

Supporting Information

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Anchoring Sub-Nanometer Pt Clusters on Crumpled Paper-Like MXene Enables High Hydrogen Evolution Mass Activity

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Experimental details

Synthesis of $Ti_3C_2T_x$ *MXene:* Ti₃AlC₂ MAX phase powder (2 g) was slowly added to a HF solution (20 mL) under magnetic stirring for 24h. (The HF is highly toxic and should be handled in the fume hood.) The suspension was then subjected to centrifugation and washed for several times with deionized water until the pH of supernatant is close to 6. Each centrifugation was performed at 10000 rpm for 3 minutes without special clarification. The black depositions was diverted to a glass bottle with 20 mL tetramethylammonium hydroxide and keep stirring for 10 days at 1600 rpm. The black suspension was centrifuged and washed for once. Then, the clay-liked precipitate was dispersed into a three-necked flask containing 200 mL deionized water with hand shaking, sonicated for 2 h under an ice bath with flowing argon to avoid the oxidation during the exfoliation. After the above processes, the suspension was subjected to centrifugation for 30 minutes at 2500 rpm. The final product was a dark green colloidal suspension, which contains few-layer Ti₃C₂T_x MXene.

Preparation of 3D crumpled MXene: To synthesize 3D crumpled MXene, 100 mL MXene colloidal suspension was stirred for a few hours and then spray dried. The spray drying was performed on a BUCHI Mini Spray Dryer B-290 using Air as the carrier gas, other relevant setting parameters include inlet temperature (200 °C), aspirator rate (90 %), pump rate (5 %), nozzle cleaner (2).

Preparation of Pt/MXene: To synthesize the Pt/MXene electrocatalysts, 1.2 mL H₂PtCl₆ $(9.65 \times 10^{-2} \text{ M})$ solution was slowly dropped into 100 mL Ti₃C₂T_x MXene colloidal suspension. The mixture was kept stirring for a few hours to achieve uniformly dispersion. Finally, the Pt/MXene was collected through spray drying.

Materials Characterization: Scanning electron microscope (SEM) images were acquired through a JEOL JSM–7100F at an acceleration voltage range of 20 kV. To explore the crystal information of the synthesized samples, X-ray diffraction (XRD) was adopted using a Bruker

D8 Discover X-ray diffractometer with a Cu K α X-ray (λ =1.5418 Å). High–resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF–STEM) images were obtained through double spherical aberration corrected transmission electron microscope (Titan Cubed Themis G2 300/ Titan Cubed Themis G2 30). Element content was detected by using an inductively coupled plasma-optical emission spectroscopy (ICP-OES) on a PerkinElmer Optima 4300DV spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos AXIS SUPRA instrument.

Electrochemical measurements: Electrochemical tests were carried out in 0.5 M H₂SO₄ by a standard three-electrode system equipped with CHI 760e electrochemical workstation. The glassy carbon electrode (GCE, 5 mm in diameter) loaded with catalysts was used as the working electrode, while a saturated calomel electrode (SCE) and an unused graphited rod were used as reference electrode and counter electrode, respectively. The synthesize of ink was prepared as follow: 5 mg Vulcan XC-72R carbon, 5 mg catalyst, 850 µL isopropanol and 50 µL Nafion solution (5 wt%) were mixed and ultrasonicated until the formation of a uniform suspension. Subsequently, the slurry was carefully dropped on the GCE. A scan rate of 5 mV s⁻¹ was applied for LSV measurement. The whole test data were converted to the reversible hydrogen electrode (RHE) according to the Nernst equation: E (RHE) = 0.24+ $0.059 \times pH+ E$ (SCE). Electrochemical impedance spectroscopy (EIS) was measured at the overpotential of 10 mA cm⁻² with a frequency range from 0.01 to 10⁵ Hz. It is necessary to point the tests were without iR corrected.

X-ray absorption measurements: X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were obtained on Beamline 12-BM-B at the Advanced Photon Source. The X-ray absorption fine structure (XAFS) raw data were processed by standard procedures with the ATHENA program.

Calculations method: All the DFT calculations on Pt and Pt/MXene were conducted by Vienna ab initio simulation package. The projector-augmented wave (PAW) method and Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) were applied to describe ionic cores and exchange–correlation effects, respectively. A cutoff energy of 450 eV was adopted and the Grimme method for DFT-D3 was used to account for van der Waals (vdW) interactions. The vacuum gap between periodic images was set to 15 Å to avoid interaction. The convergence criteria for residual force and energy were set to 0.05 eV/Å and 10^{-5} eV, respectively. The Brillouin zone was sampled with a $2 \times 2 \times 1$ Gamma centered special k points grid for geometry optimization. The free energy profile for the HER was obtained based on the computational hydrogen electrode (CHE) model proposed by Nørskov and co-workers. In this model, the free energy of proton-electron pair is equal to that of 1/2 H₂(g). The free energy change for each fundamental step was determined by

$$\Delta G = \Delta E + E_{ZPE} - T\Delta S$$

where ΔE is the difference of electronic energy directly obtained from DFT simulation. ΔE_{ZPE} is the variation of zero-point energy (ZPE), ΔS is the entropy (S) change, T is the temperature (T = 298.15K) The ZPE and S of NRR intermediates were obtained by the vibrational frequencies. For the molecular in gas phase, H₂(g), the ZPE and S were taken from NIST database.



Figure S1. SEM images of (a) Ti_3AlC_2 , (b) $Ti_3C_2T_x$ after etching (without TMAH intercalation and sonication), (c) freeze-dried $Ti_3C_2T_x$, and (d) spray-dried $Ti_3C_2T_x$.



Figure S2. TEM image of the spray-dried $Ti_3C_2T_x$.



Figure S3. (a) Photographs of initial colloidal solution after dilution with obvious Tyndall effect, initial colloidal solution (1), and MXene solution standing for 42 days (2). The concentrations of initial MXene solution and that after 42 days are 2.41 and 2.35 mg mL⁻¹, respectively. (b) Zeta potential curves of initial MXene solution, MXene solution standing for 42 days, F-Ti₃C₂T_x, S-Ti₃C₂T_x, and Pt/MXene, and (c) the corresponding scatter plot.



Figure S4. N₂ adsorption–desorption isotherm curves of $F-Ti_3C_2T_x$ and $S-Ti_3C_2T_x$.



Figure S5. The XPS survey spectrum of $S-Ti_3C_2T_x$ MXene.



Figure S6. (a) Al 2p and (b) Ti 2p XPS spectrum of MAX (Ti₃AlC₂).



Figure S7. (a) Al 2*p* XPS spectrum of $F-Ti_3C_2T_x$, (b) Ti 2*p*, (c) C 1*s*, and (d) O 1*s* XPS spectrum of Pt/MXene.



Figure S8. Magnified pre-edge profiles of Pt *L*₃-edge XANES.



Figure S9. Cyclic voltammogram curves of (a) MXene, (b) Pt/MXene, and (c) Pt/C at different scan rates of 20, 40, 60, 80, and 100 mV s⁻¹ in a non-faradaic region.



Figure S10. TOF of the Pt/C and Pt/MXene catalysts at different overpotential in the range of 50-200 mV in 0.5M H₂SO₄.



Figure S11. Chronopotentiometric response of Pt/MXene and Pt/C at -10 mA cm $^{-2}$.



Figure S12. TEM image of Pt/MXene after 10000 s durability test.



Figure S13. Comparison of overpotential (10 mA cm^{-2}) for various HER catalysts based on MXene or Pt-based electrocatalysts.



Figure S14. Structure and configuration of (a) Pt/TiCO-F–H, (b) Pt/TiCO–H, (c) Pt(111)–H, and (d) TiCO–H. Atoms in blue, white, red, cyan, gray and dark gray represent Pt, H, O, F, Ti, and C, respectively.

Туре	Atomic conc. [%]	Mass conc. [%]
F 1s	5.9	5.7
Ti 2p	17.1	41.9
O 1s	23.8	19.5
C 1s	53.3	32.8

Table S1. Elemental analysis of S-Ti₃C₂T_x MXene from XPS survey spectrum.

Region	Binding energy (eV)	Assigned to
Al 2p	71.7	Al–Ti
	74.0	Al ₂ O ₃
Ti 2p	454.0	Ti–Al
	455.0 (460.3)	Ti–C
	458.4 (464.1)	Ti–O

Table S2. XPS peak fitting results for MAX (Ti₃AlC₂).

Region	Binding energy (eV)	Assigned to
Pt 4f	71.0 (74.3)	Pt^{0}
Ti 2p	453.4 (457.6)	Ti–C
	454.4 (460.3)	C-Ti ²⁺ -(O/OH)
	456.9 (462.6)	C-Ti ³⁺ -(O/OH)
	459.4 (463.9)	$TiO_{2-x}F_{2x}$
C 1s	283.1	C-Ti/Pt
	284.5	C–C
	287.1	C-0
O 1s	528.1	Ti–O
	528.9	$TiO_{2-x}F_{2x}$
	530.3	C–Ti–O
	531.1	C-Ti-OH

Table S3. XPS peak fitting results for the Pt/MXene.

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