Supporting Information

Charge self-regulation of Ti_3C_2 MXene via rich unsaturated Ti sites for boosted photocatalytic hydrogen generation

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SI Experimental

SI-1 Photoelectrochemical measurements

Photoelectrochemical (PEC) curves were measured on an electrochemical analyzer (CHI660E, China) in a standard three-electrode configuration according to our previous works [1]. The prepared samples were loaded on fluorine-doped tin oxide (FTO) conductor glass, a standard Ag/AgCl electrode and the platinum foil as the working electrodes, reference electrode and counter electrode, respectively, with Na_2SO_4 (0.5 mol L^{-1}) as the electrolyte solution. The method of working electrodes was the same as in our previous works. Linear sweep voltammetry (LSV) curves were obtained in the potential ranging of -1.0 to -1.6 V with a scan rate of 10 mV s^{-1}. Transient photocurrent responses with time (*i-t* curves) were recorded at 0.5 V bias potential during periodic ON/OFF illumination cycles under a 3W LED lamp (365 nm). Electrochemical impedance spectroscopy (EIS) curves were conducted at the frequency range of 0.01-10^5 Hz with an ac amplitude of 10 mV under the open-circuit voltage.

SI-2 Density functional theory calculation

The calculations were carried out by using the Vienna *ab* initio simulation package (VASP) [1-3]. The generalized gradient approximation (GGA) with Purdew-Burke-Ernzerhof (PBE) functional was selected to reveal the exchange-correlation interaction. The cutoff energy and Monkhorst-Pack k-point mesh was set as 450 eV and 3 × 3 × 1, respectively. The convergence threshold d for total energy converged

within 10^{-5} eV/atom and 0.01 eV·Å^{-1} for force. The partial occupancies are determined using the Gaussian smearing smearing scheme with smearing width of 0.2 eV. To eliminate interactions between periodic structures, a vacuum of 15 Å was added. The Gibbs free energy of H atom adsorption (ΔG_{H*}) was defined as following the equation S1:

$$\Delta G_{H*} = \Delta E_{H*} + \Delta E_{ZPE} - T\Delta S_H \quad \text{(S1)}$$

where ΔE_{H*}, ΔE_{ZPE}, $T\Delta S_H$ are the differential hydrogen ΔE_{H*} adsorption energy, the change in zero-point energy and entropy between the adsorbed hydrogen and molecular hydrogen in gas phase, respectively, and T is the temperature. By default the entropy of H_2 gas at 298 K is 130 J·mol^{-1}·K^{-1}, so the term $T\Delta S_H$ was calculated to be -0.20 eV. In this work, Ti_3C_2 model was constructed by removing Al atom in the Ti_3AlC_2 (002) model. The (3 × 3 × 1) supercell containing 27 Ti and 18 C atoms of crystalline. $Ti_3C_2F_x$ structure was added 6 F atoms on the basis of Ti_3C_2 model and performed for the following theoretical calculations. On the basis of $Ti_3C_2F_x$ model, the $Ti_3C_2F_x$-U (002) model composed of 27 Ti atoms, 17 C atoms and 6 F atoms is constructed by digging out a carbon atom to simulate the broken Ti-C bonds and some surrounding saturated Ti atoms convert to unsaturated state. As a result, U in the $Ti_3C_2F_x$-U model represent the unsaturated Ti active sites with insufficient coordination. Additionally, three configurations are possible for the chemical F terminations on $Ti_3C_2F_x$-U system: (1) F functional groups located on the top of C atoms; (2) F functional groups located on the top of transition Ti metals; (3) F functional groups on top of the hollow sites (neither on the top of Ti metals nor C

atoms). The work function is defined as $\Phi = E_v - E_f$, where E_v and E_f are the electrostatic potentials of the vacuum and Fermi levels, respectively.

References

1. H. Long, P. Wang, X. Wang, F. Chen, H. Yu, *Appl. Sur. Sci.* 2022, **604**, 154457.
2. D. Gao, H. Long, X. Wang, J. Yu, H. Yu, *Adv. Funct. Mater.*, 2022, **34**, 210847.
3. W. Zhong, B. Zhao, X. Wang, P. Wang, H. Yu, *ACS Catal.*, 2023, **13**, 749-756.

Table S1 Composition of the various samples based on the XPS result.

Sample	Ti-C	Ti^{3+} + Ti^{2+}
$Ti_3C_2F_x$	32.6%	23.4%
$Ti_3C_2F_x$-20°C	28.4%	29.8%
$Ti_3C_2F_x$-60°C	23.2%	35.1%
$Ti_3C_2F_x$-100°C	21.5%	31.0%
$Ti_3C_2F_x$-140°C	6.7%	9.5%

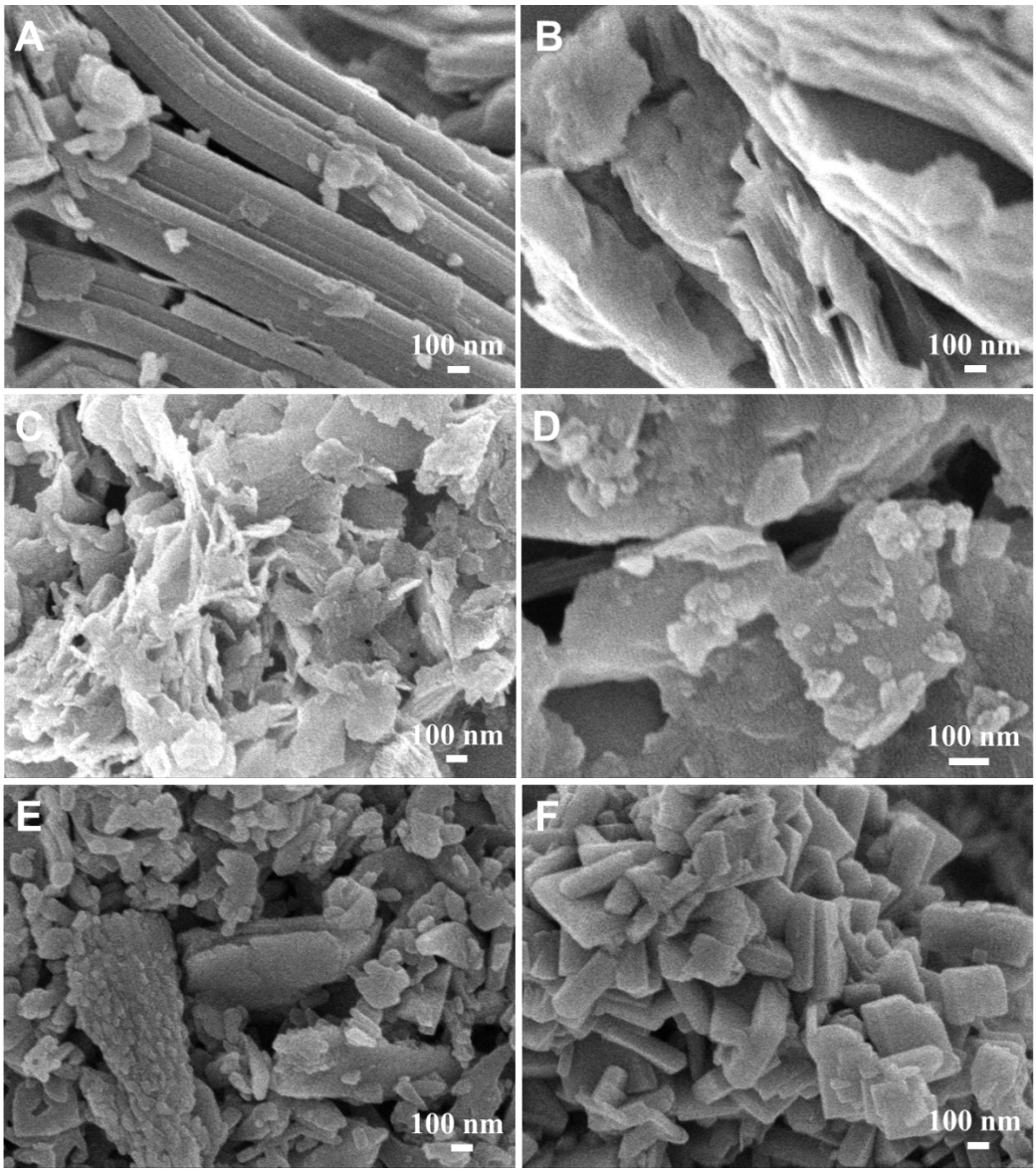

Fig. S1. FESEM images of (A) Ti_3AlC_2, (B) $Ti_3C_2F_x$, (C) $Ti_3C_2F_x$-20°C, (D) $Ti_3C_2F_x$-60°C, (E) $Ti_3C_2F_x$-100°C, and (F) $Ti_3C_2F_x$-140°C after ultrasonic intercalation.

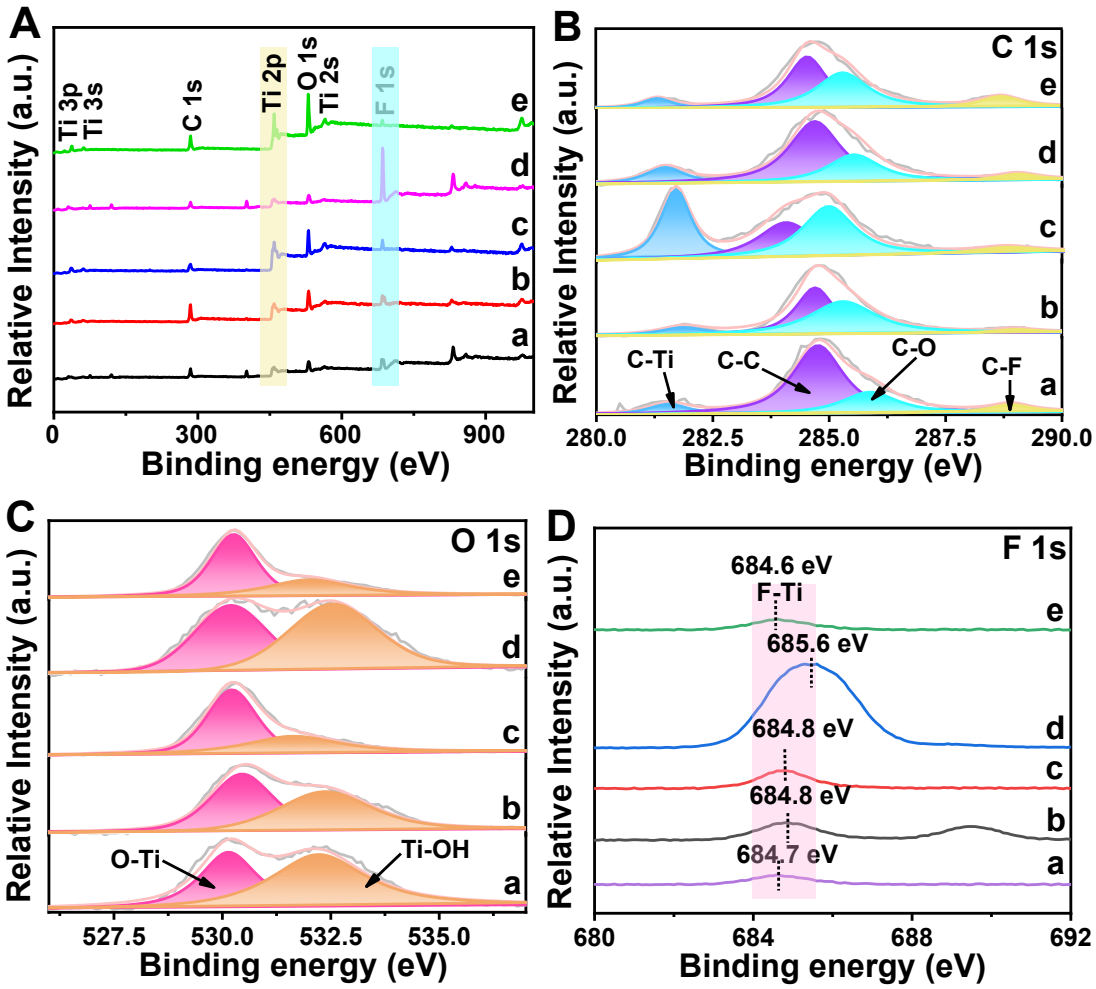

Fig. S2. (A) XPS survey spectra and the high-resolution spectra of (B) C 1s, (C) O 1s, (D) F 1s for (a) $Ti_3C_2F_x$, (b) $Ti_3C_2F_x$-20°C, (c) $Ti_3C_2F_x$-60°C, (d) $Ti_3C_2F_x$-100°C, and (e) $Ti_3C_2F_x$-140°C.

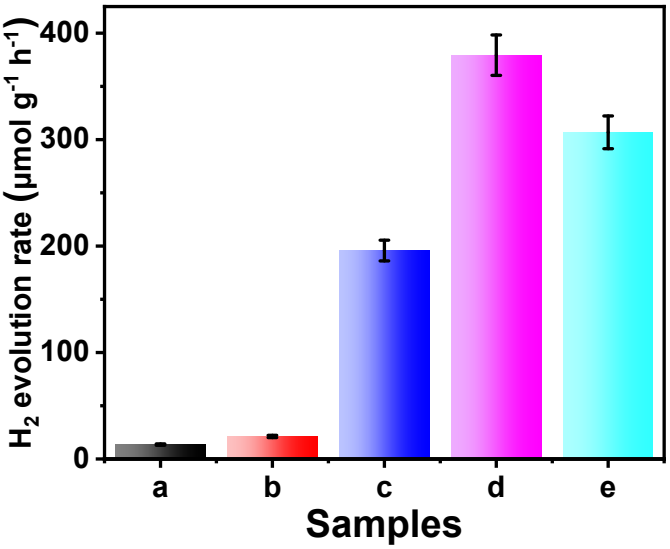

Fig. S3 Photocatalytic H_2-evolution rate of (a) TiO_2, (b) $Ti_3C_2F_x$-60°C/TiO_2(0.1 wt%), (c) $Ti_3C_2F_x$-60°C/TiO_2(1 wt%), (d) $Ti_3C_2F_x$-60°C/TiO_2(5 wt%) (as $Ti_3C_2F_x$-60°C/TiO_2), and (e) $Ti_3C_2F_x$-60°C/TiO_2(10 wt%).

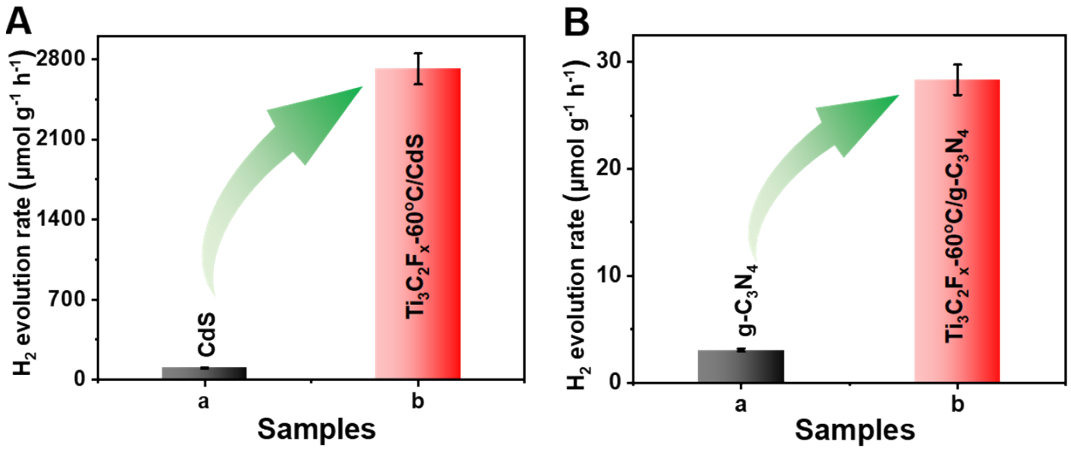

Fig. S4. The photocatalytic H_2-evolution rate of (A) (a) CdS, (b) $Ti_3C_2F_x$-60°C/CdS and (B) (a) g-C_3N_4, (b) $Ti_3C_2F_x$-60°C/g-C_3N_4.

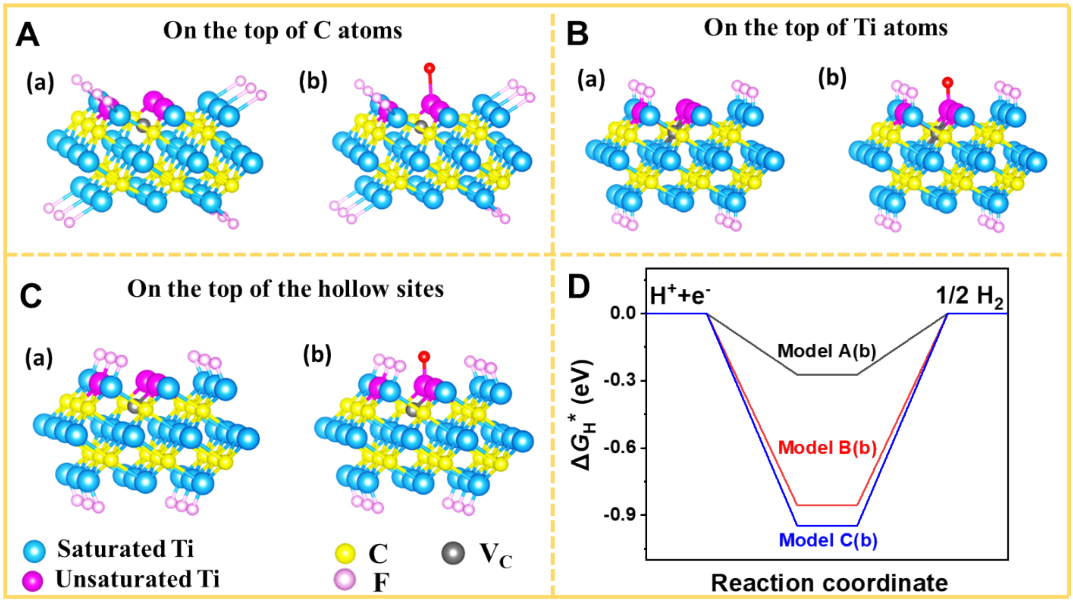

Fig. S5 (A-C) Three configurations are possible for the F chemical terminations on $Ti_3C_2F_x$-U models: (a) before H adsorption and (b) after H adsorption and (D) Gibbs free energy profiles (ΔG_{H^*}) for H_{ads} adsorption on Ti sites in different F terminated positions.

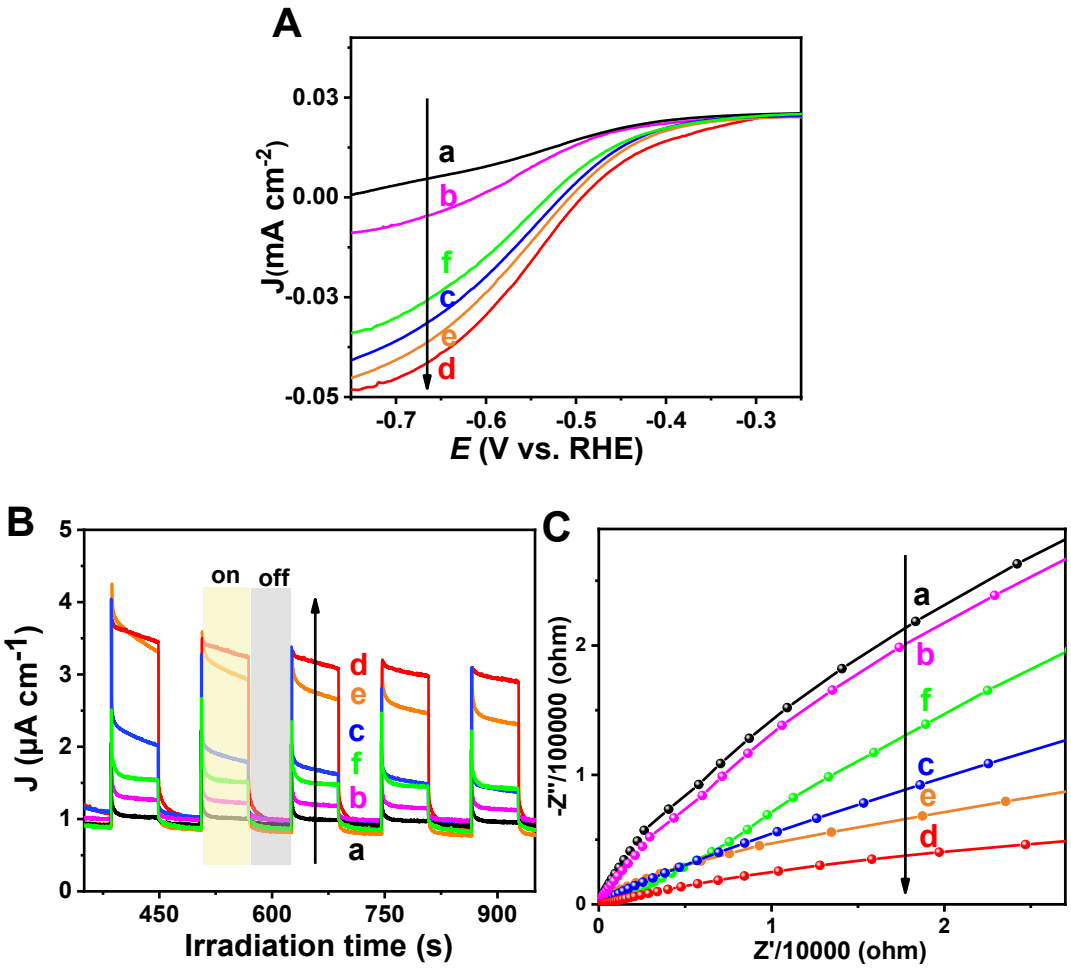

Fig. S6. (A) Linear sweep voltammetry (LSV) curves, (B) transient photocurrent response, and (C) electrochemical impedance (EIS) spectra of (a) TiO_2, (b) $Ti_3C_2F_x/TiO_2$, (c) $Ti_3C_2F_x$-20°C/TiO_2, (d) $Ti_3C_2F_x$-60°C/TiO_2, (e) $Ti_3C_2F_x$-100°C/TiO_2, and (f) $Ti_3C_2F_x$-140°C/TiO_2.