

Unraveling and Regulating Self-Discharge Behavior of Ti₃C₂T_x MXene-Based **Supercapacitors**

Zixing Wang,[§] Zhong Xu,[§] Haichao Huang,[§] Xiang Chu, Yanting Xie, Da Xiong, Cheng Yan, Haibo Zhao, Haitao Zhang,* and Weiqing Yang*



nism are still remaining issues. Herein, we propose a chemically interface-tailored regulation strategy to successfully unravel and efficiently alleviate the self-discharge behavior of $Ti_3C_2T_x$ MXene-based supercapacitors. As a result, $Ti_3C_2T_x$ MXenes with fewer F elements (~0.65 atom %) show a positive self-



discharge rate decline of ~20% in comparison with MXenes with higher F elements (~8.09 atom %). Such decline of the F elements can highly increase tight-bonding ions corresponding to an individual self-discharge process, naturally resulting in a dramatic 50% increase of the transition potential (V_T). Therefore, the mixed self-discharge rate from both tight-bonding (contain fewer F elements) and loose-bonding ions (contain more F elements) is accordingly lowered. Through chemically interface-tailored engineering, the significantly changed average oxidation state and local coordination information on MXene affected the interaction of ion counterparts, which was evidently revealed by X-ray absorption fine structures. Theoretically, this greatly improved self-discharge performance was proven to be from higher adsorption energy between the interface of the electrode and the electrolyte by density functional theory. Therefore, this chemically interface-tailored regulation strategy can guide the design of high-performance MXene-based supercapacitors with low self-discharge behavior and will promote its wider commercial applications.

KEYWORDS: supercapacitors, self-discharge behavior, self-discharge mechanism, MXene, chemically interface-tailored engineering

s an important electrochemical energy storage/ conversion device, supercapacitors are promising alternatives or complements to rechargeable batteries when high power delivery or fast energy harvesting is required. \tilde{I}^{-6} As we know, the performance of supercapacitors highly relies on the intrinsic properties of the critical electrode materials.^{7–13} In particular, MXenes have been proven to be a kind of promising electrode material used in supercapacitors.^{14–16} This electrode material is a class of two-dimensional transition metal carbides, nitrides, and carbonitrides, namely, described as $M_{n+1}X_nT_x$ (n = 1, 2, 3), where M denotes the transition metal, X is the carbon or nitrogen atoms, and T_x refers to surface-terminating functional groups (-O, -OH, -F).¹⁷⁻²⁰ It exhibits extremely rich electrochemical active sites that naturally originate from the rapid change of transition metals with different valence states and fast redox reactions of surface-terminating functional groups.^{17,21,22} A metallically conductive carbide core of MXenes can efficiently facilitate a

rapid electron transfer, which is commonly limited for most pseudocapacitive materials.

During last 8 years, some breakthroughs on realizing high volumetric capacitance (1500 F cm⁻³),^{14,23-25} ultrahigh rate capability,¹⁹ extremely rapid frequency response (0.12 ms at 120 Hz),²⁶ as well as the energy storage mechanism²² of MXene-based supercapacitors were witnessed. However, selfdischarge behavior and its mechanism, which are largely overlooked yet highly detrimental issues in supercapacitors,^{27–29} are still a remaining issue for MXenes. Self-discharge behavior commonly refers to the spontaneously decreased

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Figure 1. Disclosing and regulating the self-discharge effect of $Ti_3C_2T_x$ MXene-based supercapacitors. (a) Schematic illustration of the different tight-bonding models. (b) Different bonding models result in the mixed self-discharge mechanism. (c) Strategy of a tunable self-discharge process *via* regulating surface chemistry.

potential with time under an open-circuit condition after supercapacitors are in a high free energy state (charged state).^{28–31} Generally, self-discharge mechanisms are classified as four main categories: (i) the overpotential caused by overcharging spontaneously decreases after being shelved for a period of time, which is manifested by the activation-controlled faradaic process;^{28,32} (ii) self-discharge is caused by the "shuttle effect" of impurities (such as Fe^{2+}/Fe^{3+} , O₂), which belongs to diffusion-controlled faradaic process;^{28,31} (iii) there is ohmic leakage between the electrodes;^{27,28} (iv) there is charge redistribution, which is caused by the movement or loss of charge ions adsorbed on the electrodes.^{31,33}

However, the above-discussed self-discharge mechanisms of supercapacitors mainly focus on electric double layer (EDL) capacitance, whereas a small minority of studies are on pseudocapacitance, which actually possesses the more complex capacitance mechanism and certainly shares the more complicated self-discharge behavior. In an early research, Conway discussed the self-discharge behavior of RuO₂ electrodes.^{28,34} In RuO₂ electrodes, the near-surface region discharged first, closely followed by a recovery phenomenon that is attributed to redistribution of a high oxidation state complemented by proton and electron transitions. Subsequently, Andreas demonstrated that the self-discharge of MnO₂ was influenced simultaneously by both an activationcontrolled process and a charge redistribution.³⁵ As a kind of pseudocapacitor material, MXene presents much more complex surface structure and terminal groups, which will result in more complicated self-discharge behavior. Undoubtedly, how to unravel and regulate the self-discharge behavior of MXene-based pseudocapacitors will remain challenging. Also, it is of great significance for further exploitation and utilization of the expanded pseudocapacitor electrode materials.

In this work, we proved that the self-discharge mechanism of $Ti_3C_2T_r$ MXene-based supercapacitors should originate from a mixed potential driving process by both experiment and theoretical calculation. Experimentally, an interface chemistry engineering strategy was proposed to highly increase the ratio of tight-bonding ions corresponding to an individual slow selfdischarge process. As a result, the transition potential $(V_{\rm T})$ between the mixed and individual potential driving process dramatically increases by 50% (from 0.24 to 0.36 V). Also, it exhibits a positive decline of ~20% in self-discharge rate compared to that of a-MXene (without interface chemistry engineering). More importantly, X-ray absorption fine structures (XAFS) and density functional theory (DFT) results evidently proved that the improved self-discharge behavior of Ti₃C₂T_x t-MXene (surface-tailored MXene) should be ascribed to both the increase of the average oxidation state and the adsorption energy between the electrode and electrolyte ions. Obviously, this kind of unraveling of the self-discharge mechanism and regulating its process provides a deep insight into the self-discharge effect.

RESULTS AND DISCUSSION

Figure 1a schematically presents the close relationship among self-discharge behavior of $Ti_3C_2T_x$ MXene-based supercapacitors and the formation mechanism of pseudocapacitance as well as the surface chemistry of MXenes. When charged, electrolyte ions are attracted to the oppositely charged electrode/electrolyte interface and form different bonds in the intercalated capacitance. Specifically, electrolyte ions partially incorporated into the faradaic reaction will be chemically bonded to different degrees. Actually, the completely direct interaction between the ions and the electrode surface leads to a tight-bonding model (as shown in the top part of Figure 1a). Conversely, in the region where



Figure 2. Self-discharge performance of $Ti_3C_2T_x$ MXene-based supercapacitors. (a) Schematic illustration of assembling the MXene-based supercapacitors. (b) Variation of leakage current with time. Decay of open-circuit potential for the (c) *a*-MXene- and (d) *t*-MXene-based supercapacitors after being charged with different charge current densities from 0.5 to 5 mA cm⁻².

functional groups exist, a loose-bonding model will form (as shown in the bottom part of Figure 1a) as the increasing distance will result in the weakening of attractive force between the ions and the electrode surface. Accordingly, these two different models lead to a mixed self-discharge behavior, as shown in Figure 1b. First, both tight-bonding and loosebonding ions diffused out of the electrode surface, which can be fitted by the mixed potential driving model as follows:^{27,29,38}

$$V \propto V_1 \times e^{-t/\tau_1} + V_2 \times e^{-t/\tau_2}$$
 (1)

where V is the supercapacitor potential during self-discharge, V_1 and V_2 represent the initial potential of the self-discharge process, t is the time, and τ_1 and τ_2 correspond to the time constant of the self-discharge process. Once mostly loosebonding ions diffuse out of the electrode surface, the selfdischarge process transits into the individual potential driving model as follows:

$$V \propto V_1 \times e^{-t/\tau_1} \tag{2}$$

Interestingly, the mixed self-discharge behavior can be finely regulated through tailoring the surface chemistry of MXenes (Supporting Information (SI) Figure S1). As displayed in Figure 1c, $Ti_3C_2T_x$ t-MXene after elaborately eliminating the functional fluorine elements (~0.65 atom %) shares a positively apparent decline of 20% in the self-discharge rate in comparison to that of the high fluorine-containing (~8.09 atom % of XPS results) $Ti_3C_2T_x$ a-MXene. Moreover, the time of the mixed self-discharge process in t-MXene supercapacitors is much shorter than that in a-MXene supercapacitors, as well

as the transition potential ($V_{\rm T}$), markedly increases by 50% (from 0.24 to 0.36 V).

To further investigate the effect of surface chemistry on the electrochemical behaviors, supercapacitors were built with a-MXene and *t*-MXene and 6 M KOH as the electrolyte (Figure 2a). It should be noted that the areal capacitance of $Ti_3C_2T_x$ t-MXene is higher than that of a-MXene (SI, Figure S2). As calculated by the galvanostatic charge-discharge curves, the specific capacitance of *a*-MXene is 120.2 mF cm⁻², whereas for t-MXene, it is 138.3 mF cm⁻² at the same current density of 0.5 mA cm⁻². This increase is ascribed to the elimination of surface termination, which blocks electrolyte ion transport and decreases of the average oxidation state.^{39,40} Self-discharge measurements are conducted as either leakage current measurements or open-circuit potential measurements. As shown in Figure 2b, the leakage currents were recorded for MXene-based supercapacitors charged to 0.6 V at 0.5 mA cm^{-2} . In a short time, the leakage current is relatively high, but it will decrease with the passage of time and eventually reach a steady-state current, which is equal to the current associated with self-discharge.^{30,41} It is clear that the steady-state current of t-MXene is lower than that of a-MXene (34 μ A vs 45 μ A), exhibiting a slower self-discharge rate. Figure 2c,d shows the decays of open-circuit potential after charging at different current densities. As expected, the current density shows an effect not only on self-discharge but also on the initial voltage. The initial voltage increases linearly as the current density decreases (the inset of Figure 2c,d). A lower current density allows more time for ions to distribute and form a more stable bonding than when the ions stack together quickly to form an



Figure 3. Morphology evolution and compositions of *a*-MXene and *t*-MXene freestanding films. Representative scanning electron microscopy images of (a) *a*-MXene and (b) *t*-MXene freestanding films. (c) Energy-dispersive spectroscopy mapping of *t*-MXene films. High-resolution X-ray photoelectron spectra of the (d) *a*-MXene and (e) *t*-MXene freestanding films.

unstable state at a high current density.^{27,29} The change in the cumulative amount of ions near the surface causes the voltage drop at the beginning of the self-discharge process, hence the initial voltage at the beginning of the self-discharge process should replace the nominal voltage (0.6 V) when calculating the self-discharge rate.

We proved that the morphology, composition, structure, as well as the valence state of MXene had been changed after annealing treatment and hence affected the self-discharge behavior. The macropores are abundantly present in freestanding $Ti_3C_2T_r$ *a*-MXene prepared by solution-based etching and following vacuum filtration. Apparently, the macropores are greatly eliminated for t-MXene (Figure 3a,b and SI, Figure \$3), which is probably due to the removal of water molecules bonding between the MXene layers.⁴² On the other hand, the interlayer spacing of $Ti_3C_2T_r$ MXene was determined from the X-ray diffraction characterization. As shown in SI, Figure S4, the interlayer spacing of the *a*-MXene calculated from the 2θ value of (0 0 2) is 13.6 Å, whereas it decreases to 12.4 Å for t-MXene. Intriguingly, the appropriately lowered interlayer spacing of MXenes will promote the stronger ion adsorption effect in a much more confined space. As mentioned in the previous works, folding of the walls significantly improved the adsorption properties in comparison to ideal slit-like systems.^{43,44} The narrower the slit, the closer the ions reside to the slit wall so that the effective thickness inside the slits becomes smaller, yielding a larger capacitance. Consequently, the tight-bonding ions will be increased in *t*-MXene compared to that with a-MXene, which is one of the critical factors to cause the low self-discharge rate of the former. Notably, the elimination of macropores is beneficial to enhance the areal and volumetric properties for practical application as the relative weight of the electrolyte in the whole supercapacitors can be decreased greatly.

Energy-dispersive spectroscopy mapping was carried out to elaborately analyze the change of compositions for heat-treated $Ti_3C_2T_x$ MXene films. All of these characterizations unambiguously implied that the functional groups of F elements were largely removed for t-MXene (only 0.65 atom %) (Figure 3c). In contrast, both the surface and the inside of a-MXene are terminated with F elements, as indicated by energy-dispersive spectroscopy and X-ray photoelectron spectroscopy (XPS) results (SI, Figures S5 and S6). To specifically get rid of F elements is especially important for MXene-based 2D materials. On one hand, the absence of -F could lead to a predominant increase in ion storage capability, including both surface and bulk ion intercalation, i.e., pseudocapacitance and capacity; on the other hand, the sheet resistance of t-MXene films was significantly decreased by 42.5% in comparison with that of a-MXene films (SI, Figure S7). In addition, it can be found that t-MXene has a better affinity for water than a-MXene, which was determined from the contact angle test (SI, Figure S8).

Further, we proved that the chemical bonding and the valence state were changed as the MXene experienced annealing treatment. According to XPS measurements (Figure 3d,e), the surface chemistry of MXene after annealing changes. The Ti 2p3/2 peaks at 455.04 (Ti-C), 455.83 (Ti(II)), and 456.96 (Ti(III)) eV almost disappears, with an increase of TiO₂ for the Ti 2p spectrum as compared with a-MXene, which may be attributed to the oxidation of Ti atoms on the surface. Actually, the intensity of TiO₂ in the inner XPS spectrum is significantly weaker than the surface of t-MXene (SI, Figure S9). Correspondingly, for the spectrum of C 1s, the intensity of C-Ti centered at 281.45 eV decreases substantially. From the spectrum of O 1s, the peaks at 533.80 (H_2O) and 534.95 (O-F) almost disappear, whereas the intensity of TiO₂ centered at 206.88 eV increases sharply. Additionally, the components in the F 1s region further



Figure 4. X-ray absorption fine structures of Ti. (a) Ti K-edge XANES spectra of *a*-MXene and *t*-MXene, together with those of Ti foil and TiO_2 anatase. (b) Average Ti oxidation state determination in *a*-MXene and *t*-MXene, using the Ti K-edge energy shift of the reference Ti foil and TiO_2 anatase. (c) Corresponding EXAFS R space fitting curves of *a*-MXene and *t*-MXene.



Figure 5. DFT calculations of MXene structures. (a) Schematic illustration of suppressing self-discharge *via* regulating surface functional groups. (b) Top (upper row) views showing the different functionalized $Ti_3C_2T_x$ structures (2 × 2 supercells) with K atoms adsorbed. (c) Adsorption energy at different sites. The inset shows the different adsorbed sites from side views.

indicate that fluorine elements have been greatly reduced. Based on fitted results, the atomic percentages of Ti, C, O, and F for *a*-MXene and *t*-MXene are summarized in SI, Table S1.

In order to investigate the influences of the changes of structure and valence state on self-discharge behavior of MXene after annealing treatment, X-ray absorption near-edge structures (XANES) and extended X-ray absorption fine structures (EXAFS) were measured to confirm the intrinsic structure information at the atomic level. In Figure 4a, the XANES curves of a-MXene and t-MXene show their edge energy between those of Ti foil and TiO₂, indicating that the oxidation state of Ti is between the two references. As shown in Figure 4b, the average oxidation state of Ti can be quantitatively estimated on the basis of the measured edge energy of a-MXene, t-MXene, the reference Ti foil, and TiO₂ anatase, which is based on the fact that the edge energy is directly proportional to the average oxidation state.^{45–47} The inset of Figure 4b clearly shows that the average oxidation state of Ti decreases from 2.51 to 2.39 after being surface-tailored,

which is responsible for the increases of pseudocapacitance in t-MXene compared to that in a-MXene.^{46,47} Moreover, the lower the average oxidation state of Ti atoms, the higher the chemical potential drive to a higher oxidized state as charged, thereby forming much more tight-bonding ions in t-MXene than in a-MXene, which is one of the factors to alleviate the self-discharge effect through chemically interface-tailored regulation.

The change in local coordination information that can be determined by EXAFS is another effect on self-discharge behavior. As shown in the EXAFS curves (SI, Figure S10), the Ti–Ti peak apparently appears at 2.5 Å in the Ti foil, and the EXAFS curves of *a*-MXene and *t*-MXene show oscillations similar to those of Ti foil. It should be noted that some other peaks occur that are due to Ti–O(C) bonds.^{46,48} To obtain quantitative structural information (SI, Table S2), the Ti–O(C) and Ti–Ti peaks of the *a*-MXene, *t*-MXene, and Ti foil were fitted in the *R* space (Figure 4c), *k* space (SI, Figure S11), and wavelet transform (SI, Figure S12). Note that Ti atoms in

the *t*-MXene display a coordination number higher than that in a-MXene after eliminating F atoms. In fact, Ti–F bonds formed on the surface of a-MXene cause an increase in the distance between the ions and the electrode surface and hence lead to a decline of the attractive force, which eventually exacerbates the self-discharge effect.

To further understand the changes in adsorption energy of MXene after chemically interface-tailored regulation, we performed DFT calculations with the Ti_3C_2 monolayer functionalized by O and F groups. As shown in Figure 5a, in the region where F termination is present, a loose-bonding model forms due to the lower absorption energy, whereas in the region without F termination, a tight-bonding model forms.

Here, we mainly studied $Ti_3C_2O_2$ and $Ti_3C_2F_xO_y$ (x/y =1:2.6, which is based on the results of XPS). After full optimization, it is found that the K ions can locate at four kinds of sites (Top, Bri, Hcp, Fcc) among the O atoms (Figure 5b), and the valence electron localization function of the K- $Ti_3C_2F_xO_y$ is shown in SI, Figure S13. To explore the K absorbed capability, different absorbed energy at four sites on $Ti_3C_2O_2$ and $Ti_3C_2F_xO_y$ with a 2 × 2 supercell is studied. To assess the stabilities of K-Ti₃C₂O₂ and K-Ti₃C₂F_xO_y the absorption energy was calculated with $E_a = E_{slab-K} - \dot{E}_{slab}$ $E_{\text{K-bulk}}$, where $E_{\text{slab-K}}$ is the total energy of K-Ti₃C₂O₂ and K- $Ti_3C_2F_xO_y$, E_{slab} denotes the total energy of bare MXene slab model, and $E_{\text{K-bulk}}$ is the chemical potential of K atom.^{21,37} As shown in Figure 5c and SI, Table S3, the adsorption energy of $Ti_3C_2O_2$ at Hcp (-1.032 eV) and Top (-0.608 eV) sites are higher than those of $Ti_3C_2F_xO_y$ (-0.924 and -0.570 eV), and the adsorption energy is close to that for Bri and Fcc sites. The higher the adsorption energy is, the more stable the system is after K ions are adsorbed. Consequently, in the region where F exists, a loose bonding is formed due to the lower adsorption energy, thus accelerating the self-discharge process of a MXene-based supercapacitor.

CONCLUSION

In conclusion, the mixed potential driving process correlated with the models of tight-bonding and loose-bonding ions were proposed to shed light on the self-discharge mechanism of $Ti_3C_2T_x$ MXene-based supercapacitors. In this regard, a chemically interface-tailored strategy was employed to strengthen tight-bonding ions and hence to efficiently regulate the self-discharge process. As a result, the self-discharge rate positively decreases by ~20% for $Ti_3C_2T_x$ t-MXene with high fluorine elements (~0.65 atom %) compared to a-MXene with high fluorine elements (~8.09 atom %). Experimentally, the XAFS and XPS results evidently revealed that the improved self-discharge behavior of $Ti_3C_2T_x$ t-MXene should be ascribed to the decline of the average oxidation state. Theoretically, the DFT results adequately uncover that its greatly improved selfdischarge performance should originate from the increase of the adsorption energy between the electrode and electrolyte ions. Hence, this work provides not only an open strategy to tailor the self-discharge process of $Ti_3C_2T_x$ MXene but also a deep insight into the self-discharge mechanism.

EXPERIMENTAL SECTION

Preparation of Freestanding Ti₃**C**₂**T**_x **MXene Films.** The freestanding $Ti_3C_2T_x$ MXene films have been prepared according to the previously reported work.³⁶ First, Ti_3AlC_2 (400 mesh, purchased from 11 Technology Co. Ltd.) powders were chemically etched by hydrochloric acid (Kelong Chemical Reagent Corporation, Chengdu,

China) and lithium fluoride (Aladdin Industrial Corporation, Shanghai, China), exfoliated, and further delaminated to prepare $Ti_3C_2T_x$ MXene colloidal solutions. Then, 0.2 g of $Ti_3C_2T_x$ powders was mixed with 20 mL of deionized water and kept under ultrasound for 1 h to obtain few-layer $Ti_3C_2T_x$. After that, the dark green supernatant was collected by centrifugation at 3500 rpm for 1 h. Finally, freestanding $Ti_3C_2T_x$ MXene films (named as *a*-MXene) can be obtained by vacuum-assisted filtration of the as-prepared $Ti_3C_2T_x$ MXene colloidal solution.

Chemically Interface-Tailored Engineering of Freestanding $Ti_3C_2T_x$ MXene Films. Our previous work indicated that the surface chemistry and the electrical conductivity of $Ti_3C_2T_x$ MXene could be finely tuned through a simple annealing treatment.³⁷ In this work, for tailoring surface functional groups and the electronic structure, freestanding a-MXene films were carefully annealed at 400 °C under the protection of N_2/H_2 gas with a flow rate of 40 sccm. In fact, the $Ti_3C_2T_x$ MXene prepared by the etching and delamination method still contains some water molecules in the interlayer of MXenes. These water molecules were proven to availably promote the transfer of electrolyte ions. N_2/H_2 was used to heat-treat the MXenes, and both the pseudocapacitance and the Li-ion storage capability became stronger. After treatment, the composition changes of surface chemistry led to a different structure and consequently influenced the electrical and electrochemical properties, which we discuss in the Results and Discussion. For convenience, the samples were named t-MXene (treated MXene) according to the annealing temperature. XPS (Thermo Scientific ESCALAB 250Xi) and X-ray energy dispersive spectroscopy (JSM-7800F Prime) were performed to characterize the composition change of t-MXene in comparison with a-MXene. Field-emission scanning electron microscopy (JSM-7800F Prime) and X-ray diffraction (PANalytical X'Pert powder diffractometer) were used for morphology and crystal structure detections. The contact angle was measured using a Dataphysics DSA100 contact-angle system.

X-ray Absorption Fine Structure Measurements. The X-ray absorption fine structures were collected on the beamline BL01C1 in NSRRC and were provided for technical support by Ceshigo Research Service (www.ceshigo.com). The radiation was monochromatized by a Si(111) double-crystal monochromator. X-ray absorption near-edge structure and extended X-ray absorption fine structure data reduction and analysis of *a*-MXene and *t*-MXene were processed by Athena software.

Density Functional Theory Computations. The density functional theory calculations were performed with the Vienna Ab Initio Simulation Package (VASP). The functional of choice was Perdew-Burke-Ernzerhof, and the van der Waals contributions were obtained through the DFT-D2 method. This setup has been proven to predict the experimental adsorption energies of MXene and K. The inner electrons were represented by projector-augmented wave pseudopotentials, and the monoelectronic states were expanded in plane waves with a kinetic energy cutoff of 450 eV. Surfaces of MXene were modeled by a four-layer slab and at least $p(2 \times 2)$ supercells, where the two uppermost layers were fully relaxed and the rest fixed to the bulk distances. In the surface calculations, the Brillouin zone was sampled by a Γ -centered k point mesh from the Monkhorst–Pack method, and the k point samplings were denser than 30 Å⁻¹. The vacuum between the slabs was 15 Å, and the adsorbates were placed only on one side of the slab, and thus a dipole correction was applied to remove spurious contributions arising from this asymmetry. In all cases, the nature of the saddle points was assessed by the diagonalization of the numerical Hessian generated by 0.02 Å displacements for each coordinate. All TS structures have a single imaginary frequency. In all cases, the optimization thresholds were 10^{-5} eV and 0.02 eV Å⁻¹ for electronic and ionic relaxations, respectively. In addition, the F and O functional groups in MXene were randomly distributed on the MXene surface with the atom ratio of 2.6:1 according to the XPS measurements.

Electrochemical Measurements. Symmetric supercapacitors were assembled using 2032-type coin cells. The *a*-MXene and *t*-MXene films were punched into a 1.2 cm diameter and used as

electrodes without the current collector. A cellulose membrane (F4050, NKK) was sandwiched between two electrodes as the separator, and 6 M KOH was employed as the electrolyte.

Cyclic voltammetry curves, galvanostatic charge–discharge process, and electrochemical impedance spectra were carried out using the electrochemical workstation (CHI660E). The self-discharge measurement of the supercapacitors was conducted on an Arbin MSTAT4 multichannel galvanostat/potentiostat instrument. We mainly used leakage current measurements and open-circuit potential measurements to record the self-discharge process. In leakage current measurements, the MXene-based supercapacitors were charged to 0.6 V at a current of 1.11 mA and then maintained at a constant voltage (0.6 V) to record the change of current with time. In opencircuit potential measurements, the MXene-based supercapacitors were charged to 0.6 V at a current density of 0.5 mA cm⁻² first and then monitored for the change of potential with time under opencircuit conditions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c01056.

Chemically interface-tailored engineering of $Ti_3C_2T_x$ MXene; electrochemical performance comparison of a-MXene and t-MXene; scanning electron microscopy images of a-MXene and t-MXene; X-ray diffraction patterns of a-MXene and t-MXene; energy-dispersive spectroscopy results of a-MXene; XPS survey spectrum of a-MXene and t-MXene; sheet resistance of a-MXene and t-MXene; contact angle test of a-MXene and t-MXene; high-resolution XPS spectrum of the t-MXene with different Ar-ion etchs; XAS results of a-MXene and t-MXene; valence electron localization function of the $K-Ti_3C_2F_xO_y$; specific adsorption energies of the $Ti_3C_2T_r$ MXene (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Haitao Zhang Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, P.R. China; Email: haitaozhang@swjtu.edu.cn
- Weiqing Yang Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering and State Key Laboratory of Traction Power, Southwest Jiaotong University, Chengdu 610031, P.R. China; orcid.org/0000-0001-8828-9862; Email: wqyang@ swjtu.edu.cn

Authors

- **Zixing Wang** Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, P.R. China
- Zhong Xu Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, P.R. China
- Haichao Huang Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, P.R. China
- Xiang Chu Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science

and Engineering, Southwest Jiaotong University, Chengdu 610031, P.R. China

- Yanting Xie Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, P.R. China
- **Da Xiong** Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, P.R. China
- Cheng Yan Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, P.R. China
- Haibo Zhao Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, P.R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsnano.0c01056

Author Contributions

[§]Z.W., Z.X., and H.H. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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