Cu film on Cu foam	3.0 M NaOH/0.2 M N <sub>2</sub> H <sub>4</sub>	~ 428	1
Ni–Cu alloy film	3.0 M NaOH/0.1 M N <sub>2</sub> H <sub>4</sub>	~ 208	2
Ni nanosheet array	3.0 M KOH/0.1 M N <sub>2</sub> H <sub>4</sub>	~ 110	3
Ni nanoflower	3.0 M KOH/0.1 M N <sub>2</sub> H <sub>4</sub>	~ 190	4
Cu nanowire array	3.0 M NaOH/1.0 M N <sub>2</sub> H <sub>4</sub>	~ 365	5
polycrystalline Co	1.0 M KOH/0.1 M N <sub>2</sub> H <sub>4</sub>	~ 50	6
nanoporous Cu film	3.0 M NaOH/1.0 M N <sub>2</sub> H <sub>4</sub>	~ 343	7
Co nanoflows	1.0 M NaOH/0.03 M N <sub>2</sub> H <sub>4</sub>	~ 188	8
CoS <sub>2</sub> /TiM	1.0 M KOH/0.1 M N <sub>2</sub> H <sub>4</sub>	125	This work

**Table S2.** Comparison of HER performance in alkaline electrolytes for CoS<sub>2</sub>/TiM and some previously reported electrocatalysts.

Catalyst	Electrolyte	$\eta_{10 \text{ mA cm}^{-2}}$ (mV)	Ref.
FeP NAs/CC	1.0 M KOH	~ 218	9
bulk MoB	1.0 M KOH	~ 225	10
CoP/CC	1.0 M KOH	~ 209	11
Co-NRCNTs	1.0 M KOH	~ 370	12
Ni wire	1.0 M NaOH	~ 350	13
Ni-Mo alloy/Ti foil	1.0 M NaOH	~ 80	13
CoO <sub>x</sub> @CN on GCE	1.0 M KOH	~ 235	14
CoS <sub>2</sub> /TiM	1.0 M KOH	178	This work

**Movie S1.** This movie shows continuous evolution of H<sub>2</sub> and N<sub>2</sub> at cathode and anode, respectively, using a CoS<sub>2</sub>/TiM || CoS<sub>2</sub>/TiM electrolyzer at 0.8 V in 1.0 M KOH with 100 mM hydrazine.

## References

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