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Nitrogen Doped Intercalation $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ Nanocomposite Electrodes with Enhanced Pseudocapacitance

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Abstract: Layered two-dimensional titanium carbide ($\text{Ti}_3\text{C}_2\text{T}_x$), as an outstanding MXene member, has captured increasing attention in supercapacitor applications due to its excellent chemical and physical properties. However, the low gravimetric capacitance of $\text{Ti}_3\text{C}_2\text{T}_x$ restricts its rapid development in such applications. Herein, this work demonstrates an effective and facile hydrothermal approach to synthesize nitrogen doped intercalation $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ with greatly improved gravimetric capacitance and excellent cycling stability. The hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) in hydrothermal environment acted as the nitrogen source and intercalants, while the $\text{Ti}_3\text{C}_2\text{T}_x$ itself was the titanium source of TiO_2 and TiN . We tested the optimized nitrogen doped intercalation $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ electrodes in H_2SO_4 , Li_2SO_4 , Na_2SO_4 , LiOH and KOH electrolytes, respectively. The electrode in H_2SO_4 electrolyte delivered the best electrochemical performance with high gravimetric capacitance of 361 F g^{-1} at 1 A g^{-1} and excellent cycling stability of 85.8% after 10,000 charge/discharge cycles. A systematic study of material characterization combined with the electrochemical performances disclosed that TiO_2/TiN nanoparticles, the introduction of nitrogen and the NH_4^+ intercalation efficaciously increased the specific surface areas, which is beneficial for facilitating electrolyte ions transportation. Given the excellent performance, nitrogen doped intercalation $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ bodes well as a promising pseudocapacitor electrode for energy storage applications.

Keywords: MXenes; $\text{Ti}_3\text{C}_2\text{T}_x$; intercalation; TiO_2 ; TiN ; supercapacitor

1. Introduction

Supercapacitors, bridged the gap between lithium-ion batteries and conventional capacitors, have been considered to be a class of state-of-the-art energy storage devices with characteristics of high power density, long cycle life, and fast charge/discharge properties [1,2]. Electric double layer capacitors (EDLCs) based on carbon or carbon derivatives store charges via ions electro-sorption. EDLCs commonly exhibit excellent cyclic stability due to the high electrical conductivity and extraordinary chemical stability, while withstanding relatively low specific capacitance because of the limitation of charge accumulation in electrical double layers [3]. By contrast, pseudocapacitors enable the charge storage by mainly taking advantage of fast redox reactions based on metal oxides, sulfides

and conducting polymers [4–7]. Pseudocapacitors can achieve substantially high specific capacitances through surface redox reactions but usually suffer from short cyclic lifetimes [8]. Two-dimensional (2D) materials, like graphene-based composites, have been used in redox capacitors and have shown impressive pseudocapacitance on account of their large electrochemically active surfaces [9]. Yet these pseudocapacitive materials display serious volume changes during the fast charge/discharge processes, resulting in deterioration in cyclability, which curtails their wide scale use [10,11]. Therefore, researchers have focused on the development of redox-active materials with high specific capacitance and good stability for pseudocapacitors.

MXenes, a new but quickly expanding class of 2D transition metal carbides and nitrides, have showed great potential in supercapacitor electrodes applications because of their enriched features of good electrical conductivity, remarkable chemical durability, hydrophilic nature, and intercalation characteristics [12–21]. Generally, MXenes are referred to formula $M_{n+1}X_nT_x$ (where M is an early transition metal, X is C or N, T is a surface termination –OH, –F and/or –O, and n is 1, 2, or 3.) and can be synthesized by selectively etching “A” element layer from MAX phases in acidic fluoride containing solutions, such as HF, NH_4HF_2 and LiF in HCl [22–26]. To date, MXenes have been reported to exhibit high volumetric capacitance up to 900 F cm^{-3} and no measurable capacitance losses even after 10,000 cycles for $Ti_3C_2T_x$ in aqueous electrolyte, which means a better performance than those of the carbon electrodes [26]. Nevertheless, the gravimetric capacitances of MXenes electrodes are usually low because the adjacent layers are easy to restack owing to the van der Waals interaction, which limits the accessibility of ions and utilization of the active sites [27,28].

To meet the practical requirements of high gravimetric capacitance and long cyclic life for MXenes supercapacitors, exploiting more pseudocapacitances by increasing the active sites has been considered as a valid tactic [29]. On the one hand, a high-efficiency strategy using heteroatoms incorporation into MXene-based electrodes can promote the surface properties and enhance the electrochemical reactivity and the electrical conductivity of MXenes [30–36]. Rufford and co-workers synthesized nitrogen-doped $Ti_3C_2T_x$ supercapacitor electrode by annealing in ammonia gas [32]. Que’s group reported nitrogen-doped delaminated $Ti_3C_2T_x$ and nitrogen and sulfur co-doped $Ti_3C_2T_x$ electrodes through urea-assisted and thiourea-assisted carbonization, respectively [33,34]. These experimental results suggested that the introduction of heteroatoms into the $Ti_3C_2T_x$ led to a remarkable increase of specific capacitance due to the strong electronegativity of heteroatoms compared with those of carbon atoms, which affected the surficial electrical and chemical properties of MXenes [30].

On the other hand, modifying the surface structures of MXenes with pseudocapacitive materials (like RuO_2 and MnO_2) is an effective strategy to prevent the re-stacking of sheets and meanwhile bring additional pseudo reactive sites, jointly imparting enhanced performances [37–43]. The redox-based metal cations are the key active ions carrying out redox reaction in the electrolyte, which deliver pseudocapacitance. For instance, Rakhi et al. synthesized $\epsilon\text{-MnO}_2/Ti_2CT_x$ and $\epsilon\text{-MnO}_2/Ti_3C_2T_x$ electrodes for aqueous pseudocapacitors [37]. Jiang et al. reported MXene- RuO_2 asymmetric supercapacitors, which displayed enhanced device performance [41]. Moreover, recent researches have demonstrated that MXenes can be intercalated by a variety of cations [23–26]. The MXene electrodes undergo a large dilatation during Li^+ , K^+ , Na^+ or Mg^{2+} intercalation, resulting in volumetric expansion and –F surface groups reduction [29]. The cation intercalated MXene electrodes show a significant enhancement in the gravimetric capacitance performance than its non-intercalated counterpart in pseudocapacitor application.

Pseudocapacitive materials modifying and heteroatoms doping are promising supports for faradic reactions and the cation intercalation can create open pathways for ions transport. These measures are promising for enhancing the gravimetric capacitances in supercapacitor electrode applications. Herein, in order to improve the gravimetric capacitance, we fabricated nitrogen doped intercalation $TiO_2/TiN/Ti_3C_2T_x$ ($N\text{-}TiO_2/TiN/Ti_3C_2T_x$) via a facile $C_6H_{12}N_4$ solution-assisted hydrothermal process. The combination of cations intercalating, heteroatoms doping and pseudocapacitive materials addition collectively produced high gravimetric capacitance MXenes pseudocapacitor. The $N\text{-}TiO_2/TiN/Ti_3C_2T_x$

demonstrated high gravimetric capacitance of 361 F g^{-1} at 1 A g^{-1} coupled with good cycling stability of 85.8% after 10,000 cycles.

2. Materials and Methods

2.1. Preparation of $\text{Ti}_3\text{C}_2\text{T}_x$

Typically, 3 g Ti_3AlC_2 (−200 mesh, Forsman, Beijing, China) powder was slowly added into 30 mL HF solution (40 wt%) and magnetically stirred at a speed of 450 rpm for 36 h at 40°C . Afterwards, the multi-layered $\text{Ti}_3\text{C}_2\text{T}_x$ was obtained after washing with deionized (DI) water and centrifuging until the supernatant reached a PH value about 6–7, and followed by drying in a vacuum oven at 80°C for 12 h.

2.2. Synthesis of N Doped Intercalation $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$

For the preparation of N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$, the multi-layered $\text{Ti}_3\text{C}_2\text{T}_x$ was treated in a hydrothermal environment with hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) solution. Briefly, 50 mmol $\text{C}_6\text{H}_{12}\text{N}_4$ was dispersed in 50 mL DI water and stirred until it completely dissolved. Then 0.8 g multi-layered $\text{Ti}_3\text{C}_2\text{T}_x$ was added and stirred in $\text{C}_6\text{H}_{12}\text{N}_4$ solution. Subsequently, the mixed solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and the hydrothermal reactions were conducted at 150°C for 6 h, 12 h, 20 h, respectively. After the autoclave cooled to room temperature, the obtained N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ was washed with DI water until neutral. Finally, the wet sediments were dried at 60°C for 8 h.

2.3. Material Characterization

X-ray diffraction (XRD, Rigaku D/Max-2000, Rigaku, Tokyo, Japan) was performed with Cu $K\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) to characterize the crystalline structure. Scanning electron microscopy (SEM, FEI Nova 400, Peabody, MA, Netherland) and transmission electron microscopy (TEM, JEM-2100, JEOL, Tokyo, Japan) were used to examine the morphologies and microstructures. Chemical compositions and states were further analysed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi, Thermo Fisher, Madison, USA) with monochromated Al $K\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$). Raman spectroscopic (Raman, LabRAM HR Evolution, Horiba, Lille, France) and Fourier transform infrared spectroscopy (FTIR, Nicolet iS50, Thermo Fisher, Madison, USA) were employed to probe the functional groups. Nitrogen adsorption/desorption measurements were performed to investigate the surface characteristics at 77 K using a surface area analyser (BET, Quadrasorb 2MP, Quantachrome Instruments, FL, USA).

2.4. Preparation of Electrodes and Electrochemical Measurements

Pseudocapacitive electrodes were fabricated by dispersing 80 wt% active materials ($\text{Ti}_3\text{C}_2\text{T}_x$, 6 h, 12 h and 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$), 10 wt% carbon black, and 10 wt% polyvinylidene fluoride in N-methyl-2-pyrrolidone to form a slurry. The resulting slurry was coated on the conductive carbon paper collector (area of 1 cm^2 , TGP H-60, Toray Industries, Tokyo, Japan) with a mass loading of 1.52 mg and then dried in a vacuum oven at 60°C for 8 h. The electrochemical properties including cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) were measured in a three-electrode cell by using a CHI 660E electrochemical workstation, in which a platinum plate served as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and the $\text{Ti}_3\text{C}_2\text{T}_x$ based active material as the working electrode. 1 M H_2SO_4 , 1 M KOH, 1 M LiOH, 1 M Na_2SO_4 , and 1 M Li_2SO_4 were selected as electrolytes to investigate the influence of ionic radius on supercapacitor performance. Cycling stability was measured by repeating the GCD tests for 10,000 cycles at 8 A g^{-1} . The electric impedance spectroscopy (EIS) was performed with an amplitude of 5 mV from 10 mHz to 100 kHz.

3. Results and Discussion

3.1. Material Characterizations and Analysis

We successfully fabricated N-TiO₂/TiN/Ti₃C₂T_x by the exfoliation and following facile hydrothermal treatment. The schematic diagram of fabrication process for N-TiO₂/TiN/Ti₃C₂T_x is shown in Figure 1. The multi-layered Ti₃C₂T_x was firstly obtained by exfoliating Al layer from Ti₃AlC₂ with 40 wt% HF solution. The dried and neutral Ti₃C₂T_x powder was dispersed into C₆H₁₂N₄ solution under a hydrothermal condition at 150 °C for 6 h, 12 h and 20 h, respectively. During the hydrothermal process, the Ti₃C₂T_x itself as titanium source was partly oxidized to TiO₂ and nitrated to TiN. In addition, NH₄⁺ ions decomposed from C₆H₁₂N₄ intercalated spontaneously between Ti₃C₂T_x layers and the N atoms doped into Ti₃C₂T_x layers. After the treated suspensions naturally cooled to room temperature, the reaction products were washed with DI water until neutral and then were dried.

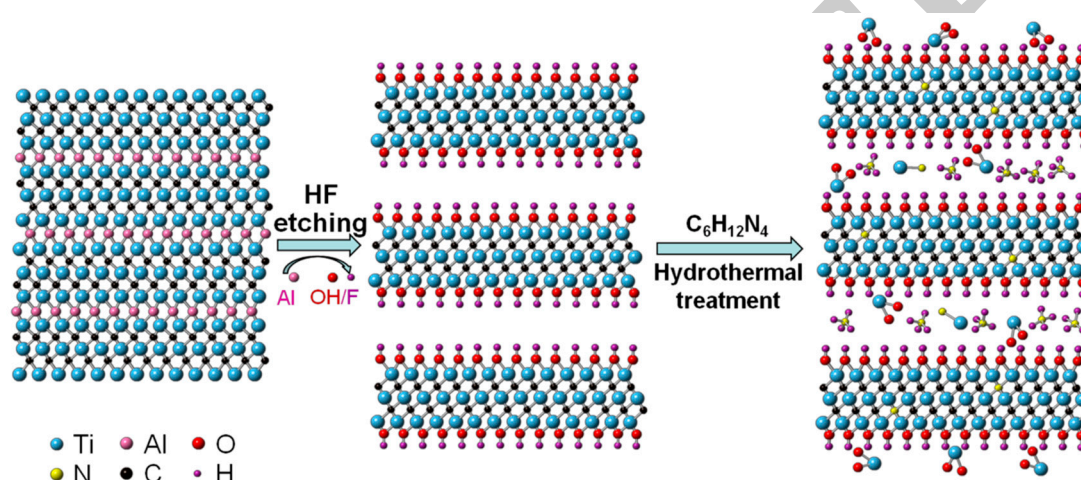


Figure 1. Schematic illustration of the preparation process for N-TiO₂/TiN/Ti₃C₂T_x.

XRD was carried out to characterize the crystal structure and orientation of the as-prepared Ti₃C₂T_x and N-TiO₂/TiN/Ti₃C₂T_x. Figure 2a shows major peaks of (002), (004), (008) and (110), validating the formation of Ti₃C₂T_x [44]. Additionally, despite the main peaks of Ti₃C₂T_x retain in 20 h N-TiO₂/TiN/Ti₃C₂T_x sample, new peaks at 2θ values of 35.98° and 43.42° might be readily attributed to (101) and (210) plane of TiO₂ (JCPDS card No. 21-1276), and 34.46°, 40.78° and 63.58° are assigned to (101), (210) and (301) plane of TiN (JCPDS card No. 17-0386), respectively. When the Ti₃C₂T_x treated with C₆H₁₂N₄ solution, some Ti atoms of Ti₃C₂T_x were oxidized into TiO₂ and nitrated into TiN nanoparticles. Moreover, it is noteworthy that the (002) peak of 20 h N-TiO₂/TiN/Ti₃C₂T_x narrowed and moved by a significant shift of 1.58° towards a lower angle in Figure 2b comparing with Ti₃C₂T_x. This shift signs an increase in the d-spacing from 1.01 nm to 1.24 nm, demonstrating an expansion of the interlayer spacing. The enlarged interlayer space is expected to increase ion diffusion or active site accessibilities, which may lead to a high capacitance. Moreover, the crystallite size of the Ti₃C₂T_x and 20 h N-TiO₂/TiN/Ti₃C₂T_x are calculated about to be 12 and 18 nm based on the Scherrer formula, respectively [45]. The 20 h N-TiO₂/TiN/Ti₃C₂T_x is expected better conductivity because the grain boundary widths decrease as crystallite size increases [46]. Figure S1 shows the XRD patterns of Ti₃C₂T_x with different hydrothermal treatment time periods in C₆H₁₂N₄ solutions. The 6 h and 12 h samples possess the same peaks of the 20 h N-TiO₂/TiN/Ti₃C₂T_x, but the 20 h sample displays a lower angle at (002) peak.

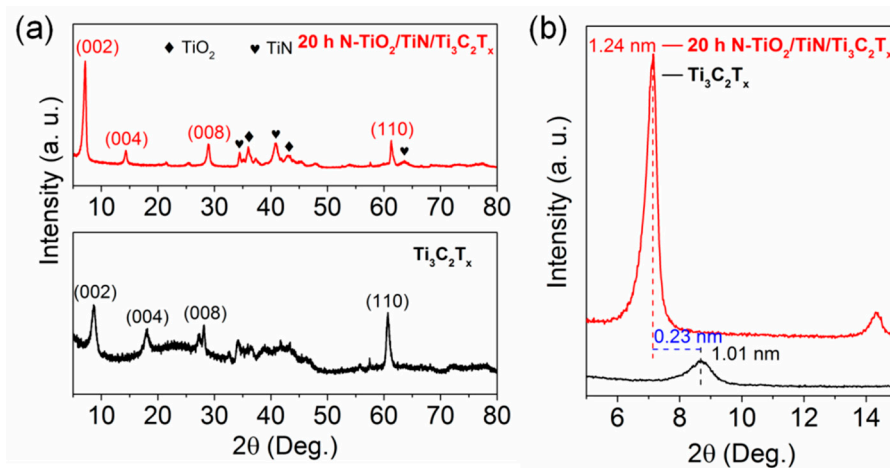


Figure 2. (a) XRD patterns of $\text{Ti}_3\text{C}_2\text{T}_x$ and 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$, (b) XRD patterns of $\text{Ti}_3\text{C}_2\text{T}_x$ and 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ over a small range of 2θ from $5\text{--}15^\circ$.

The morphology evolution is shown in the SEM images of Figure 3. Different from Ti_3AlC_2 without any layers (Figure S2), Figure 3a reveal the loosely stacked multilayer structure with smooth surface of $\text{Ti}_3\text{C}_2\text{T}_x$ because of the broken metallic Ti–Al bond binding the neighboring layers [47]. The SEM images of the N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ (Figure 3b–d) also feature well-stacked nanosheets. Specifically noting that a large number of TiO_2/TiN nanoparticles homogeneously disperse on the surfaces and between the $\text{Ti}_3\text{C}_2\text{T}_x$ layers, and the average size about 46 nm of particles of 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ is much larger than those of 6 h and 12 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$. Comparing with $\text{Ti}_3\text{C}_2\text{T}_x$, the lateral size of N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ evidently diminished, which transformed to a much more delaminated structure. Such a layered structure is beneficial for ions transport and improving the pseudocapacitance performance [39].

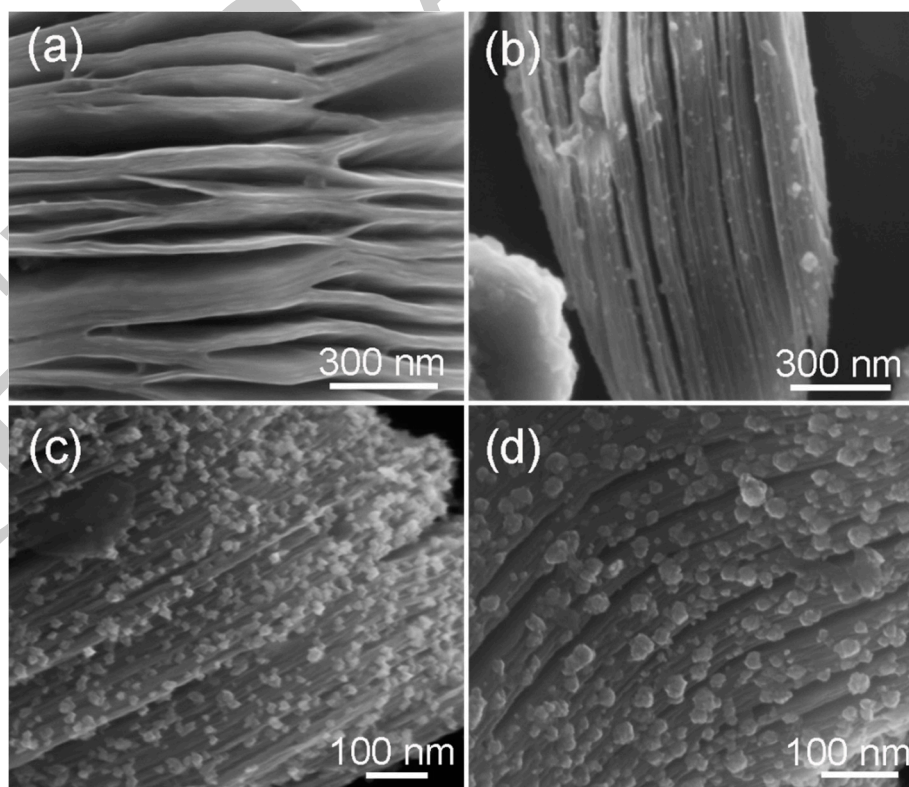


Figure 3. SEM images of (a) $\text{Ti}_3\text{C}_2\text{T}_x$, (b) 6 h, (c) 12 h and (d) 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$.

TEM images provide further insights into the microstructures of the $\text{Ti}_3\text{C}_2\text{T}_x$ and the 20 h N-TiO₂/TiN/Ti₃C₂T_x samples. The $\text{Ti}_3\text{C}_2\text{T}_x$ manifests a typically multi-layered structure, and the interlayer spacing from Figure 4b is about 1.01 nm. While the interlayer spacing of the 20 h N-TiO₂/TiN/Ti₃C₂T_x is measured to be 1.24 nm in Figure 4d. The expansion distance of 20 h N-TiO₂/TiN/Ti₃C₂T_x is highly coincide with the XRD results. In Figure 4c, it could be observed that 20 h N-TiO₂/TiN/Ti₃C₂T_x exhibits layered structure and numerous TiO₂ and TiN nanoparticles evenly fasten on $\text{Ti}_3\text{C}_2\text{T}_x$ layers. The lattice spacing of 0.26 nm and 0.24 nm were measured from Figure 4e, which could be identified as the (101) plane of TiN and (210) plane of TiO₂, respectively. Both element maps of Figure 4f demonstrate the homogeneous element distribution of titanium, nitrogen, carbon, oxygen and fluorine of 20 h N-TiO₂/TiN/Ti₃C₂T_x. Table 1 lists the atomic concentrations of the elements of $\text{Ti}_3\text{C}_2\text{T}_x$ and N-TiO₂/TiN/Ti₃C₂T_x samples. The results indicate that the 20 h N-TiO₂/TiN/Ti₃C₂T_x has the highest N concentration and lowest fluorine content.

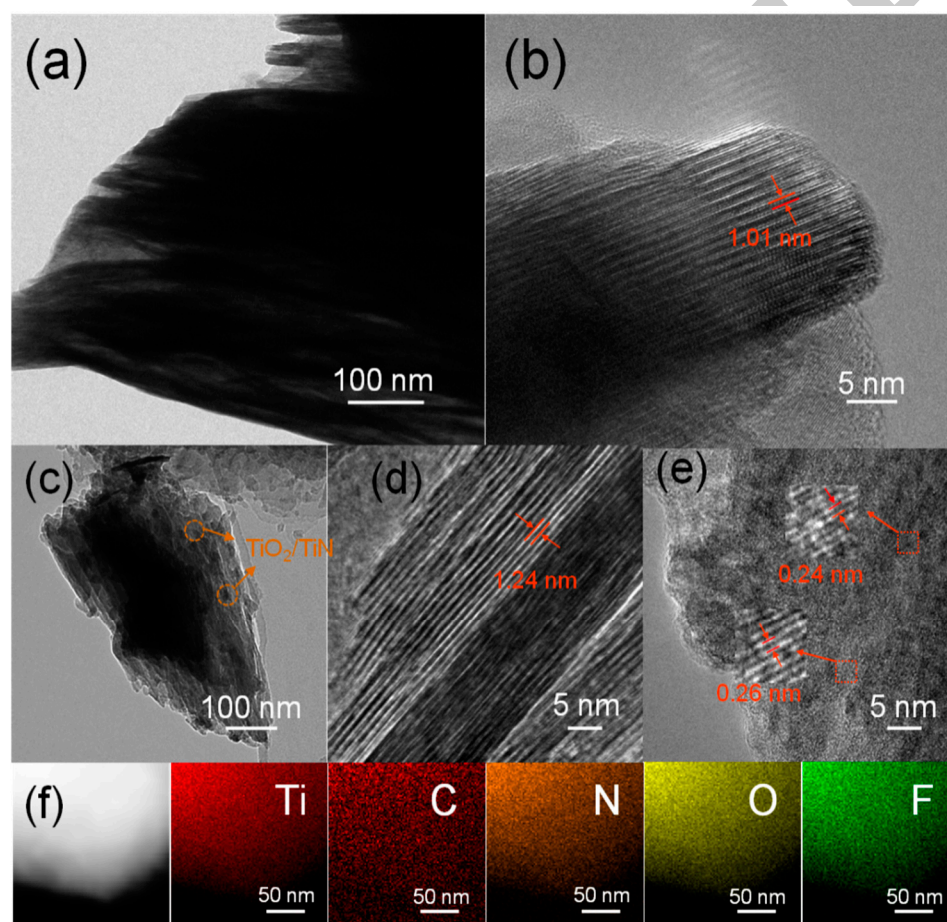


Figure 4. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of (a,b) $\text{Ti}_3\text{C}_2\text{T}_x$ and (c–e) 20 h N-TiO₂/TiN/Ti₃C₂T_x. (f) EDS element mapping of 20 h N-TiO₂/TiN/Ti₃C₂T_x.

Table 1. The atomic concentration (at %) of elements from $\text{Ti}_3\text{C}_2\text{T}_x$ and N-TiO₂/TiN/Ti₃C₂T_x.

Materials	Contents					
	Ti	C	O	F	Al	N
$\text{Ti}_3\text{C}_2\text{T}_x$	32.2	28.3	20.1	15.6	3.8	-
6 h N-TiO ₂ /TiN/Ti ₃ C ₂ T _x	27.8	34.5	23.5	10.5	2.9	1.3
12 h N-TiO ₂ /TiN/Ti ₃ C ₂ T _x	23.7	38.1	25.4	9.4	0.6	2.8
20 h N-TiO ₂ /TiN/Ti ₃ C ₂ T _x	23.8	39.2	24.1	7.9	0.8	4.2

Raman and FTIR spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ and 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ are displayed in Figure 5a,b. Three broad Raman bands at approximately 205, 381, and 608 cm^{-1} are detected from $\text{Ti}_3\text{C}_2\text{T}_x$, which are consistent with the reported data [48,49]. It is noted that a new peak at 154 cm^{-1} emerges of 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$, which can be assigned to the vibrational mode of TiO_2 [49]. Peaks at 1352 cm^{-1} and 1580 cm^{-1} correspond to D and G bands of graphitic carbon become more obviously, suggesting that the hydrothermal treatment promote the formation of amorphous carbon and the thinner nanosheets with more structural defects. This result may be beneficial for the improvement of the conductivity of the sample. The FTIR spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ and 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ directly proved the existence of identical stretching vibrations of C-F (1033 cm^{-1}), O-H (1390 cm^{-1}), C-O (1636 cm^{-1}) and -OH (3447 cm^{-1}), as shown in Figure 5b [50,51]. The comparison of these two spectra clearly shows the disappearance of the broadband around 3447 cm^{-1} , suggesting that the terminal -OH groups are reduced to some extent after the treatment. In addition, the fluorine content has also been proved to be decreased by the EDS. The lower terminated surface group concentration on the surface leads to more Ti atoms participating in redox reactions [29]. Particularly, the peak at 3112 cm^{-1} is account for the vibration of -NH, revealing the surfaces of the 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ were passivated by -NH groups [50]. A stretching vibration of Ti-O bond appears at 660 cm^{-1} and proves the formation of TiO_2 [51]. No sharp absorption peak corresponding to stretching vibrations of Ti-N is observed due to its high reflectivity of infrared light [52].

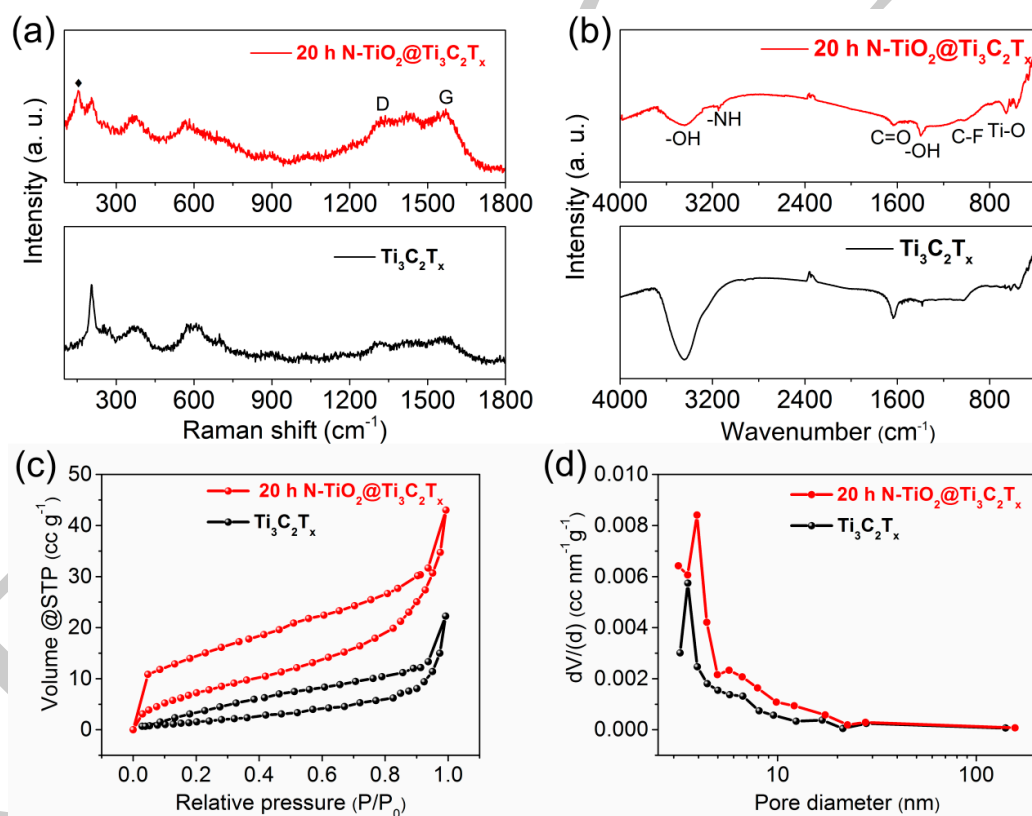


Figure 5. (a) Raman spectra, (b) Fourier transform infrared spectroscopy (FTIR) spectra, (c) Nitrogen (77 K) adsorption-desorption isotherms and (d) the corresponding pore size distribution curves of $\text{Ti}_3\text{C}_2\text{T}_x$ and 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$.

Nitrogen adsorption/desorption isotherms were measured to characterize the specific surface areas and pore size distributions of $\text{Ti}_3\text{C}_2\text{T}_x$ and 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$. As shown in Figure 5c, the Brunauer-Emmett-Teller (BET) surface areas of $\text{Ti}_3\text{C}_2\text{T}_x$ and 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ are $6.32 \text{ m}^2 \text{ g}^{-1}$ and $29.93 \text{ m}^2 \text{ g}^{-1}$, respectively. The large increased surface area is due to the formation of numerous TiO_2/TiN nanoparticles and the expanded interlayer spacing distance after the hydrothermal treatment.

The increased surface area is beneficial for improving the electrochemical performance through enhancing ion diffusion and active site accessibilities during the electrochemical reaction processes [53]. Figure 5d exhibits pore size distributions of the $\text{Ti}_3\text{C}_2\text{T}_x$ and 20 h $\text{N-TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$, suggesting that most pores of the both samples are in a range of 3–6 nm.

Further details about surface chemical states were characterized by XPS technique in Figure 6. As shown in Figure 6a, peaks of Ti, C, O, and F elements in both $\text{Ti}_3\text{C}_2\text{T}_x$ and 20 h $\text{N-TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ are visualized. Specifically, the 20 h $\text{N-TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ disclosed an additional remarkable N 1s peak at about 400 eV. The intensity of the F 1s peak decreased quickly while the O 1s peak increased significantly, indicating that a large amount of F terminal groups were removed and TiO_2 formed after the treatment. The deconvolutions of N 1s, Ti 2p, C 1s, O 1s, and F 1s levels are presented in Figure 6b–f, respectively. The high-resolution N 1s core level spectra can be fitted into three main constituent peaks, as shown in Figure 6b, including N–Ti bond at 396.4 eV, N–H peak at 399.5 eV, and quaternary–N at 401.3 eV, respectively [33,34]. The N–H bond is assigned to the thermal decomposition of $\text{C}_6\text{H}_{12}\text{N}_4$ solution. Fractional N atoms originated from the amino groups transform into the doped nitrogen in carbon, which also react with Ti to form N–Ti covalent bonds. In Figure 6c, the Ti 2p core level can be fitted with three doublets of (Ti $2p_{3/2}$ –Ti $2p_{1/2}$), and Ti–N, TiO_2 peaks. The Ti $2p_{3/2}$ components located at 454.8, 455.6, and 456.3 eV correspond to Ti–C, Ti–F and Ti–O, respectively. Peaks at 457.3 and 459.1 eV can be assigned to Ti–N and TiO_2 , respectively [31,54–58]. It could be seen that the TiO_2 peak becomes stronger and a Ti–N peak emerges after the hydrothermal treatment, which could be a sign of formation of TiO_2 and TiN particles. The C 1s spectra present five peaks related to C–Ti (281.4 eV), C–Ti–O (282.2 eV), C–C (283.9 eV), C–O (285.6 eV) and C–F (287.0 eV) [55]. The O 1s core level is fitted with O–Ti, C–Ti–Ox, C–Ti–(OH)x and H_2O –Ti bonds, which are located at 529.4, 530.4, 531.4 and 532.5 eV, respectively [54,58]. In Figure 6f, the F 1s peaks at 684.8 and 686.1 eV are correspond the Ti–F and C–F bonds, respectively.

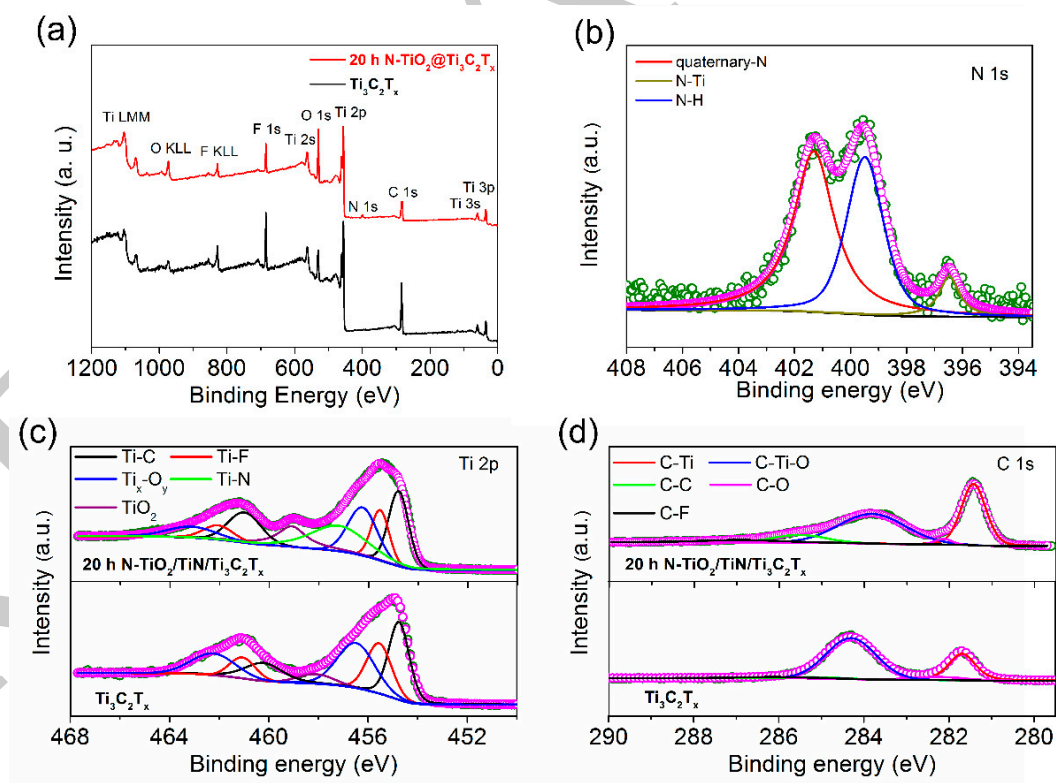


Figure 6. Cont.

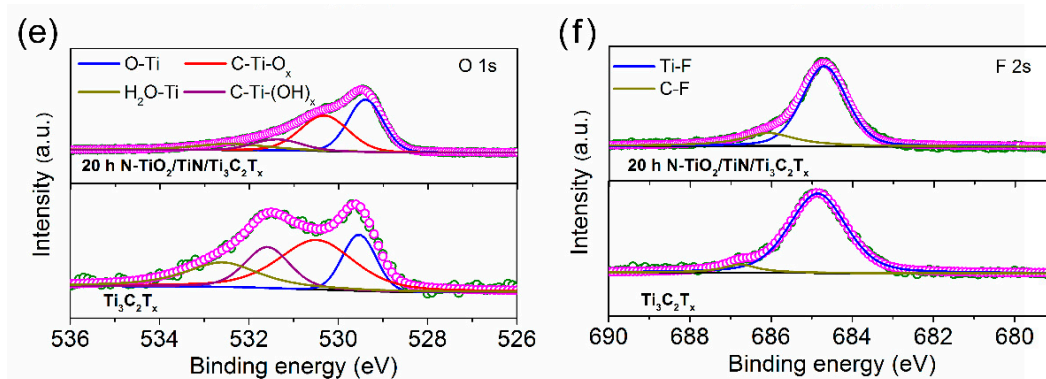


Figure 6. (a) X-ray photoelectron spectroscopy (XPS) survey spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ and 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$. High resolution (b) N 1s, (c) Ti 2p, (d) C 1s, (e) O 1s, and (f) F 1s of $\text{Ti}_3\text{C}_2\text{T}_x$ and 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$.

On the basis of the material characterizations and analysis, we confirmed that the hydrothermal process induced Ti oxidation and nitration, NH_4^+ intercalation and N doping between the $\text{Ti}_3\text{C}_2\text{T}_x$ layers. The incorporation of TiO_2 and TiN nanoparticles, the intercalation of NH_4^+ and N doping not only increased the surface areas of the N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ and enlarged interlayer space between the $\text{Ti}_3\text{C}_2\text{T}_x$ layers, but also provided additional diffusion paths for ionic migration. Therefore, the N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ are expected to have enhanced supercapacitive performances compared with $\text{Ti}_3\text{C}_2\text{T}_x$.

3.2. Electrochemical Properties

Enlightened by the advantageously structural features, N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ forebodes its potential application on supercapacitors. We conducted cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electric impedance spectroscopy (EIS) experiments in the three-electrode configurations to appraise the electrochemical performance of the $\text{Ti}_3\text{C}_2\text{T}_x$, 6 h, 12 h and 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$, which are labelled as 0 h, 6 h, 12 h and 20 h in Figures 7–10, respectively. A series of pre-experiments were performed to select a suitable potential range and an activated treatment after multiple cycles was needed to reach a steady state.

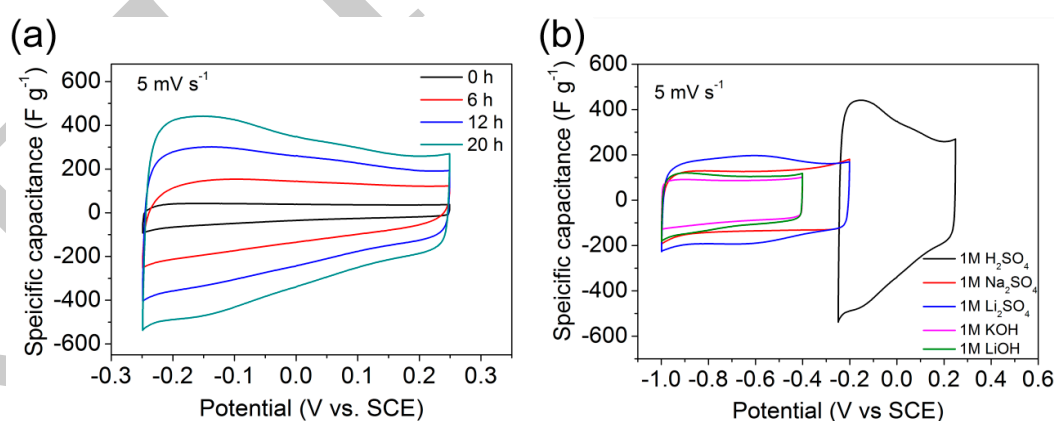


Figure 7. Electrochemical performance of $\text{Ti}_3\text{C}_2\text{T}_x$ and N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ electrodes in a three-electrode system. (a) CV profiles at 5 mV s^{-1} for N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ electrodes in 1 M H_2SO_4 . (b) CV profiles at 5 mV s^{-1} for 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ in different electrolytes.

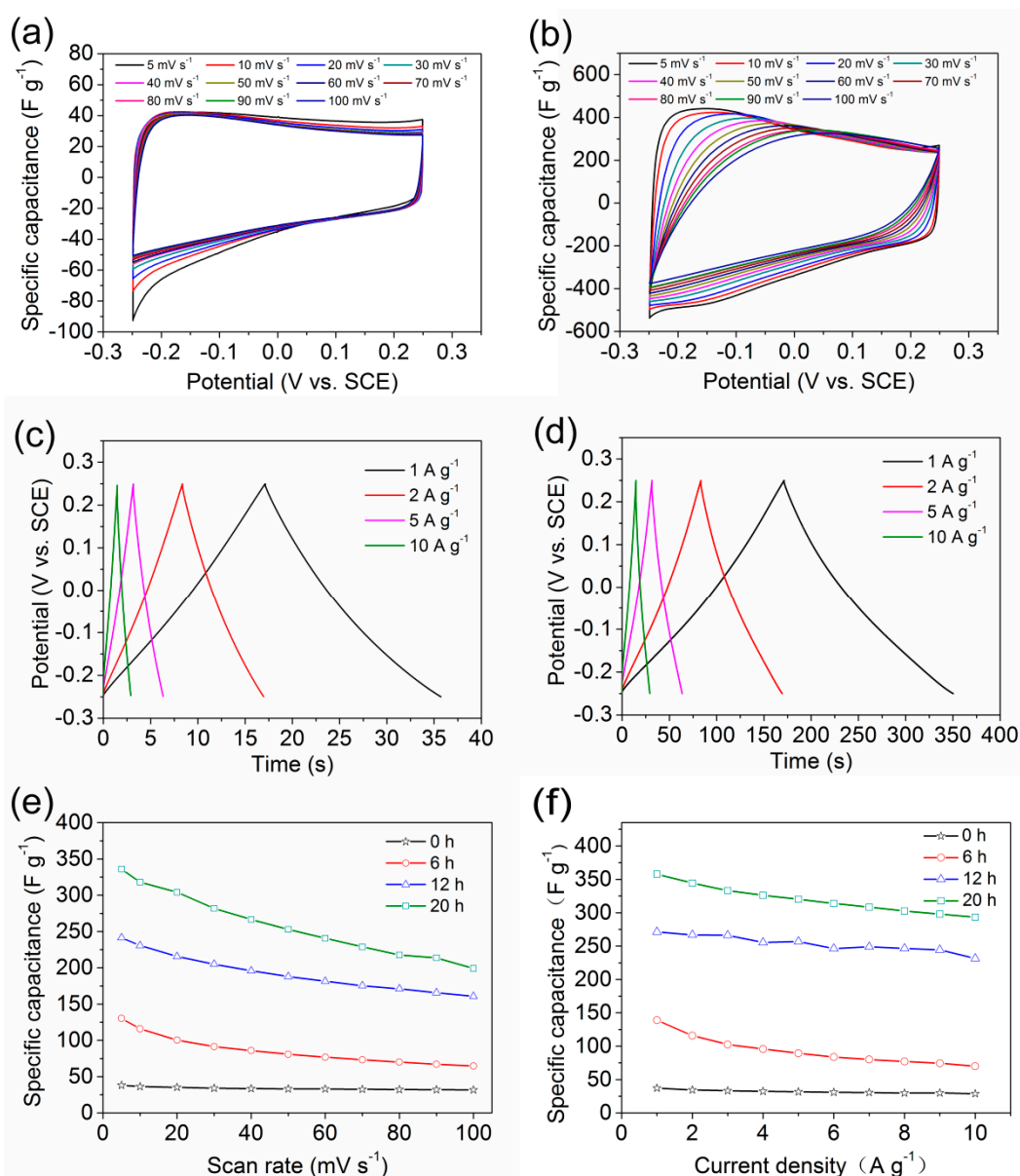


Figure 8. CV profiles of (a) $\text{Ti}_3\text{C}_2\text{T}_x$ and (b) 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ at different scan rates. The GCD curves for (c) $\text{Ti}_3\text{C}_2\text{T}_x$ and (d) 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ at current densities of 1, 2, 5, and 10 A g^{-1} . (e) Gravimetric specific capacitances at different scan rates. (f) Gravimetric specific capacitances at different current densities of $\text{Ti}_3\text{C}_2\text{T}_x$, 6 h, 12 h and 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ electrodes.

Figure 7a displays a comparison of the CV loops of $\text{Ti}_3\text{C}_2\text{T}_x$, 6 h, 12 h and 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ at a fixed scan rate of 5 mV s^{-1} with a potential window confined between -0.25 and 0.25 V in $1 \text{ M H}_2\text{SO}_4$ electrolyte. The capacitance contribution of conductive carbon paper can be negligible as shown in Figure S3. Apparently, regardless of $\text{Ti}_3\text{C}_2\text{T}_x$, all N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ CV profiles behave similarly and feature capacitance humps at potentials of -0.25 V to -0.1 V (vs. SCE). It is demonstrated that these humps derive from the combination of bonding/debonding of hydronium with the terminal oxygen in the $\text{Ti}_3\text{C}_2\text{T}_x$ electrode and the additional pseudocapacitive effect is related to valence change of Ti species [59]. Meanwhile, CV curves exhibit intuitive tendency that the integrated area augments with the increase of hydrothermal treatment time, in which the 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ possesses the largest integrated area among these electrodes. This significant improvement in gravimetric capacitance most likely originated from two reasons: (a) The increased specific surface areas and enlarged interlayer distance between $\text{Ti}_3\text{C}_2\text{T}_x$ layers improved the ion diffusion or the active site

accessibilities. (b) The replacement of N atoms and the formation of graphite carbon bring better electrical conductivity, which is favorable for rate performances [32].

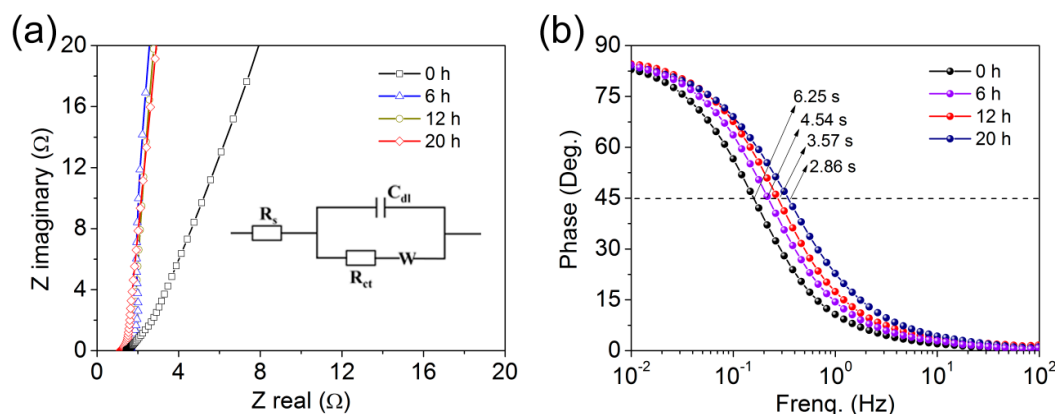


Figure 9. (a) Nyquist impedance spectra of different $\text{Ti}_3\text{C}_2\text{T}_x$ -based electrodes in magnified high-frequency region. (b) Bode plots of phase angle versus frequency. The inset of (a) is the corresponding equivalent circuit mode.

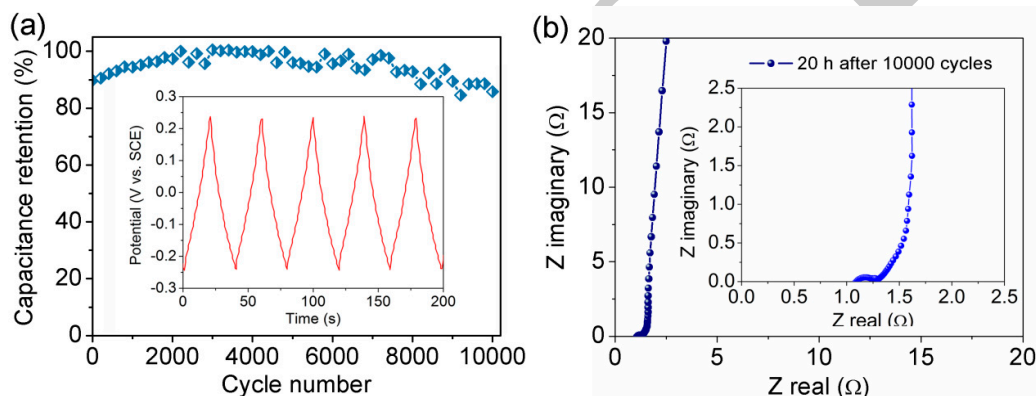


Figure 10. (a) Life cycle test in 1 M H_2SO_4 up to 10,000 cycles at the charge/discharge rate of 8 A g^{-1} . (b) Nyquist spectrum of 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ after 10,000 cycles. The insets are (a) the last five GCD cycling data at a current density of 8 A g^{-1} and (b) the magnified high-frequency region.

To shed light on the effects of cations diffusion, the influence of ionic radius in different electrolytes was investigated in Figure 7b. Clearly, the responses in the H^+ , Na^+ , Li^+ and K^+ ionic electrolytes were different, which means the cations rather than the anions were intercalating. The specific capacitances decrease in the order of H_2SO_4 , Li_2SO_4 , Na_2SO_4 , LiOH and KOH at the same scan rate of 5 mV s^{-1} , and the detailed CV and GCD profiles of $\text{Ti}_3\text{C}_2\text{T}_x$ and 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ electrodes in Li_2SO_4 , Na_2SO_4 , LiOH and KOH electrolytes are plotted in Figures S4 and S5, respectively. The 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ electrode in H_2SO_4 electrolyte delivered the best electrochemical performance among all the electrolytes in Figure 7b. The H_2SO_4 electrolyte possessed excellent conductivity and the H^+ , the smallest cations, might empower faster and easier surface redox reactions, which brought about greater contributions to intercalation-pseudocapacitance at the same scan rate. The intercalation/de-intercalation processes of H^+ are based on the following reactions [60–62].

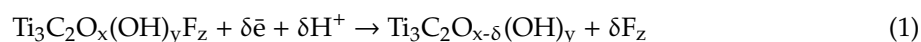


Figure 8a,b illustrate CV curves of $\text{Ti}_3\text{C}_2\text{T}_x$ and 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$ electrodes at scan rates from 5 to 100 mV s^{-1} , respectively. Figure 8a shows better symmetric properties than Figure 8b due to the reversible redox reaction which will affect the stability of the electrodes. However, the $\text{Ti}_3\text{C}_2\text{T}_x$ possesses smaller rectangular curves, corresponding to lower capacitances, while the 20 h N- $\text{TiO}_2/\text{TiN}/\text{Ti}_3\text{C}_2\text{T}_x$

exhibits superior capacitive performance. Across all scan rates, the CV curves of $\text{Ti}_3\text{C}_2\text{T}_x$ and 20 h N-TiO₂/TiN/Ti₃C₂T_x electrodes maintain similar shapes, which displays a slight shift of the anodic and cathodic peaks. The GCD curves of $\text{Ti}_3\text{C}_2\text{T}_x$ and 20 h N-TiO₂/TiN/Ti₃C₂T_x electrodes at current densities of 1, 2, 5, and 10 A g⁻¹ are shown in Figure 8c,d, respectively. All of the curves are nearly linear symmetrical and exhibit typical triangular shapes with inconspicuous voltage drops (iR drop) at different current densities, which indicates that the little overall resistance and excellent electrochemical reversibility are achieved.

Figure 8e,f compared the variation in specific capacitance as a function of scan rates and current densities of the $\text{Ti}_3\text{C}_2\text{T}_x$, 6, 12 and 20 h N-TiO₂/TiN/Ti₃C₂T_x electrodes, respectively. The detailed experiment data of 6 h and 12 h N-TiO₂/TiN/Ti₃C₂T_x electrodes are placed in Figure S6. From the CV plots, the 20 h N-TiO₂/TiN/Ti₃C₂T_x electrode shows enhanced capacitive performance of 336 F g⁻¹ at a scan rate of 5 mV s⁻¹ compared with $\text{Ti}_3\text{C}_2\text{T}_x$ electrode of 38 F g⁻¹ at the same scan rate. The pure $\text{Ti}_3\text{C}_2\text{T}_x$ are easy to agglomerate, impeding the ion transport. The $\text{Ti}_3\text{C}_2\text{T}_x$ electrode yields a similar specific capacitance to those HF etched $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes in the previous reports [63,64]. The specific capacitances calculated from GCD curves of the 20 h N-TiO₂/TiN/Ti₃C₂T_x electrode are 361, 343, 321, and 297 F g⁻¹ at 1, 2, 5 and 10 A g⁻¹, respectively. These results are mainly consistent with the order calculated by the CV curves. The decreasing trend in gravimetric capacitance suggests that parts of the electrode surfaces are inaccessible at higher charge/discharge rates.

Figure 9a records the Nyquist impedance of EIS spectra to investigate the ion-transport behavior and the internal resistance of the electrodes. The Nyquist plots are consisted of a high frequency semicircle and a low frequency linear branch, corresponding to charge transfer resistance R_{ct} and Warburg impedance W , respectively. Equivalent series resistances of $\text{Ti}_3\text{C}_2\text{T}_x$, and 6, 12 and 20 h N-TiO₂/TiN/Ti₃C₂T_x electrodes are found to be 1.43 Ω, 1.41 Ω, 1.38 Ω, and 1.13 Ω, respectively. It suggests that 20 h N-TiO₂/TiN/Ti₃C₂T_x electrode exhibits best conductivity because of its larger electroactive surface areas and lower charge transfer resistance [29]. Nyquist plots of 20 h N-TiO₂/TiN/Ti₃C₂T_x in different electrolytes are plotted in Figure S7. Figure 9b shows the Bode plots of all electrode materials. The phase angle of the 20 h N-TiO₂/TiN/Ti₃C₂T_x electrode is close to -83.0° at a frequency of 0.01 Hz, indicating that the capacitive performance of the electrode is close to that of an ideal capacitor. The characteristic frequencies, f_0 , for the phase angle of -45° are 0.16, 0.22, 0.28 and 0.35 Hz for the $\text{Ti}_3\text{C}_2\text{T}_x$, and 6 h, 12h, and 20 h N-TiO₂/TiN/Ti₃C₂T_x. The corresponding time constants τ_0 ($=1/f_0$) were calculated to be 6.25, 4.54, 3.57 and 2.86 s, respectively. The fast frequency response of 20 h N-TiO₂/TiN/Ti₃C₂T_x may owing to the nitrogen doping, which can enhance the electrolyte ion transport rates [65,66].

Electrochemical stability is one of the most important factors in practical application of pseudocapacitor electrodes. Figure 10a shows the GCD cycling stability of the 20 h N-TiO₂/TiN/Ti₃C₂T_x electrode at a current density of 8 A g⁻¹ along with the triangular shape of the last five GCD cycles in the inset of Figure 10a. It is found that above 85.8% of the capacitance remained after 10,000 cycles for the 20 h N-TiO₂/TiN/Ti₃C₂T_x electrode, possessing a prominent cycling stability. Nyquist plot of the 20 h N-TiO₂/TiN/Ti₃C₂T_x electrode after 10,000 charge/discharge cycles (Figure 10b) shows that the 20 h N-TiO₂/TiN/Ti₃C₂T_x electrode still maintains well low equivalent series resistance of 1.08 Ω. The above-mentioned results reveal that the 20 h N-TiO₂/TiN/Ti₃C₂T_x electrode is very stable and relatively invertible during cycling. Hence, it can be concluded that the 20 h N-TiO₂/TiN/Ti₃C₂T_x electrode is promising for supercapacitor application.

With the aim to assess the practical application of 20 h N-TiO₂/TiN/Ti₃C₂T_x, a symmetric supercapacitor was fabricated in 1 M H₂SO₄ aqueous electrolyte. The CV curves with the suitable potential window of 0–0.7 V from 5 to 100 mV s⁻¹ and the GCD profiles at current densities of 1, 2, 3, 4, 5 A g⁻¹ are plotted in Figure 11a and Figure S8, respectively. The Ragone plot, which is correlated containing/covering the energy density with power density, is depicted in Figure 11b. It can be seen that the symmetric supercapacitor cell delivers an energy density of 4.42 Wh kg⁻¹ at a power density of 1.14 kW kg⁻¹ and remains an energy density of 2.93 Wh kg⁻¹ at a high power density of 13.4 kW kg⁻¹.

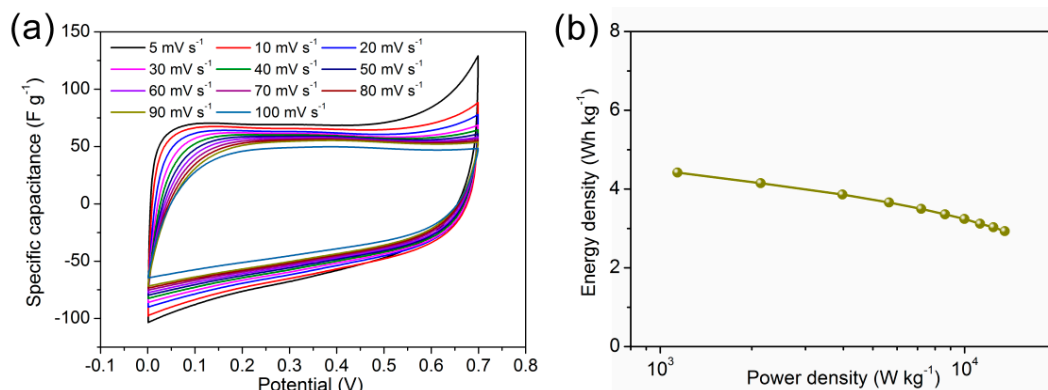


Figure 11. Electrochemical performance of the symmetric 20 h N-TiO₂/TiN/Ti₃C₂T_x//20 h N-TiO₂/TiN/Ti₃C₂T_x supercapacitor in 1 M H₂SO₄. (a) CV profiles at different scan rates under the potential of 0.7 V. (b) Power density versus energy density plot of the symmetric supercapacitor by CV test.

4. Conclusions

In summary, we reported a facile synthesis of nitrogen doped intercalation TiO₂/TiN/Ti₃C₂T_x via 6 h, 12 h and 20 h hydrothermal treatments of C₆H₁₂N₄ solution. TiO₂/TiN nanoparticles inserted between the Ti₃C₂T_x layers, which effectively prevent the self-restacking of Ti₃C₂T_x during fabrication and enable more pseudocapacitances. Moreover, benefiting from the introduction of nitrogen and the NH₄⁺ intercalation, the accessibility of the Ti₃C₂T_x layers to electrolyte ions is also enhanced. When employed as electrode materials for supercapacitors, the 20 h N-TiO₂/TiN/Ti₃C₂T_x electrode exhibited high performances with a specific capacitance of 361 F g^{−1} at 1 A g^{−1} and a capacitance retention of 85.8% after 10,000 charge/discharge cycles when used in a three-electrode configuration in 1 M H₂SO₄. Besides, the assembled symmetric supercapacitor delivered an energy density of 4.42 Wh kg^{−1} at a power density of 1.14 kW kg^{−1}. Furthermore, the influence of ionic radius in different electrolytes were studied by using H₂SO₄, Li₂SO₄, Na₂SO₄, LiOH and KOH electrolytes. The H₂SO₄ electrolyte possessed excellent conductivity and empowered faster and easier surface redox reactions, which brought about greater contributions to intercalation-pseudocapacitance. The excellent electrochemical performance could be attributed to the unique architecture with physical confinement preventing the restacking of Ti₃C₂T_x, and the minimized pass path between electrolyte and electrodes. This facile synthesis paves a new strategy to achieve promising pseudocapacitance MXene electrode materials in practical applications.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2079-4991/10/2/345/s1>, Figure S1: XRD patterns of Ti₃C₂T_x and 6 h, 12 h, 20 h N-TiO₂/TiN/Ti₃C₂T_x, Figure S2: High-magnification SEM images of pristine Ti₃AlC₂, Figure S3: CV curves at scan rate of 50 mV s^{−1} of conductive carbon paper, Figure S4: CV and GCD curves of Ti₃C₂T_x in different electrolytes of (a,b) Na₂SO₄, (c,d) Li₂SO₄, (e,f) KOH and (g,h) LiOH, Figure S5: CV and GCD curves of 20 h N-TiO₂/TiN/Ti₃C₂T_x in different electrolytes of (a,b) Na₂SO₄, (c,d) Li₂SO₄, (e,f) KOH and (g,h) LiOH, Figure S6: CV and GCD curves of (a,b) 6 h, (c,d) 12 h N-TiO₂/TiN/Ti₃C₂T_x in H₂SO₄ electrolyte, Figure S7: Nyquist plots of 20 h N-TiO₂/TiN/Ti₃C₂T_x in different electrolytes. 1 M H₂SO₄ have lower resistance of the bulk electrolyte solution compared with Na₂SO₄, Li₂SO₄, KOH and LiOH, Figure S8: GCD plots at different current densities of the symmetric 20 h N-TiO₂/TiN/Ti₃C₂T_x//20 h N-TiO₂/TiN/Ti₃C₂T_x supercapacitor in 1 M H₂SO₄.

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Conflicts of Interest: The authors declare no conflict of interest.

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