# Supporting Information for

# Rhenium anchored $Ti_3C_2T_X$ (MXene) nanosheets for electrocatalytic hydrogen production

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### Experimental

#### Synthesis of $Ti_3C_2T_x$ (MXene)

2D Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets were produced by etching Ti<sub>3</sub>AlC<sub>2</sub> (MAX) phase using concentrated hydrofluoric acid (HF) according to an established method.<sup>1, 2</sup> In this process, powder MAX (2.5 g) was stirred in an aqueous HF (XiLong Chemistry) with a concentration of 10% (25 mL) for 18 h at room temperature (25 °C). After the etching process, the mixture was washed with deionized (DI) water and centrifuged until reaching a pH of >6. It should be noted that this washing procedure was repeated 10-12 times. After removing aluminum (Al) layers from the MAX phase, the sample was gently stirred in dimethylsulfoxide (DMSO) (25 mL) for 24 h at room temperature to obtain few-layer  $Ti_3C_2T_x$  sheets. After DMSO was removed by centrifugation, the supernatant was sonicated in DI water for 1 h. Then, the solution was centrifuged at 100 g for 30 min (two cycles) to remove any unetched MAX phase. The final dispersion of MXene flakes was degassed with Ar for 10 min and stored in the fridge.

# Preparation of Re@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>

For the synthesis of Re@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, the as-prepared Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> flakes were mixed with Re<sub>2</sub>O<sub>7</sub> (Alfa Aeser) in a flask containing DI water. The weight ratio of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and Re<sub>2</sub>O<sub>7</sub> was 4:1. After freeze-drying, the mixture was annealed in a quartz tube under an Ar gas flow. Specifically, the sample was heated at 200 °C (ramped up at the rate of 2°C/min) for 1 h and annealed at 500 °C for 3 h (ramped up at the rate of 4°C/min). During the annealing process, Re<sub>2</sub>O<sub>7</sub> is thermally reduced to Re nanoparticles. The heating rate can be lower to prevent Re<sub>2</sub>O<sub>7</sub> evaporations leading to deposits to form a mirror-like surface at the end of the cooler tube part.

# Materials characterization

UV–vis spectroscopy (UV-vis Carry 1100) was carried out at wavelengths ranging from 200 to 950 nm to scan the UV-vis absorption spectra of the  $Ti_3C_2T_x$  dispersion. For X-ray diffraction (XRD) analysis, the samples were scanned at a fixed sample illumination mode (5 mm illumination length), and the data were collected using a Bruker D8 Advance diffractometer. X-ray photoelectron spectroscopy (XPS) scans were obtained using a Kratos Axis ULTRA X-ray photoelectron spectrometer incorporating a 165 mm hemispherical electron energy analyzer. The incident radiation was monochromatic Al K $\alpha$  X-rays (1486.6 eV) at 225 W (15 kV, 15 mA). Survey scans were carried out at binding energies between 1200 and 0 eV with an interval of 1.0 eV and a dwell time of 100 ms, while high resolution (HR) scans

were conducted with 0.05 eV steps and 250 ms dwell time. Transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) elemental mapping were acquired using a FEI Titan Themis. The scanning transmission electron microscope (STEM) probe was aberration-corrected, enabling sub-Angstrom spatial resolution, and high-angle annular dark-field (HAADF) images were obtained. Inductively coupled plasma-optical emission spectrometry (ICP-OES) (Perkin Elmer, 7300DV) was used to determine the content of Ti and Re in the sample. Only 0.02450 g sample was used for ICP-OES test.

#### **Electrochemical Measurements**

All the electrochemical measurements were carried out on an electrochemical workstation (DY2300) in a standard three-electrode system at room temperature using 0.5 MH<sub>2</sub>SO<sub>4</sub> as the electrolyte. Ag/AgCl (saturated KCl) electrode and platinum wire were used as the reference and counter electrode, respectively. To prepare the working electrode, 5 mg of catalyst was first dispersed in a 1 mL mixture of water (800  $\mu$ L)/ isopropanol (200  $\mu$ L) in the presence of 50  $\mu$ L Nafion solution (5 wt%). Then the as-prepared catalyst ink was loaded onto a glassy carbon (GC) electrode. The catalyst loading was 0.708 mg cm<sup>-2</sup>. For comparison, Pt disk electrode was used. Linear sweep voltammetry (LSV) was recorded at a scan rate of 5 mV s<sup>-1</sup> with an interval of 1 mV. The potentials obtained against an Ag/AgCl electrode were converted to the reversible hydrogen electrode (RHE) using the Nernst formula.<sup>3</sup>

### **Theoretical calculation details**

Density functional theory (DFT) calculations were performed within the framework of plane wave and projector augmented wave (PAW) pseudopotential methods, implementing the Vienna Ab initio Simulation Package (VASP) (version 5.4.4) code.<sup>4, 5</sup> The exchangecorrelation functional was treated with spin-polarized PBE+U (U=4.2 eV) including Grimme's D3 dispersion interactions. The  $\Gamma$ -centered 12 × 12 × 1 k-meshes for a sampling of irreducible Brillouin Zone and the 520 eV cut-off for plane wave basis were used in the calculations. The 2D-Ti<sub>3</sub>C<sub>2</sub>O<sub>2</sub> slab was constructed by adding a 20 Å vacuum thickness in the direction normal to the (3 × 3) basal plane. The slab was optimized until the total energy of the system was less than 1 µeV and the forces on atoms were less than 1 meV Å<sup>-1</sup>.

Three possible locations of the Rhenium atom to the surface of  $Ti_3C_2O_2$  are commonly assumed, as illustrated in Fig. S5: (1) on top of the hollow site above the C atom, (2) on top of

the Ti atom, and (3) on top of the O atom. Before structural optimization, the Re atom was placed 3 Å above the surface. After full geometrical optimization by quantum mechanical first-principle calculation, the Re atom prefers to locate on the hollow site rather than the other two locations. Specifically, the Re atom is bound to three O atoms on the surface of  $Ti_3C_2O_2$ , resulting in a Rhenium-anchored MXene structure that is energetically more favorable (Fig. S5c-d).

The hydrogen chemisorption energy of HER intermediate is described by the following equation:

$$\Delta E_H = E_{(surf+H)} - E_{(surf)} - \frac{1}{2}E_{H_2}$$

where  $E_{(surf + H)}$  and  $E_{(surf)}$  are the total DFT energies of the surface with and without adsorbed hydrogen,  $E_{H_2}$  is the energy for an H<sub>2</sub> molecule in gas phase.

The calculation of reaction free energy is defined as

$$\Delta G_{H*} = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H$$

where  $\Delta E_H$  is the differential hydrogen adsorption energy which is directly obtained from DFT calculations,  $\Delta E_{ZPE}$  is the difference in zero-point energy between atomic hydrogen adsorption and gaseous hydrogen molecule, and  $\Delta S_H$  is change in entropy at 298 K.

The  $\Delta G_{H*}$  quantity of H\* intermediate on the surface is the key descriptor to investigate the catalytic activity for HER and should be near-zero for an ideal surface since hydrogen does not efficiently bind to the catalyst in the adsorption step or forms a strong bond at the desorption step, which will decrease the HER catalytic activity.

To clarify the change of the charge density in terms of Re-defects, we evaluated the charge density difference ( $\Delta \rho$ ), where  $\Delta \rho$  is obtained as follows:

$$\Delta \rho = \rho_{H/Re-dual} - \rho_{Re-dual} - \rho_{H}$$

where  $\rho_{H/Re-dual}$ ,  $\rho_{Re-dual}$ , and  $\rho_{H}$  represent the charge density distribution of dual Reanchored Ti<sub>3</sub>C<sub>2</sub>O<sub>2</sub> before and after H adsorption as well as an isolated hydrogen atom, respectively.



Fig. S1 XRD pattern of MAX phase  $(Ti_3AlC_2)$ .



Fig. S2 High resolution C1s XPS spectrum of  $Ti_3C_2T_x$ .



Samples

Fig. S3 Current densities (@500 mV) of the four catalysts including GC (green),  $Ti_3C_2T_x$  (blue),  $Re@Ti_3C_2T_x$  (red) and Pt wire(black).



Fig. S4 LSV curves of  $Ti_3C_2T_x$  before and after storing in water for 30 days.



**Fig. S5** a) Top and b) side views of the  $Ti_3C_2O_2$ , specifying three possible locations for the Re atom exists. c) Top and d) side views of the single Re-anchored  $Ti_3C_2O_2$ , where the inset illustrates the zoomed-in view of Re atom bound to three O atoms on the surface of  $Ti_3C_2O_2$ .



**Fig. S6** a) Top and b) side structural views of the single Re-anchored  $Ti_3C_2O_2$ , c) The band structure and d) DOS of the single Re-anchored  $Ti_3C_2O_2$ . e) Charge difference for H adsorption on the single Re-anchored  $Ti_3C_2O_2$ , where the yellow (gray) distribution reflects the charge accumulation (depletion) in the density of 0.035 e/bohr<sup>3</sup>. (f) Gibbs free energy  $(\Delta G_{H^*})$  diagram of  $Ti_3C_2O_2$  (pure) and single Re-anchored  $Ti_3C_2O_2$  (single Re-anch) for the HER at the equilibrium potential.

Catalyst	Potential required to achieve 10 mA cm <sup>-2</sup>	Electrolyte	Reference
$Re@Ti_3C_2T_x$	298 mV	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	This work
$Ti_3C_2T_x$	584 mV	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	This work
$\operatorname{Re}_2\operatorname{O}_7$	365 mV	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	This work
B-doped $Ti_3C_2T_x$	504 mV	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	[6]
Ru@rGO	260 mV	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	[6]
Ti <sub>2</sub> CT <sub>x</sub>	609 mV	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	[7]
N-doped $Ti_3C_2T_x$	198 mV	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	[8]
Rhenium wire	~324 mV	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	[9]
p-Si(100)/Re	200 mV	$0.1 \text{ M H}_2\text{SO}_4$	[10]
poly-Re	~336 mV	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	[11]
Re-NPC/a-C	133 mV	$0.5 \mathrm{~M~H_2SO_4}$	[12]

**Table S1**. Catalytic performances of different HER electrocatalysts prepared in this work and other literature.

# References

- 1. M. Naguib, V. N. Mochalin, M. W. Barsoum and Y. Gogotsi, *Adv Mater*, 2014, **26**, 992-1005.
- 2. Q. Peng, J. Guo, Q. Zhang, J. Xiang, B. Liu, A. Zhou, R. Liu and Y. Tian, *Journal of the American Chemical Society*, 2014, **136**, 4113-4116.
- 3. A. Alarawi, V. Ramalingam, H.-C. Fu, P. Varadhan, R. Yang and J.-H. He, *Opt. Express*, 2019, **27**, A352-A363.
- 4. G. Kresse and J. Furthmüller, *Physical Review B*, 1996, **54**, 11169-11186.
- 5. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1996, 77, 3865-3868.
- 6. M. Bat-Erdene, M. Batmunkh, B. Sainbileg, M. Hayashi, A. S. R. Bati, J. Qin, H. Zhao, Y. L. Zhong, J. G. Shapter. *Small.*, **2021**, *17*, 2102218.
- Z. W. Seh, K. D. Fredrickson, B. Anasori, J. Kibsgaard, A. L. Strickler, M. R. Lukatskaya, Y. Gogotsi, T. F. Jaramillo, A. Vojvodic. ACS Energy Lett. 2016, 1, 589-594.
- 8. T. A. Le, Q. V. Bui, N. Q. Tran, Y. Cho, Y. Hong, Y. Kawazoe, H. Lee. *ACS Sustainable Chem. Eng.* **2019**, *7*, 16879-16888.
- 9. R. Garcia-Garcia, J. G. Rivera. R. Antaño-Lopez, F. Castañeda-Olivares, G. Orozco. *Int. J. Hydrogen Energy* **2016**, 41, 4660-4669.
- 10. E. C. Muñoz, R. S. Schrebler, M. A. Orellana, R. Córdova. J. Electroanal. Chem. 2007, 611, 35-42.
- 11. J. H. Chun, S. K. Jeon, K. H. Ra, J. Y. Chun. Int. J. Hydrogen Energy 2005, 30, 485-499.
- 12. M. Kim, Z. Yang, J. H. Park, S. M. Yoon, B. A. Grzybowski. *ACS Appl. Nano Mater*. **2019**, *2*, 2725-2733.