

Graphical Abstract

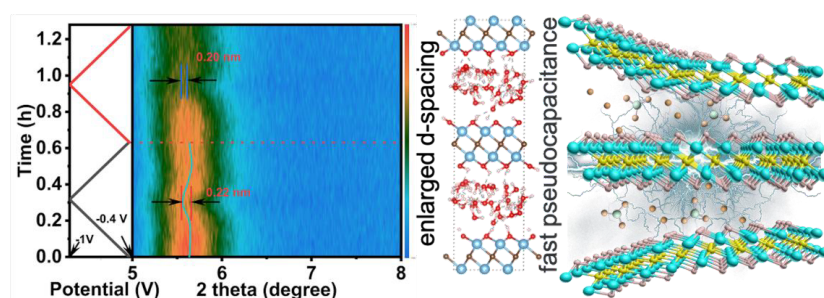
Reproducible and flexible Ti_2CT_x MXene films for high-rate proton-coupled pseudocapacitance in acidic aqueous electrolytes

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A highly conductive, flexible, freestanding Ti_2CT_x film is developed, revealing its reversible interlayer “breathing” behavior, driven by $\text{H}^+/\text{H}_3\text{O}^+$ intercalation in acidic electrolyte, enabling fast pseudocapacitive charge storage.

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ABSTRACT

Ti_2CT_x MXene presents significant fabrication challenges, including difficulties in producing freestanding films, high susceptibility to oxidation under ambient conditions, and inadequate mechanical toughness, which results in brittleness. Here, through optimization of post-etch solution selection and physical delamination, binder-free freestanding electrodes with a high electronic conductivity of $1098 \text{ S} \cdot \text{cm}^{-1}$ are fabricated. The electrode exhibits high-rate specific capacitance and excellent rate capability, along with significant electrolyte-dependent behavior. In H_2SO_4 , surface-dominated pseudocapacitance involving protons/hydronium ions prevails, delivering a specific capacitance of $617 \text{ F} \cdot \text{g}^{-1}$ at $2 \text{ mV} \cdot \text{s}^{-1}$ and $680 \text{ F} \cdot \text{g}^{-1}$ at $1 \text{ A} \cdot \text{g}^{-1}$, while retaining $298 \text{ F} \cdot \text{g}^{-1}$ at $100 \text{ A} \cdot \text{g}^{-1}$. This rate capability is comparable to that of previously reported Ti_2CT_x and many $\text{Ti}_3\text{C}_2\text{T}_x$ -based electrodes. In contrast, electric double-layer capacitance dominates in NaCl or NaOH electrolytes. A rapid proton-coupled pseudocapacitance mechanism is confirmed using *in situ* X-ray diffraction, which reveals a reversible interlayer expansion–contraction of 0.22 nm during electrochemical cycling. First-principles analysis indicates strong coupling between the oxygen terminations and H_3O^+ , which lowers the ion migration barrier, enabling a high-rate response. These advancements in fabrication reliability, mechanistic insight, and rate capability offer a viable strategy for designing Ti_2CT_x -based flexible MXene electrodes with enhanced high-rate performance for high-power supercapacitors. Overall, this work provides a reproducible fabrication strategy, mechanistic insight, and competitive high-rate performance for Ti_2CT_x -based flexible MXene electrodes.

KEYWORDS

Ti_2CT_x MXene, freestanding film, proton-coupled pseudocapacitance, *in situ* XRD, energy storage mechanism

1 Introduction

The rapid advancement of portable, wearable, and flexible electronics has driven significant interest in energy storage devices that simultaneously deliver high energy density, high power density, and outstanding mechanical flexibility. Among electrochemical energy-storage systems, supercapacitors offer much higher capacitance than conventional capacitors and superior power capability and cycle life compared with batteries, affording unique application potential^[1,2]. To function as lightweight and deformable power sources in flexible integrated systems, devices must maintain a high energy and power output under mechanical deformation, which places stringent requirements on the electrode materials and device architectures^[3–5]. The electrode material is the core component governing the electrochemical performance. Commercial supercapacitors generally use carbon-based electrodes,

which exhibit excellent power and cycling stability. However, their charge storage is largely confined to electric double-layer adsorption, resulting in intrinsically limited capacitance and constrained device-level energy density. In contrast, pseudocapacitive materials store charge through fast, reversible surface and near-surface redox processes, offering a higher theoretical specific capacitance and providing a viable route to boosting the energy density^[6–8].

Two-dimensional transition-metal carbides and nitrides (MXenes) have emerged as promising pseudocapacitive electrode materials, combining high electronic conductivity, tunable surface chemistry, hydrophilicity, and robust mechanical properties^[9–11]. As an MXene, $\text{Ti}_3\text{C}_2\text{T}_x$ has been extensively studied owing to its exceptional electrical conductivity, mechanical flexibility, and hydrophilicity, enabling applications in catalysis, optoelectronics, and beyond^[12–14]. In recent years, MXene systems beyond

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$\text{Ti}_3\text{C}_2\text{T}_x$ have also demonstrated promising pseudocapacitive energy-storage properties. For example, non- $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes such as Nb_2CT_x and Mo_2CT_x exhibit excellent pseudocapacitive behavior, further expanding the compositional diversity of MXene-based supercapacitors^[15–18]. Theoretically, low-molar-mass M_2X -type MXenes, such as Ti_2CT_x , Nb_2CT_x , Mo_2CT_x , and Sc_2CT_x , are especially attractive for achieving high specific capacitance because of their reduced formula weight compared with M_3X_2 and M_4X_3 counterparts^[19,20]. Within this family, Ti_2CT_x , with a relatively low molar mass, stands out as a particularly compelling candidate. However, systematic studies on flexible freestanding Ti_2CT_x films that simultaneously possess high electronic conductivity and excellent rate capability remain limited, restricting their practical application potential^[16]. Existing studies have focused primarily on multilayer powder materials, whereas reports on high-quality, binder-free, flexible freestanding Ti_2CT_x films remain scarce, particularly in terms of achieving both high electronic conductivity and outstanding high-rate electrochemical performance. Multiple strategies for synthesizing high-performance MXenes have been developed. Notably, in 2014, mild HCl/LiF etching of MAX phases enabled the production of multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ and catalyzed subsequent advances in MXene research^[21]. Research on Ti_2CT_x has similarly focused on multilayer powders and their properties. For example, Guan et al.^[22] reported a volumetric capacitance of $452 \text{ F}\cdot\text{cm}^{-3}$ for multilayer Ti_2CT_x in KOH, and Li et al.^[23] obtained multilayer Ti_2CT_x via HCl + LiF etching, yielding a gravimetric and volumetric capacitance of $515.3 \text{ F}\cdot\text{g}^{-1}$ and $694 \text{ F}\cdot\text{cm}^{-3}$ at $2 \text{ mV}\cdot\text{s}^{-1}$, respectively. However, the multilayer MXene nanosheets are prone to restacking, which reduces the accessible surface area and active sites, limiting their electrochemical performance. Binder- and additive-free freestanding films enable better utilization of the active material, often delivering superior performance. Thus, delaminating multilayer MXene into single-/few-layer nanosheets followed by film formation is an effective strategy for achieving enhanced performance. Despite the theoretical advantages of Ti_2CT_x , systematic electrochemical studies of its flexible freestanding films in various aqueous electrolytes remain scarce, and deeper insight into its charge-storage mechanisms is required^[24]. Moreover, existing reports on flexible Ti_2CT_x have limited reproducibility, the materials exhibit low electronic conductivity, and the storage mechanisms are ambiguous. In this study, the aforementioned challenges are addressed by establishing a reproducible route for fabricating flexible, freestanding Ti_2CT_x films with high electronic conductivity for high-rate MXene-based energy storage applications.

This work establishes a reproducible route to flexible Ti_2CT_x MXene films through optimized post-etch solution selection and physical delamination. The resulting films exhibit an electronic conductivity of $1098 \text{ S}\cdot\text{cm}^{-1}$, which translates into markedly improved rate capability. In acidic media, Ti_2CT_x delivers specific capacitances of $617 \text{ F}\cdot\text{g}^{-1}$ at $2 \text{ mV}\cdot\text{s}^{-1}$ and $680 \text{ F}\cdot\text{g}^{-1}$ at $1 \text{ A}\cdot\text{g}^{-1}$, while retaining $298 \text{ F}\cdot\text{g}^{-1}$ at $100 \text{ A}\cdot\text{g}^{-1}$. The electrochemical performance surpasses that of previously reported freestanding Ti_2CT_x electrodes. The excellent high-rate capability is attributed to the high electronic conductivity and rela-

tively low molar mass of Ti_2CT_x . Furthermore, *in situ* X-ray diffraction (XRD) measurements and first-principles calculations provide additional evidence of proton-coupled pseudocapacitive behavior in acidic electrolytes, offering deeper insight into the charge-storage mechanism of Ti_2CT_x MXene electrodes.

2 Experimental

2.1 Fabrication of flexible Ti_2CT_x films

Ti_2CT_x , an MXene, was synthesized by selectively etching the Al layers of the Ti_2AlC MAX phase (Foshan Xinxin Technology Co., Ltd.) using the conventional HCl + LiF route^[23]. To ensure reproducibility, a detailed protocol for preparing flexible, freestanding Ti_2CT_x films was established^[25]. In a typical procedure, 5 mL of deionized water was mixed with 15 mL of HCl (12 mol/L), followed by the addition of 1.5 g LiF. After LiF completely dissolved, 1.0 g of Ti_2AlC precursor powder was slowly added. The resulting mixture was stirred at 400 rpm for 24 h at room temperature. The etched suspension was then transferred to 15 mL centrifuge tubes and centrifuged at 8500 rpm for 5 min, after which the supernatant was discarded. The sediment was redispersed in deionized water by vortexing or shaking, and the centrifugation–washing cycles were repeated until the supernatant turned dark-purple/black, indicating sufficient removal of residual salts and byproducts. To obtain single-/few-layer Ti_2CT_x nanosheets, deionized water was added to the final sediment to reach a total volume of 15 mL, followed by vigorous shaking for 10 min to ensure complete dispersion. The resulting suspension was then centrifuged at 3000 rpm for 10 min, and the supernatant enriched with two-dimensional nanosheets was collected. Freestanding films were fabricated by vacuum filtration of approximately 1 mL of the supernatant through a mixed cellulose ester membrane ($0.22 \mu\text{m}$), which is compatible with aqueous systems. After complete removal of the water, a flexible, freestanding Ti_2CT_x film formed on the membrane, which could be directly peeled off for subsequent use.

2.2 Electrode assembly and electrochemical testing

The flexible Ti_2CT_x film was punched into disks (diameter = 0.5 cm) for use as working electrodes, and their mass was accurately determined. Electrochemical measurements were performed in a three-electrode configuration. An activated carbon electrode (with 5 wt% polytetrafluoroethylene [PTFE]) was used as the counter electrode. The reference electrodes were selected according to the electrolyte: Hg/Hg₂SO₄ in 1 mol/L H₂SO₄, Hg/Hg₂Cl₂ in 1 mol/L NaOH, and Ag/AgCl in 1 mol/L NaCl. Cyclic voltammetry (CV) was conducted at scan rates ranging from 2 to 1000 $\text{mV}\cdot\text{s}^{-1}$ within the following potential windows: -1.0 to -0.43 V (vs. Hg/Hg₂SO₄ in 1 mol/L H₂SO₄), -1.0 to -0.6 V (vs. Hg/Hg₂Cl₂ in 1 mol/L NaOH), and -1.0 to -0.8 V (vs. Ag/AgCl in 1 mol/L NaCl). Galvanostatic charge–discharge (GCD) tests were performed at current densities from 1 to 100 $\text{A}\cdot\text{g}^{-1}$. Electrochemical impedance spectroscopy (EIS) and long-term cycling stability tests (at 10 $\text{A}\cdot\text{g}^{-1}$) were also performed. All

electrochemical measurements were conducted using a DH7000D electrochemical workstation. The specific capacitance was directly calculated from the experimentally obtained GCD curves without additional iR-drop correction, unless otherwise stated. Because the freestanding Ti_2CT_x films possess relatively high electronic conductivity, the observed voltage drop in the GCD curves is small, and its influence on the calculated specific capacitance can be considered negligible.

2.3 In situ electrochemical XRD

In situ XRD coupled with electrochemical measurements was conducted using a modified three-electrode cell. The freestanding Ti_2CT_x film served as the working electrode; the counter electrode was excess-capacity activated carbon; the reference was $\text{Hg}/\text{Hg}_2\text{SO}_4$. The electrolyte was 1 mol/L H_2SO_4 . A Kapton window was used to prevent leakage and evaporation while ensuring X-ray transmission. CV scanning was conducted from -0.43 to -1.0 V. XRD patterns were recorded on a Bruker D8 diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å) over the 2θ range of 5° – 10° , synchronized with the electrochemical scan. Data were acquired over two consecutive cycles, with a total collection time of approximately 2 h.

2.4 Characterization of materials

The crystallinity of the films was evaluated via powder XRD using a D8 Advance diffractometer (Bruker, Karlsruhe, Germany) with Cu K α radiation ($\lambda = 1.5406$ Å) over the 2θ range of 5° – 65° . Scanning electron microscopy (SEM) was conducted using an SU8020 microscope (Hitachi High-Tech, Tokyo, Japan). Transmission electron microscopy (TEM) was performed using a Talos transmission electron microscope (Thermo Fisher Scientific, Waltham, MA, USA). X-ray photoelectron spectroscopy (XPS) was performed using a K-Alpha XPS system (Thermo Fisher Scientific, East Grinstead, UK). Four-point probe conductivity was measured using a ST2263 four-point probe instrument (Suzhou Jingge Electronic Co., Ltd., Suzhou, China). Atomic force microscopy (AFM) was performed using a Dimension Icon system (Bruker, Santa Barbara, CA, USA).

2.5 First-principles calculations

Density functional theory (DFT) calculations were performed using CASTEP. The exchange–correlation was treated with the GGA-PBE functional. On-the-fly generated ultrasoft pseudopotentials (OTFG ultrasoft) were employed. Monkhorst–Pack k-point meshes were used for Brillouin-zone sampling. The plane-wave cutoff energy

was 540 eV. The convergence criteria were set as follows: total energy = 1×10^{-5} eV/atom, maximum force = 0.02 eV·Å $^{-1}$, and pressure = 0.02 GPa, ensuring reliable structural optimization and calculation of the electronic parameters.

3 Discussion and analysis

Figure 1 illustrates the fabrication of the flexible Ti_2CT_x films. Briefly, the Ti_2AlC MAX phase was selectively etched using a HCl/LiF mixture. The upper colloidal dispersion containing delaminated MXene nanosheets was collected and vacuum-filtered to assemble freestanding, flexible Ti_2CT_x membranes (see Experimental section for details). As shown in Fig. S1a in the Electronic Supplementary Material (ESM), the etched Ti_2CT_x MXene suspension exhibits a characteristic purple–black color and a clear Tyndall effect, confirming its colloidal nature.

The structural evolution from Ti_2AlC to Ti_2CT_x was analyzed using XRD^[26]. After HCl/LiF etching, the product displays the characteristic MXene (002) reflection of MXene at $2\theta \approx 7.5^\circ$ (Fig. 2a), corresponding to an inter-layer spacing of 11.78 Å, confirming successful preparation of Ti_2CT_x . Vacuum filtration of the colloidal dispersion produced freestanding flexible films. The optical image in Fig. S1b in the ESM reveals a dark-green film with a metallic luster. The as-prepared Ti_2CT_x film could be readily bent without fracture (inset of Fig. 2a), further confirming its excellent freestanding flexibility and mechanical integrity.

The topography of the Ti_2CT_x nanosheets was examined using AFM (Fig. 2b). The lateral size of representative nanosheets is approximately 0.55 μm , with a thickness of approximately 3.2 nm, as determined from the height profile (Fig. 2c). The area-averaged roughness values ($R_q = 2.25$ nm; $R_a = 1.83$ nm) indicate a relatively smooth interface, which is beneficial for reducing the interfacial contact resistance, facilitating ion transport, and enhancing the rate capability. These morphological features provide a favorable structural basis for high-performance flexible electrodes.

XPS was used to probe the surface chemical composition and electronic states of the Ti_2CT_x films^[27] (Figs. 2d–2f). Deconvolution of the C 1s spectrum (Fig. 2d) reveals four distinct components at 281.9 eV (corresponding to Ti–C bonds intrinsic to the MXene framework), 284.8 eV (C–C), 286.3 eV (C–O), and 288.9 eV (C=O). The O 1s spectrum (Fig. 2e) exhibits three main components at 529.9, 530.8, and 532.2 eV, attributable to lattice oxygen (Ti–O), hydroxyl oxygen (Ti–OH), and adsorbed water (H–O–H), respectively, indicating abundant O– and

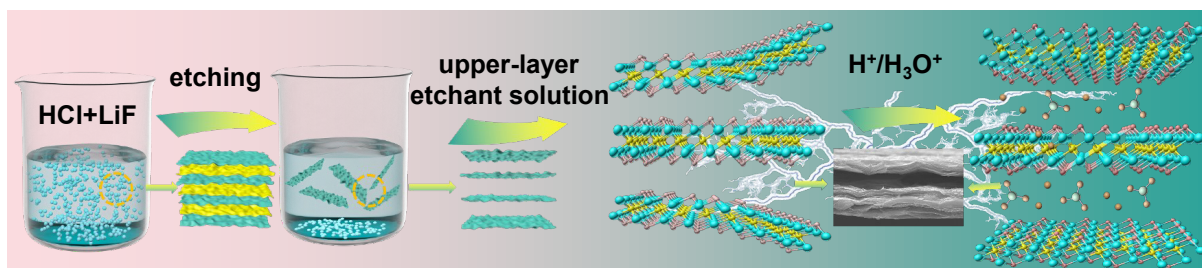


Figure 1 Schematic of preparation of Ti_2CT_x .

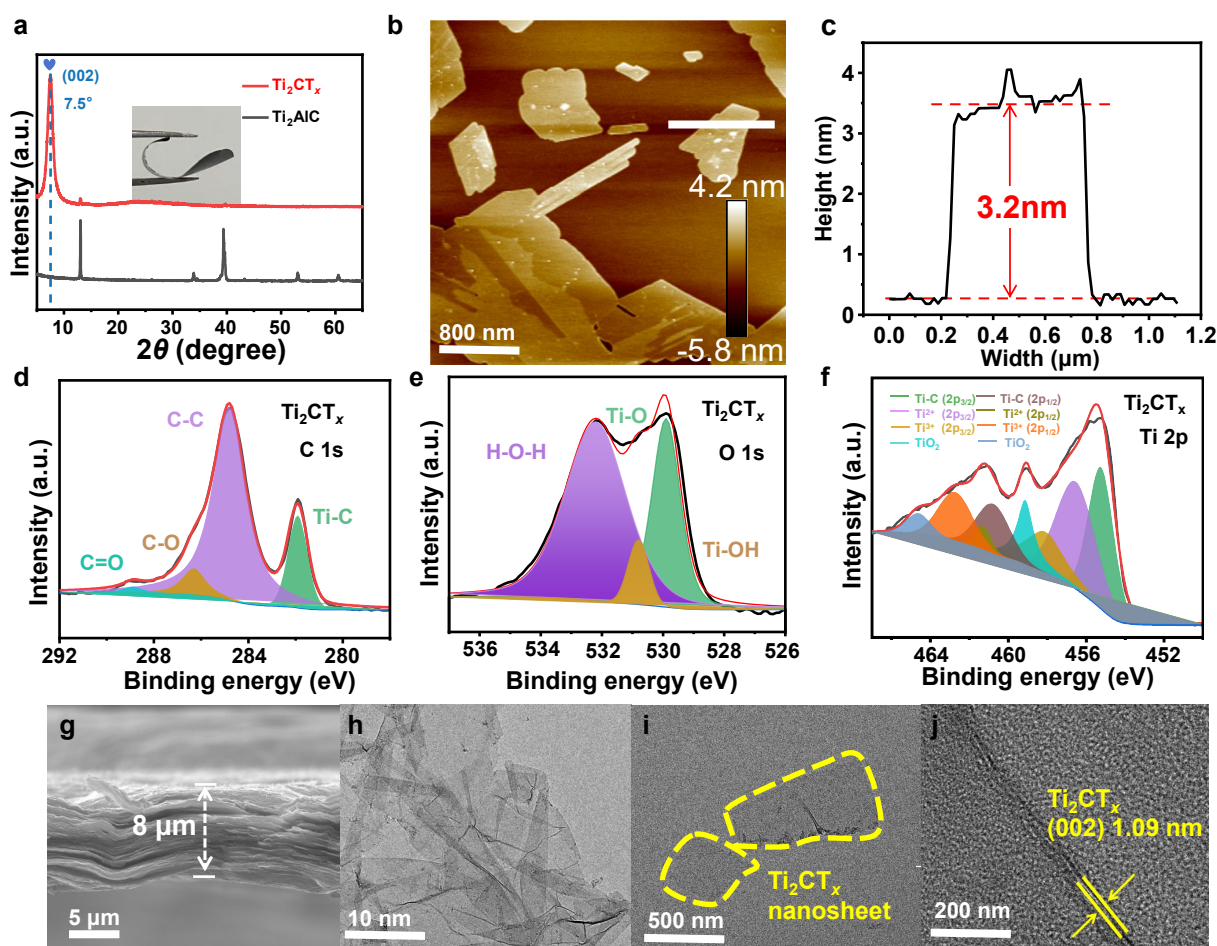


Figure 2 XRD pattern (a), AFM image (b), height distribution (c), XPS profiles (d–f), SEM image (g), and TEM images of Ti_2CT_x (h–j).

OH[−] terminal groups on the surface of the MXene. The Ti 2p spectrum (Fig. 2f) was resolved into four doublets, assigned to Ti–C (455.2/460.8 eV), Ti^{2+} (456.5/461.3 eV), Ti^{3+} (458.1/462.7 eV), and TiO_2 (459.1/464.6 eV), in good agreement with previously reported values for Ti_2CT_x MXene^[28–30]. Although the specific contributions of different surface terminations to the electrochemical performance were not systematically investigated in this study, residual –F terminations from the LiF/HCl etching process may still be present on the surface of Ti_2CT_x , as reported previously for MXene materials^[31,32].

Further insight into the microstructure of the material was provided by Raman spectroscopy (Fig. S2b in the ESM)^[33,34]. The sharp peak at approximately 224 cm^{-1} corresponds to the E_g in-plane vibration of the Ti_2CT_x phase^[35,36], which is dominated by surface atoms; the signal arises primarily from coupled vibrations of Ti with surface –O/–OH groups^[37]. The feature at 278.5 cm^{-1} may originate from constrained vibrations of interlayer water or intercalated Li^+ . The weak mode at 405.8 cm^{-1} , which exhibits strong orientation dependence, is indicative of impurity-related vibrations^[38]. The signal at 616.9 cm^{-1} is mainly associated with C vibrations (E_g and A_{1g})^[37,39].

The morphology and architecture of the films were evaluated using SEM. The cross-sectional image (Fig. 2g) reveals a densely stacked structure assembled from single-layer Ti_2CT_x nanosheets, with a total film thickness of

approximately 8 μm . Discernible interlayer voids are observable, which are expected to facilitate electrolyte infiltration and ion transport during electrochemical operation. Elemental mapping (EDS, Fig. S3 in the ESM) confirms the uniform distribution of Ti, C, O, and F throughout the film. TEM provided further insight into the microstructure of single-layer Ti_2CT_x (Figs. 2h–2i)^[40]. The high-resolution TEM profile (HRTEM; Fig. 2j) displays lattice fringes with a spacing of approximately 1.09 nm, corresponding to the (002) plane of Ti_2CT_x , consistent with the XRD data. The selected-area electron diffraction (SAED, Fig. S3f in the ESM) image displays concentric ring patterns characteristic of a hexagonal lattice, confirming the good crystallinity and preserved symmetry of the MXene structure.

The electrochemical potential windows used for the different aqueous electrolytes were selected based on the electrochemical stability of the Ti_2CT_x electrode/electrolyte systems while avoiding significant side reactions. In acidic electrolytes, the operating potential window is primarily limited by hydrogen evolution at negative potentials and oxidation-related reactions at positive potentials. In alkaline and neutral electrolytes, oxygen evolution and possible electrolyte decomposition further constrain the accessible potential range. The selected potential windows correspond to the regions where relatively stable and reversible electrochemical responses were observed during

the CV and GCD measurements. Note that although higher specific capacitance can be achieved in acidic electrolytes, the relatively narrow operating potential window may limit the practically attainable energy density. These potential windows were selected based on the electrochemical stability of the Ti_2CT_x electrode/electrolyte systems, and the selection was further guided by previously reported operating potential windows for aqueous MXene electrodes^[41,42].

The electrochemical performance of the Ti_2CT_x films was systematically evaluated in acidic, neutral, and alkaline electrolytes using a three-electrode configuration. A three-electrode system with 1 mol/L H_2SO_4 as the acidic electrolyte was chosen based on prior reports of superior Ti_2CT_x performance and high ionic conductivity^[43]. The CV curves obtained within the potential window of -1.0 to -0.43 V (vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) at scan rates of 2–1000 $\text{mV}\cdot\text{s}^{-1}$ (Fig. 3a) exhibit two pairs of broad and symmetric redox peaks. The reduction peaks are located at approximately -0.71 V and -0.59 V, while the corresponding oxidation peaks appear at -0.68 V and -0.56 V, respectively. The characteristic peaks are indicative of typical pseudocapacitive behavior, where charge storage originates from the rapid and reversible insertion/deinsertion of H^+ , hydronium ions, or hydrated protons uniformly within the electrode interior^[44]. The unique layered structure

shortens the proton diffusion pathway, ensuring that the redox peaks remain clearly discernible even at a high scan rate of 1000 $\text{mV}\cdot\text{s}^{-1}$, demonstrating excellent high-rate capability^[45–47]. Furthermore, the CV profiles exhibit negligible changes across a wide range of scan rates from 2 to 1000 $\text{mV}\cdot\text{s}^{-1}$, conclusively confirming the fast ion-transport kinetics of the flexible film electrode and accounting for its superior rate performance^[22,48]. In contrast, the CV curve acquired in 1 mol/L NaOH and 1 mol/L NaCl electrolyte exhibits a nearly rectangular shape (Figs. 3b and 3c), indicating that the dominant charge-storage mechanism is electric double-layer capacitance. A comparative analysis of the gravimetric capacitance in different electrolytes is presented in Fig. 3g. The electrode achieves optimal electrochemical performance in 1 mol/L H_2SO_4 , delivering a high specific capacitance of 617 $\text{F}\cdot\text{g}^{-1}$ at a scan rate of 2 $\text{mV}\cdot\text{s}^{-1}$. Remarkably, even when the scan rate is increased to 1000 $\text{mV}\cdot\text{s}^{-1}$, a capacitance of 204 $\text{F}\cdot\text{g}^{-1}$ is retained, demonstrating exceptional rate capability. The areal mass loading of the freestanding Ti_2CT_x film is approximately 1.53 $\text{mg}\cdot\text{cm}^{-2}$, with a film density of approximately 1.9 $\text{g}\cdot\text{cm}^{-3}$. Based on the measured specific capacitance, the corresponding areal capacitance is approximately 0.94 $\text{F}\cdot\text{cm}^{-2}$ at 2 $\text{mV}\cdot\text{s}^{-1}$. These parameters demonstrate the good electrochemical performance and practical application potential of the film, where excellent high-rate

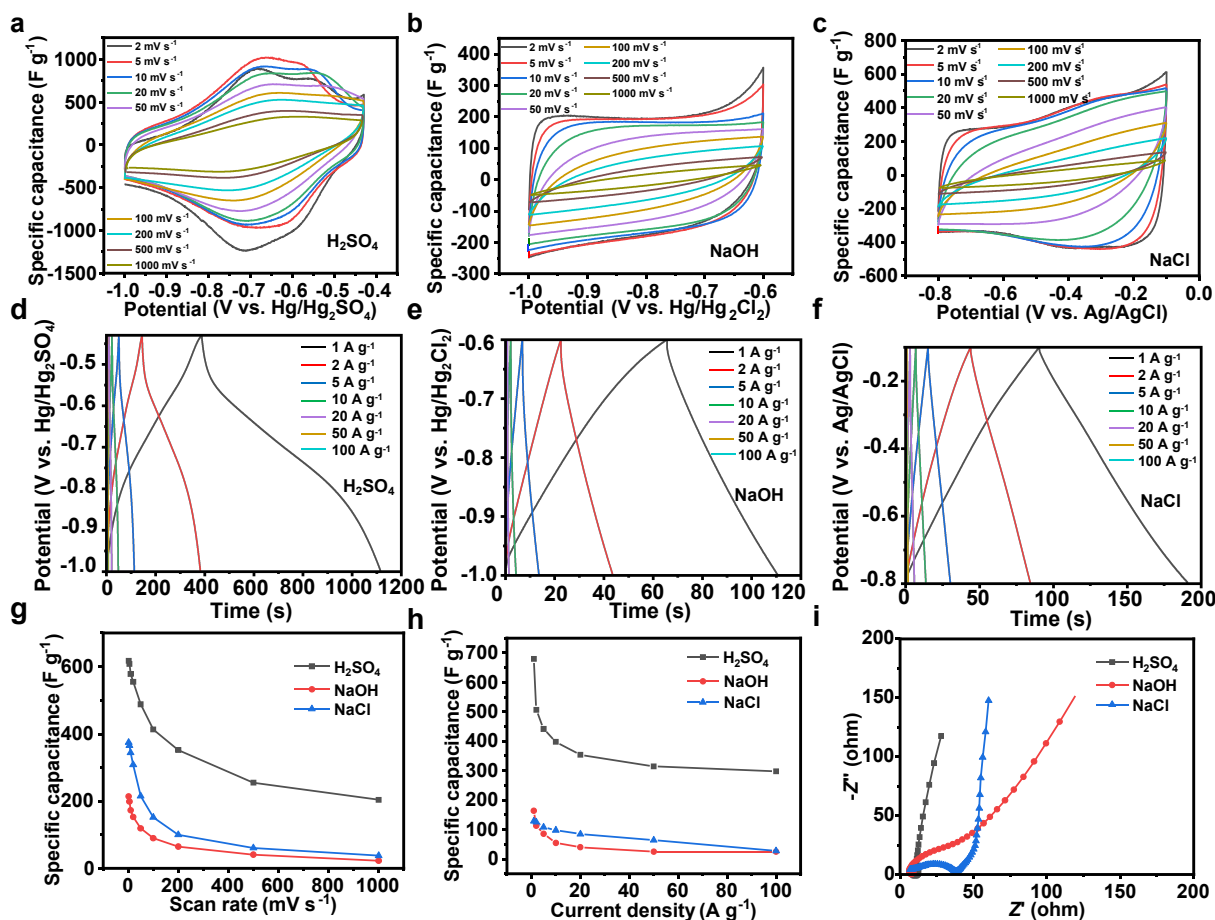


Figure 3 CV curves of the Ti_2CT_x films in 1 mol/L H_2SO_4 (a), 1 mol/L NaOH (b), and 1 mol/L NaCl (c) electrolyte at different scan rates. GCD curves in 1 mol/L H_2SO_4 (d), 1 mol/L NaOH (e), and 1 mol/L NaCl (f) electrolyte at various current densities. Specific capacitance in each electrolyte at different scan rates (g) and various current densities (h). (i) EIS curves in different electrolytes.

electrochemical performance is achieved under a reasonable active material loading rather than being obtained with an extremely low mass loading, thereby demonstrating greater practical relevance. The simultaneous achievement of high capacitance and excellent rate performance in the acidic electrolyte is attributed to the proton-coupled pseudocapacitance, the high electronic conductivity, and the relatively low molar mass of the Ti_2CT_x material.

The GCD profiles recorded at 1–100 $\text{A}\cdot\text{g}^{-1}$ (Figs. 3d–3f) further corroborate the CV data. In H_2SO_4 , the GCD curves exhibit distinct charge–discharge plateaus (Fig. 3d), characteristic of pseudocapacitive behavior. In contrast, the linear GCD curves observed in NaOH and NaCl are indicative of electrical double-layer capacitor (EDLC)-dominated storage. The gravimetric capacitances as a function of current density are summarized in Fig. 3h. The electrode delivers superior capacitance in the acidic electrolyte across the entire range of current densities, compared to those in neutral and alkaline media. Specifically, it achieves a high capacitance of $680\text{ F}\cdot\text{g}^{-1}$ at $1\text{ A}\cdot\text{g}^{-1}$ and retains $298\text{ F}\cdot\text{g}^{-1}$ even at a high current density of $100\text{ A}\cdot\text{g}^{-1}$, demonstrating excellent rate capability. These values are in good agreement with those derived from the CV measurements. In contrast, the capacitances in the neutral and alkaline electrolytes are substantially lower, retaining only 25 and $28\text{ F}\cdot\text{g}^{-1}$, respectively, at $100\text{ A}\cdot\text{g}^{-1}$.

EIS was used to elucidate the interfacial kinetics (Fig. 3i). In H_2SO_4 , the EIS profile of the electrode exhibits no discernible semicircle in the high-frequency region, indicating an extremely low charge-transfer resistance (R_{ct}) and consequently fast interfacial kinetics. In contrast, in alkaline and neutral electrolytes, the R_{ct} of the electrode is significantly larger, suggesting slower interfacial charge transfer. In the low-frequency region, the system in H_2SO_4 exhibits the largest slope, indicating the lowest diffusion resistance. This implies the shortest ion diffusion paths and fastest transport within the electrode^[49]. From four-point probe measurements, the electronic conductivity of the Ti_2CT_x film was $1098\text{ S}\cdot\text{cm}^{-1}$. Given the high capacitance and outstanding rate capability in H_2SO_4 , the long-term cycling of the electrode was evaluated at $10\text{ A}\cdot\text{g}^{-1}$ (Fig. S4 in the ESM). The electrode delivered an initial capacitance of $493\text{ F}\cdot\text{g}^{-1}$. However, after 600 charge–discharge cycles, the retained capacitance was $86\text{ F}\cdot\text{g}^{-1}$.

To evaluate the reproducibility of the fabrication method, Ti_2CT_x films independently prepared from different batches were systematically characterized. As shown in Fig. S5 in the ESM, these films exhibit highly consistent electronic conductivity and electrochemical behavior, including similar CV and GCD responses, as well as comparable specific capacitance. These results demonstrate the good reproducibility of the optimized fabrication and delamination process. A quantitative comparison with previously reported MXene-based supercapacitor electrodes is presented in Table S1 in the ESM. The as-prepared Ti_2CT_x films exhibit competitive high-rate electrochemical performance, particularly at ultrahigh current densities.

To further evaluate the practical applicability of the free-standing Ti_2CT_x films, a flexible symmetric supercapacitor was assembled using two identical Ti_2CT_x films as both the positive and negative electrodes with a poly(vinyl alcohol)

(PVA)– H_2SO_4 gel electrolyte. The CV curves recorded at different scan rates within a voltage window of 0–0.6 V maintain a nearly rectangular shape (Fig. S6a in the ESM), indicating typical capacitive behavior and fast charge-storage kinetics. The device delivers a specific capacitance of $341.1\text{ F}\cdot\text{g}^{-1}$, calculated from the CV curve at $5\text{ mV}\cdot\text{s}^{-1}$, demonstrating good charge-storage capability.

The galvanostatic charge/discharge curves acquired at different current densities are shown in Fig. S6b in the ESM. All curves exhibit good symmetry, indicating highly reversible charge-storage behavior. In the two-electrode configuration, the device can operate stably within the voltage window of 0–0.6 V, as deduced from the CV measurements. However, during GCD testing, complete charge/discharge profiles could not be reliably obtained across the 0–0.6 V voltage range, making accurate determination of the discharge time difficult. Therefore, the specific capacitance from the GCD measurements was evaluated in the 0–0.4 V voltage range, where stable discharge was observed. Under these conditions, the device delivers a specific capacitance of $117.3\text{ F}\cdot\text{g}^{-1}$ at $2\text{ A}\cdot\text{g}^{-1}$ and retains $37.5\text{ F}\cdot\text{g}^{-1}$ at $100\text{ A}\cdot\text{g}^{-1}$, demonstrating excellent rate capability.

Based on the GCD results, the device achieves an energy density of approximately $2.61\text{ Wh}\cdot\text{kg}^{-1}$ at a corresponding power density of approximately $200\text{ W}\cdot\text{kg}^{-1}$. Although the attainable device-level energy density is limited by the relatively narrow operating voltage window of the acidic gel electrolyte, the excellent rate capability and rapid charge/discharge response highlight the potential of the free-standing Ti_2CT_x films for high-power, flexible energy storage devices.

The EIS profiles of the Ti_2CT_x films are shown in Fig. S6c in the ESM. The Nyquist plot exhibits a small semicircle in the high-frequency region and an approximately vertical line in the low-frequency region, indicating low charge-transfer resistance and efficient ion-transport characteristics. These features are consistent with the high electronic conductivity of the Ti_2CT_x films and the presence of accessible ion-transport pathways, both of which facilitate rapid charge storage. Furthermore, as shown in Fig. S6d in the ESM, the device retains approximately 81% of its initial capacitance after 2000 continuous charge/discharge cycles, demonstrating good device-level cycling stability and structural robustness.

The structural evolution and charge-storage mechanisms of the films were characterized via *in situ* XRD during cycling in 1 mol/L H_2SO_4 . Figure 4a presents a comparison of the XRD patterns obtained after the 1st and 35th cycles. After 35 cycles, the (002) diffraction peak shifts by approximately 0.07° toward lower angles, indicating a net expansion of the interlayer spacing, resulting from repeated insertion/extraction. This irreversible expansion is accompanied by a minor contraction component, attributed to incomplete ion extraction and localized structural collapse upon extended cycling^[50]. Figure 4b shows the *in situ* XRD pattern at $2\theta = 5^\circ\text{--}8^\circ$ over the first two CV cycles. No new reflections emerge during charging/discharging, suggesting that charge storage proceeds without detectable phase transformation and remains highly reversible. Thus, charge storage primarily stems from pseudocapacitive behavior and EDLC contributions,

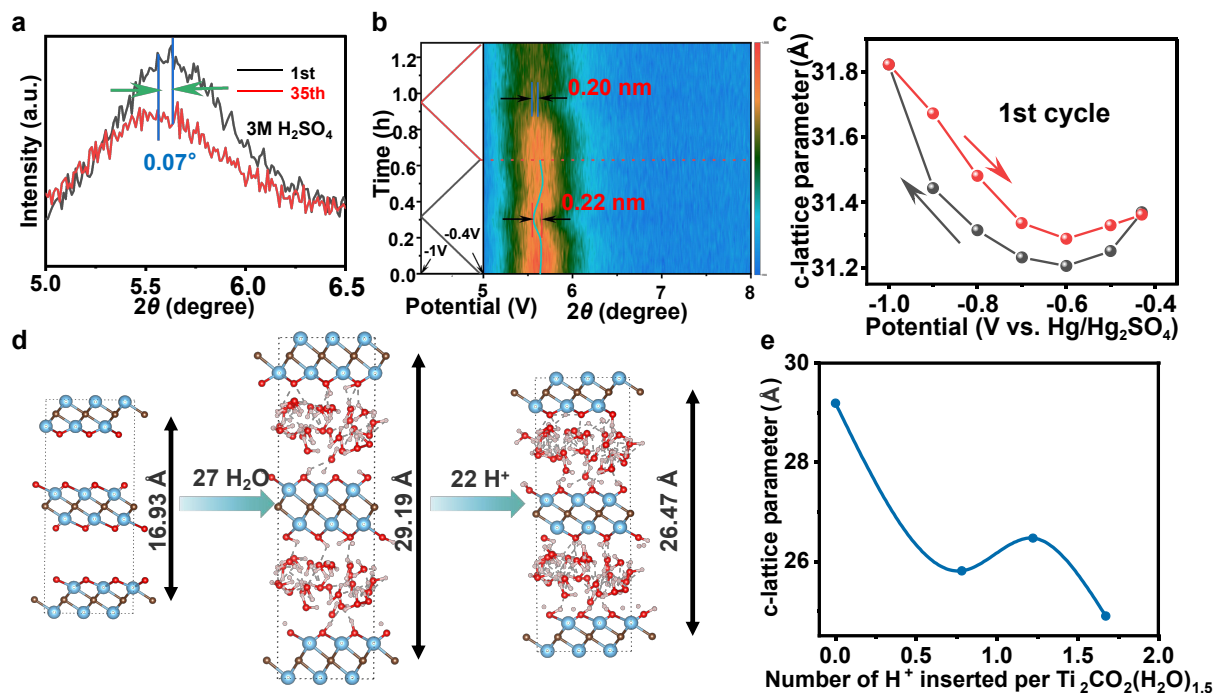


Figure 4 (a) Comparison of *in situ* XRD patterns of Ti₂CT_x. (b) *In situ* XRD pattern of Ti₂CT_x. (c) Variation of the *c*-lattice constant of Ti₂CT_x. (d) and (e) Variation of interlayer spacing in H⁺-intercalated Ti₂CO₂(H₂O)_{1.5}.

accompanied by reversible evolution of the interlayer, consistent with proton/hydronium insertion and extraction. Notably, during the potential sweep from -0.43 to -1.0 V (insertion), the (002) peak initially shifts to higher angles and then reversibly shifts to lower angles. The maximum interlayer expansion reaches approximately 0.22 nm, followed by contraction upon discharge, evidencing reversible interlayer “breathing”. In the second cycle, the maximum change is approximately 0.20 nm, which is 0.02 nm smaller than that in the first cycle, suggesting a minor degree of irreversible insertion/extraction. The initial decrease in the interlayer spacing may originate from the electrostatic screening effect associated with proton insertion, which partially reduces the electrostatic repulsion between adjacent Ti₂CT_x layers. In addition, the rearrangement and/or partial desolvation of confined interlayer water molecules during the early stage of proton intercalation may also contribute to this transient interlayer contraction behavior^[51]. Moreover, the gradual attenuation of the (002) diffraction peak intensity during cycling suggests progressive structural disordering and reduced interlayer ordering of Ti₂CT_x under acidic electrochemical conditions. The gradual loss of crystallinity during prolonged cycling plausibly arises from repeated H⁺/H₃O⁺ intercalation/deintercalation, accompanied by partial oxidation and irreversible interlayer structural evolution^[52]. The reversible interlayer “breathing” behavior of the Ti₂CT_x electrode is interpreted as being associated with the insertion/extraction of H⁺/H₃O⁺ ions. This interpretation is based on: (i) the electrolyte-dependent electrochemical behavior, (ii) the observation of reversible lattice expansion/contraction only in acidic electrolytes, and (iii) the small ionic size and rapid transport characteristics of H⁺/H₃O⁺, which are consistent with previously reported proton intercalation in MXene materials^[53].

Collectively, these observations support a proton-coupled pseudocapacitive charge-storage mechanism in Ti₂CT_x films operating in acidic electrolytes. Figure 4c presents the quantitative changes in the lattice parameter as a function of potential, further supporting the reversible modulation of the interlayer space and proton-coupled pseudocapacitive behavior in acidic electrolytes.

Density functional theory (DFT) was further used to provide qualitative insight into the pseudocapacitive mechanism of Ti₂CT_x in an acidic electrolyte. A $3 \times 3 \times 2$ Ti₂CO₂ supercell was constructed as the structural model (Fig. 4d). Upon intercalating 27 H₂O molecules into the model (i.e., 1.5 H₂O per Ti₂CO₂ formula unit), the calculated *c* lattice parameter expanded from 16.93 to 29.19 Å, closely matching the experimental value. This result suggests that H₂O effectively expands the interlayer spacing of Ti₂CT_x. Based on this hydrated configuration, proton insertion was further investigated. Upon introducing 22 H⁺ (equivalently, 1.22 H⁺ per Ti₂CO₂(H₂O)_{1.5}) into the hydrated model, the *c*-lattice parameter decreased to 26.47 Å, indicating a degree of interlayer contraction. The detailed DFT results are shown in Fig. 4e. These calculations demonstrate that varying the proton content can induce both expansion and contraction of the interlayer spacing, consistent with the *in situ* XRD data. Collectively, the theoretical findings are consistent with the proposed proton/hydronium-coupled pseudocapacitive storage mechanism. Notably, the DFT calculations were performed using an idealized Ti₂CO₂-terminated model to provide qualitative insight into the structural evolution of the proton-coupled interlayer space. The surface of the actual Ti₂CT_x system may be characterized by mixed O/OH/F surface terminations and partial surface oxidation (as revealed by the XPS analysis), which are not fully captured by the simplified computational model. There-

fore, the present DFT calculations primarily provide qualitative structural information rather than a rigorous description of proton-transport kinetics or ion-migration barriers. In addition, the involvement of protons/hydronium ions proposed in this study is mainly inferred from the combined observations of electrochemical behavior, *in situ* XRD observations, and the simplified DFT calculations. More rigorous investigations of the proton-transport kinetics and migration pathways will be pursued in future experimental and theoretical studies.

Based on the combined results of the cycling tests and *in situ* XRD analysis, the observed performance degradation is attributed to repeated $\text{H}^+/\text{H}_3\text{O}^+$ -associated interlayer cycling and structural evolution, leading to performance decay and partial irreversible changes of the interlayer. To further investigate this phenomenon, the electrode was subjected to post-mortem analysis after 100 cycles. The shift of the (002) peak from 7.5° to 7.7° indicates a decrease in the interlayer spacing (Fig. 5a). This shift is mainly ascribed to structural relaxation associated with frequent and reversible proton/hydronium transport through the confined water channels between the MXene layers, accompanied by partial irreversible ion trapping and structural changes^[54].

XPS analysis after 100 cycles provides further insight

into the surface chemical evolution of the electrode (Figs. 5b–5d). The C 1s spectrum retains components assigned to Ti–C, C–C, C–O, and C=O at binding energies of 281.9, 284.8, 286.6, and 288.7 eV, respectively, similar to those observed before cycling. In the O 1s spectrum, peaks of Ti–OH, Ti–O, and H–O–H appear at 531.3, 529.3, and 532.6 eV, respectively. The Ti 2p region displays four doublets at 453.9/459.5, 455.4/460.9, 457.2/462.7, and 457.9/463.7 eV^[28–30], consistent with previous assignments. Notably, following extended cycling, the TiO_2 -related component becomes more pronounced, whereas the carbide (Ti–C) component becomes less intense. This evolution indicates rupture of the Ti–C bonds, which constitute the structural backbone of MXene and underpin its electrochemical activity. This bond cleavage generates structural defects, drives localized collapse of the MXene lattice, and forms amorphous TiO_2 and hydroxylated species (Ti–OH)^[55]. Hydroxylation of the surface reduces the capacitance and impedes ion transport, accelerating capacity decay during long-term cycling^[56], as further evidenced in Fig. S7 in the ESM. The concurrent decreases in the relative intensity of the H–O–H and Ti–O signals do not reflect absolute reductions in the proportion of these species; rather, these changes arise from dilution effects caused by the substantial increase in the

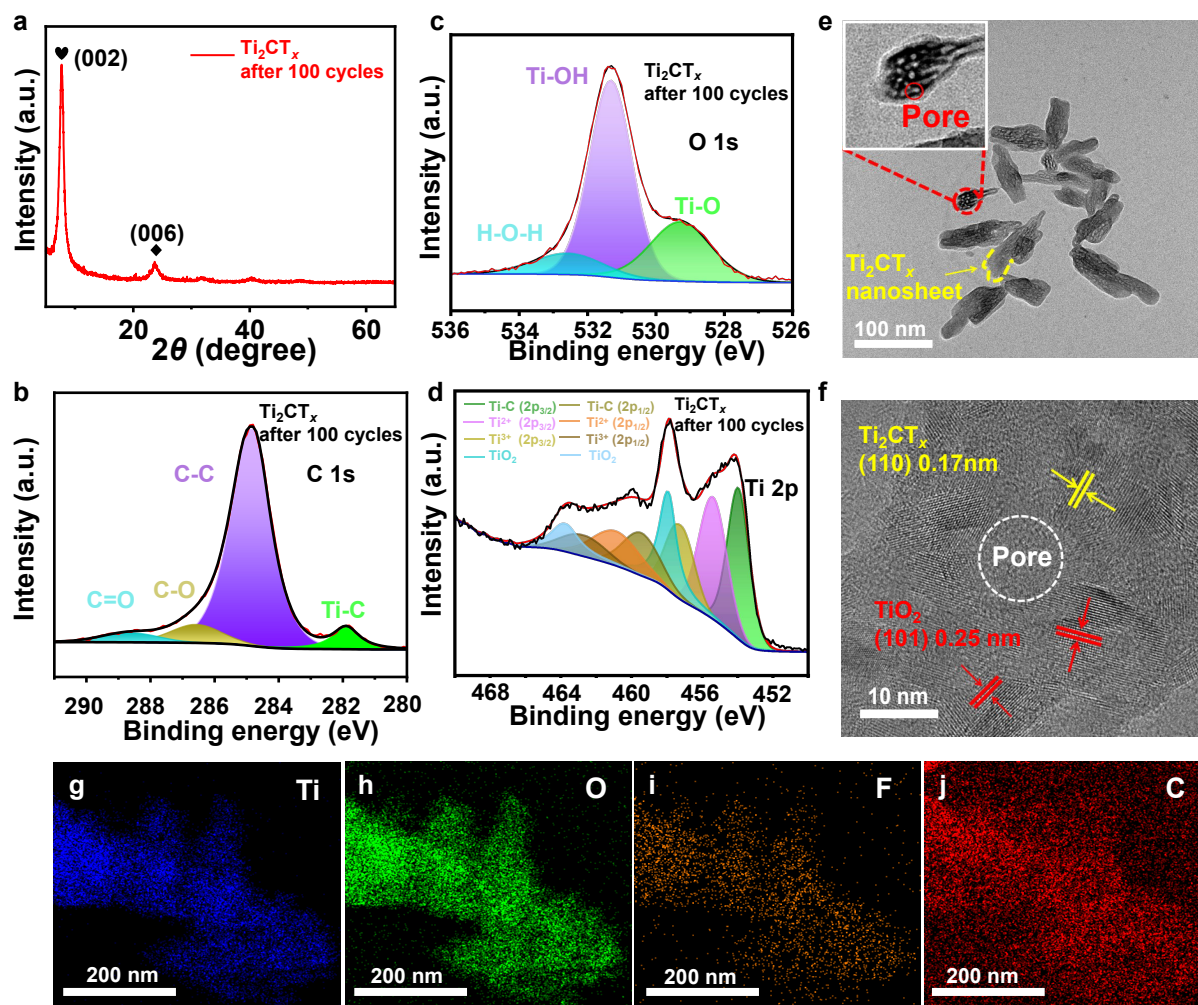


Figure 5 XRD pattern (a), XPS profiles (b–d), TEM images (e–f), and EDS profiles (g–j) of Ti_2CT_x after 100 cycles.

number of Ti–OH bonds and TiO₂ content resulting from electrochemical degradation^[40].

The morphological and structural degradation of the electrode was further elucidated using TEM (Fig. 5e). The pronounced pore formation after extended cycling indicates structural collapse and damage resulting from repeated ion insertion/extraction. The irreversible formation of these pores not only reduces the number of active sites but also reduces the electrical conductivity and retards the reaction kinetics. This finding is consistent with reports indicating that abundant voids in MXene films detrimentally affect their mechanical and electrical properties^[57]. The microstructural evolution of the electrode after 100 electrochemical cycles was further investigated by comparative analysis of the SAED and HRTEM data with those of the pristine Ti₂CT_x sample. The SAED pattern of pristine Ti₂CT_x (Fig. S3f in the ESM) exhibits three well-defined diffraction rings with interplanar spacings of 0.94, 0.70, and 0.40 nm, corresponding to the (002), (003), and (006) planes of Ti₂CT_x, respectively. The outermost (006) diffraction ring is the most intense, indicating a relatively high degree of layered crystallinity. No detectable diffraction features are observed at higher scattering angles ($d < 0.4$ nm), which defines the diffraction cutoff of pristine Ti₂CT_x. In contrast, the characteristic (001) diffraction rings of Ti₂CT_x were retained in the SAED pattern of the cycled sample (Fig. S8 in the ESM), with measured d -spacings of 0.93, 0.62, and 0.51 nm, corresponding to the (002), (003), and (004) planes, respectively. The slight decrease in the (002) spacing from 0.94 to 0.93 nm is consistent with the small shift of the (002) XRD peak from 7.5° to 7.7° in the *in situ* XRD measurements, reflecting a subtle structural change in the interlayer spacing, induced by repeated H⁺/H₃O⁺ insertion–extraction and possible irreversible ion trapping. HRTEM observations further confirm the preservation of the layered Ti₂CT_x structure. The clear lattice fringes with a spacing of approximately 0.17 nm for the layered domains correspond to the Ti₂CT_x (100) plane, indicating that the in-plane crystal structure remains largely intact after cycling. More importantly, a new diffuse diffraction ring emerges beyond the diffraction cutoff of Ti₂CT_x in the pattern of the cycled sample. The measured d -spacing of approximately 0.34 nm agrees well with the (101) plane of anatase TiO₂ (standard d -spacing = 0.352 nm, deviation ≈ 3.3%). The diffuse nature of this diffraction ring suggests the formation of nanocrystalline TiO₂. This observation is consistent with the oxidation behavior of Ti₃C₂T_x in aqueous environments, reported by Sunderiya et al.^[58], where the characteristic MXene (001) diffraction rings gradually weakened, accompanied by the appearance of polycrystalline TiO₂ diffraction rings, indicating the formation of nanoscale oxidation products. Further evidence is provided by the localized HRTEM images, where the lattice fringes with a spacing of approximately 0.25 nm are assigned to the (004) plane of anatase TiO₂, consistent with the SAED analysis. These results indicate partial oxidation of Ti₂CT_x during electrochemical cycling in acidic electrolytes, leading to the formation of nanocrystalline anatase TiO₂ and accompanying pore formation. The oxidized regions gradually lose their ability to reversibly store H⁺/H₃O⁺ ions, thereby contributing to performance degradation. Overall, the combined SAED and HRTEM analyses provide

compelling evidence of the formation of nanocrystalline anatase TiO₂, while demonstrating that a portion of the layered Ti₂CT_x structure remains intact after cycling. This structural evolution offers a reasonable explanation of the observed decline in electrochemical performance during long-term cycling.

4 Conclusion

In summary, a reproducible route to freestanding, flexible Ti₂CT_x films is developed, and the electrochemical performance of the films in aqueous electrolytes (H₂SO₄, NaOH, and NaCl) is systematically evaluated. Through a combination of *in situ* XRD and first-principles calculations, the proton/hydronium insertion–extraction-coupled pseudocapacitive behavior in acidic medium is elucidated. The flexible Ti₂CT_x electrodes deliver a high gravimetric capacitance of 680 F·g^{−1} in H₂SO₄ and retain 204 F·g^{−1} even at a high scan rate of 1000 mV·s^{−1}, demonstrating excellent rate capability. The superior performance arises from two key factors: (i) the high ionic conductivity of the acidic electrolyte, which facilitates rapid charge transport, and (ii) the strong coupling between hydronium (H₃O⁺) and oxygen-terminated Ti₂CT_x surfaces, which activates efficient proton-coupled pseudocapacitance. Furthermore, a degradation pathway in the acidic environment is revealed, involving 2D surface oxidation of Ti₂CT_x and subsequent pore formation. This insight provides a basis for developing strategies to mitigate capacity fading. Moreover, the structural degradation observed during extended cycling underscores the remaining stability limitations of Ti₂CT_x MXene in strongly acidic environments, motivating further investigation into strategies for improving its long-term durability and practical applicability. Overall, the reproducible synthesis and the elucidated charge-storage mechanism establish a robust foundation for the fabrication and application of high-power MXene electrodes, opening promising avenues for flexible energy storage devices.

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None.

Author contribution statement

Huajun Xu: Writing – review & editing, Visualization, Validation, Supervision, Software, Project administration, Funding acquisition, Formal analysis, Conceptualization. **Yaxuan Jin:** Writing – original draft, Methodology, Investigation. **Ruyi Chai:** Formal analysis, Data curation. **Quzhi Song:** Resources. **Jiankang Xu:** Formal analysis, Data curation. **Chang Li:** Formal analysis, Data curation. **Hui Zhang:** Methodology, Investigation. **Lu Li:** Writing – review & editing. **Shuo Liang:** Methodology. **Dong Luo:** Writing – review & editing, Project administration. All the authors have approved the final manuscript.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declaration of competing interest

Quzhi Song is employed by Hunan Valin Wire and Cable Co., Ltd. This work did not receive financial support from this company, and the company had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript. All the other authors declare no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Use of AI statement

During the preparation of this work, the authors used Grammarly for language polishing. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

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