Supporting Information

The Synthesis and Supercapacitor Application of Flexible Free-Standing $Ti_3C_2T_x$, $Mo_2TiC_2T_x$, and $V_4C_3T_x$ MXene Films

Xiaoqing Bin [#, 1], Minhao Sheng [#, 1], Binshan Kong[1], Yijia Luo[1], Jing Xiao [2], and Wenxiu Que[*, 1]

[1]*Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, International Center for Dielectric Research, Shaanxi Engineering Research Center of Advanced Energy Materials and Devices, School of Electronic Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China*

[2] *College of Physics and Electronic Engineering, Taishan University, Taian, Shandong 271000, People's Republic of China*

[*] Email address: wxque@xjtu.edu.cn (W. Que), [#]These authors contributed equally to this work.

Physical Characterizations: The X-ray diffraction (XRD) patterns of the as-prepared samples were measured by Rigaku D/max 2200pc diffractometer with Cu Kα radiation (λ = 1.5406 Å) in a 2θ angular range of 3-80°. The morphological properties of the samples were observed by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800 and FEI company Tecnai G220 S-twin) and transmission electron microscopy (TEM) coupled with elemental mapping. The element compositions and valence states of the samples were characterized by X-ray photoelectron spectroscopy (XPS, VG Thermo ESCALAB 250 spectrometer) with an Al Kα X-ray radiation.

Electrochemical Measurements: The electrochemical performances of the electrodes were tested in a three-electrode system using a CHI 660E electrochemical workstation, and the temperature change test was carried out in a thermostat (SPX-150 B I). The MXene films were used as the working electrode, and the activated carbon (AC) films were used as the counter electrode. Considering that H_2SO_4 (acidic), KOH (alkaline) and Na_2SO_4 (neutral) electrolytes were selected, hence, different reference electrodes were also used to obtain ideal electrochemical data. That is, when the electrolyte was acidic (3 M H_2SO_4) solution, Hg/Hg_2SO_4 was selected as the reference electrode. When the electrolyte was alkaline (3 M KOH) solution, Hg/HgO was selected as the reference electrode. When the electrolyte was neutral (3 M Na_2SO_4) solution, Ag/AgCl was selected as the reference electrode. Thus, the electrochemical behaviors of the electrodes were explored by CV, GCD and other test methods. In addition, the Landian CT2001A tester was used to evaluate the long cycling stability of the electrode material.

Preparation of working electrode (negative electrode): A certain volume of delaminated MXene (d-$Ti_3C_2T_x$, d-$Mo_2TiC_2T_x$, d-$V_4C_3T_x$) suspension was filtered on mixed cellulose ester (MCE) membrane (Φ50 mm, 0.22 μm pore size), and then the delaminated MXene nanosheets were self-assembled into a flexible and free-standing films. After being dried in a vacuum oven for 12 h, the MXene films were peeled off from the MCE membranes, and the film electrodes of three types of MXenes were prepared as shown in Figure 1. Finally, the MXene films were punched into Φ0.54 mm small films by punching machine, which is used as the working electrode in the three-electrode system (as the negative electrode in the device). The masses of the d-$Ti_3C_2T_x$, d-$Mo_2TiC_2T_x$, and d-$V_4C_3T_x$ electrodes are about 0.42 mg, 0.32 mg, and 0.25 mg, respectively.

Preparation of the counter electrode: Firstly, the pre-mixed slurry was prepared by 95 wt% of the activated carbon (YP-50F), 5 wt% of polytetrafluoroethylene (PTFE) binder (50 wt% in ethanol).

Then, the slurry was then rolled into flat film using a glass cylinder. The next step was to put it in a vacuum oven at 60°C for 12 h. Lastly, the activated carbon film with a diameter of 5.4 mm (counter electrode) was obtained using a hole punch.

Preparation of the positive electrode: It should be mentioned here that in order to match the charge with the negative electrode, the quality of the activated carbon needs to be precisely controlled. Firstly, the pre-mixed slurry was prepared by 95 wt% of the activated carbon (YP-50F), 5 wt% of polytetrafluoroethylene (PTFE) binder (50 wt% in ethanol). Then, the as-prepared slurry was coated on carbon cloth (Φ 5.4 mm in diameter) to prepare positive electrode. Finally, it was dried in a vacuum oven at 60°C for 12 h.

Device assembly and Calculation

Gravimetric capacitance (C_g, F g^{-1}) of the working electrode in the three-electrode system can be calculated by the following formula:

$$C_g = \int I \, dV / (2 \, m \, s \, \Delta V)$$

where I (A) is the applied current of the CV curve, s (V s^{-1}) is the scan rate, ΔV (V) is the potential window, and m (g) is the mass of the working electrode (the film wafer).

A two-electrode cell was set up to evaluate the electrochemical performance of supercapacitor devices in 3 M H_2SO_4 electrolyte. The symmetric supercapacitor (SSC) was assembled by two identical MXene films separated by a fiberglass membrane. The asymmetric supercapacitor (ASC) was assembled by using AC as the positive electrode and MXene films as the negative electrode. The conditions of electrochemical test were the same as those of the three-electrode system. Differently, potential window of the test was from 0 V to 0.6 V for SSC, and from 0 V to 1.4 V for ASC. In addition, prior to the assembly of the MXene // AC ASC, the mass loading of the positive and negative electrodes was balanced based on the following formula:

$$m_+/m_- = C_{s+}/C_{s-}$$

where m_+ and m_- are the masses of the film or active material (g), and C_{s+} and C_{s-} are the specific capacitances (F g^{-1}) of the positive and negative electrodes, respectively.

Gravimetric capacitance, $C_{g,c}$ (F·g^{-1}), of the supercapacitor was calculated by the following formula:

$$C_{g,c} = \int I \, dV / (2 \, m_c \, s \, \Delta V),$$

where m_c (g) is the total mass of electrodes for the supercapacitors.

Energy density (E) and power density (P) of the symmetric supercapacitor can be calculated via the following equations:

$E_g = 1/2\ C_{g,c}\ \Delta V^2$

$P = 3600\ E/\Delta t$,

where ΔV is the voltage range of one sweep segment and Δt is the time for a sweep segment.

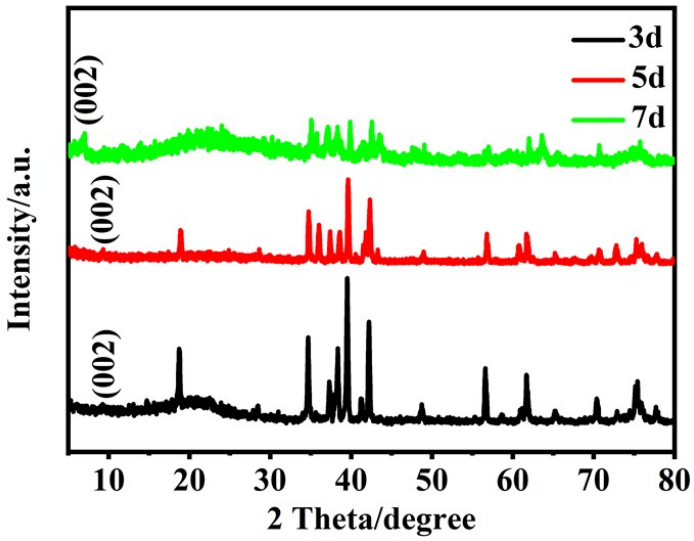

Fig. S1. XRD patterns of multilayer $Mo_2TiC_2T_x$ MXene in different etching days.

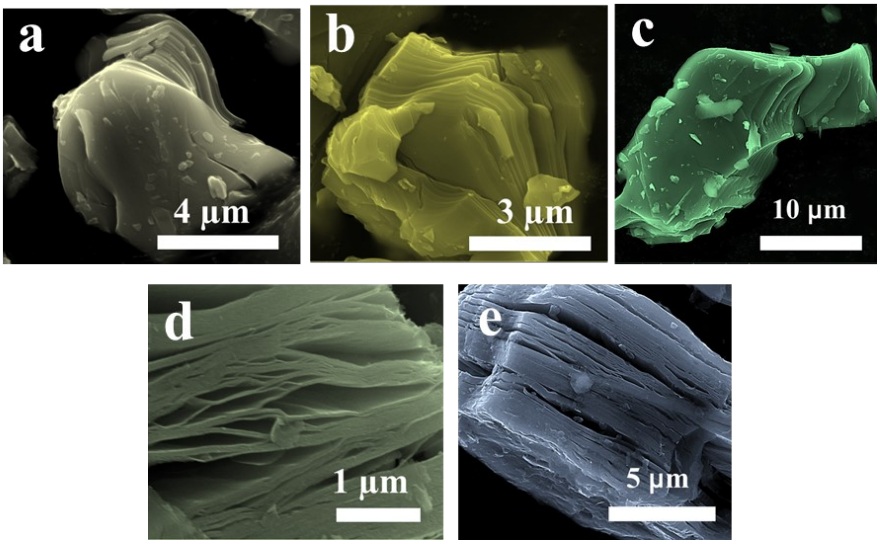

Fig. S2. (a) SEM images of (a) Ti_3AlC_2, (b) Mo_2TiAlC_2, (c) V_4AlC_3, (d) multilayer $Mo_2TiC_2T_x$, and (e) multilayer $V_4C_3T_x$.

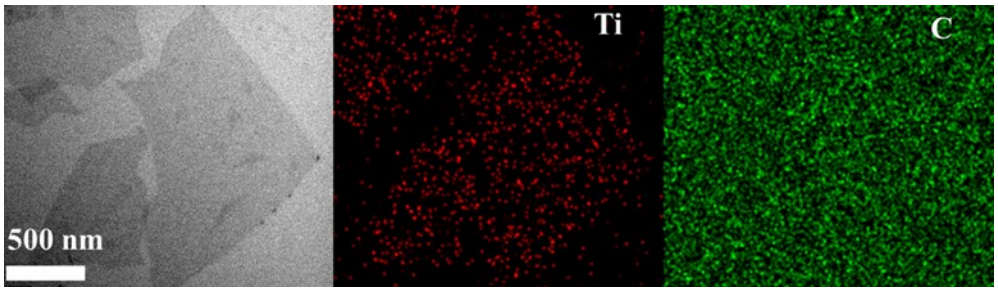

Fig. S3. EDS elemental mappings of d-$Ti_3C_2T_x$ MXene.

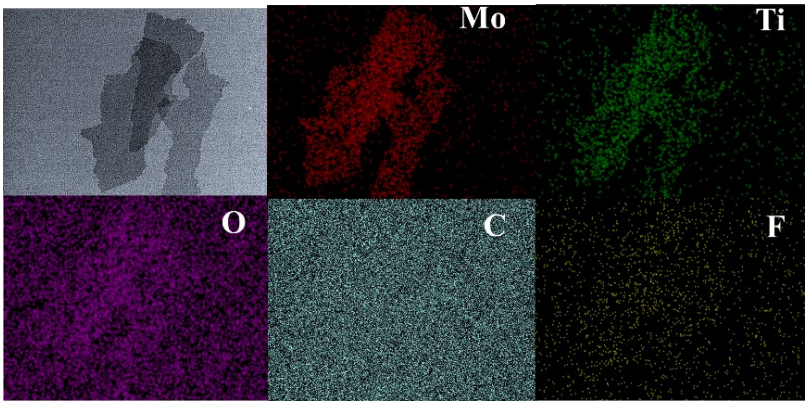

Fig. S4. EDS elemental mappings of d-$Mo_2TiC_2T_x$ MXene.

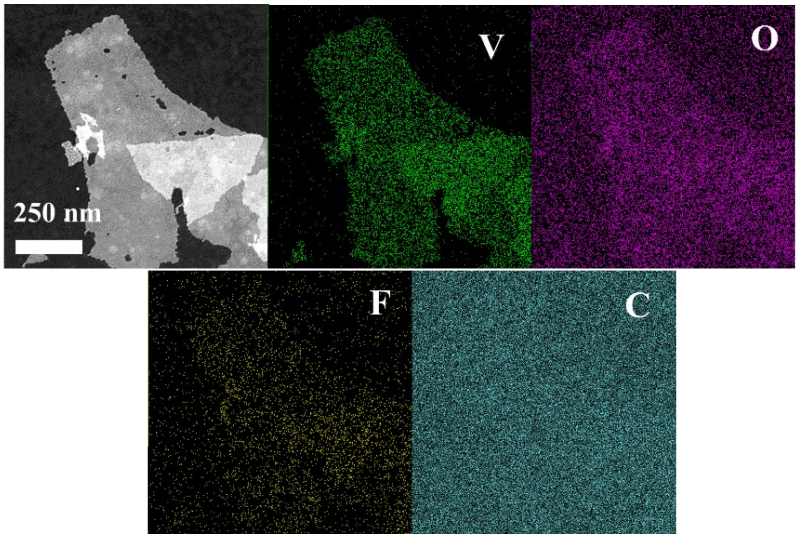

Fig. S5. EDS elemental mappings of d-$V_4C_3T_x$ MXene.

The 1st day The 10th day The 20th day

Fig. S6. The stability test for d-$V_4C_3T_x$ MXene nanosheets at room temperature.

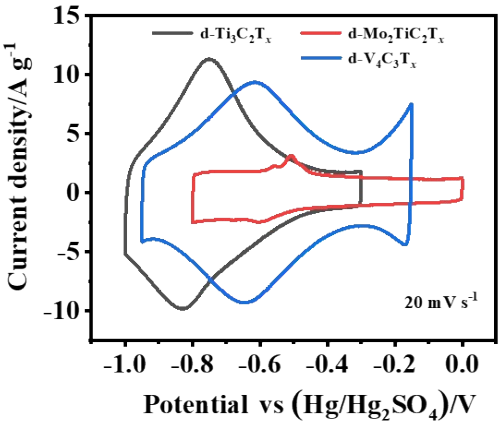

Fig. S7. The cyclic voltammetry (CV) curves for three types of MXenes at 20 mV s^{-1} in 3 M H_2SO_4.

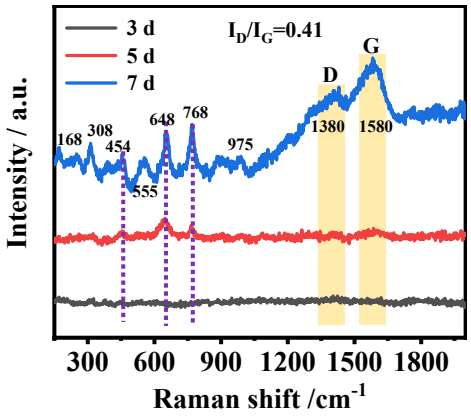

Fig. S8. Raman spectrums of multilayer $Mo_2TiC_2T_x$ MXene in different etching days.

A Raman study for multilayer $Mo_2TiC_2T_x$ MXene in different etching days was performed, as shown in Fig. S8. In Raman spectroscopy, the characteristic peaks of MXene typically appear in the 100-1000 cm^{-1} range.[1] For the multilayer $Mo_2TiC_2T_x$ MXene etched for three days (3 d), no characteristic peaks were observed. However, the multilayer $Mo_2TiC_2T_x$ MXene etched for five days (5 d) exhibited partial characteristic peaks of the $Mo_2TiC_2T_x$ MXene (454 cm^{-1}, 648 cm^{-1}, and 768 cm^{-1}). Only the multilayer $Mo_2TiC_2T_x$ MXene etched for seven days (7 d) displayed the complete characteristic peaks of the $Mo_2TiC_2T_x$ MXene (168 cm^{-1}, 308 cm^{-1}, 454 cm^{-1}, 555 cm^{-1}, 648 cm^{-1}, 768 cm^{-1}, and 975 cm^{-1}), also, obvious D and G characteristic peaks (1380 cm^{-1}, and 1580 cm^{-1}) appeared, with an intensity ratio of (I_D/I_G) 0.41. The D peak reflects the carbon defects in the lattice, while the G peak reflects the graphitization degree of the material. A higher intensity ratio of the D peak to the G peak indicates a greater number of defects in the carbon atomic crystal. The Raman results suggest that the multilayer $Mo_2TiC_2T_x$ MXene etched for seven days (7 d) exists partial carbon defects and over-etching.

Table S1. Performance comparison of d-$V_4C_3T_x$ and d-$Nb_4C_3T_x$ electrodes

Electrodes	interlayer spacing	Electrolyte	Potential window	Specific capacitance	Rate performance	Cycling stability	Flexible film	Refs.
d-$V_4C_3T_x$	**2.10 nm**	**3 M H_2SO_4**	**-0.95 ~ -0.15 vs (Hg/Hg_2SO_4)/ V**	**292.0 F g^{-1} at 2 mV s^{-1}**	**86.0% @ 200 mV s^{-1}, 78.4% @ 500 mV s^{-1}.**	**40000 (93.1%)& 60000 (82.9%).**	**Yes**	**This work**
d-$Nb_4C_3T_x$	1.77 nm	1 M H_2SO_4	-0.9 ~ 0.1 vs (Ag/AgCl)/V	275.0 F g^{-1} at 5 mV s^{-1}	27.3% @ 100 mV s^{-1}	5000 (76.1%)	Yes	[2]

Table S2. The specific capacitances of different MXenes at different temperatures

	d-$Ti_3C_2T_x$ (F g^{-1})			d-$Mo_2TiC_2T_x$ (F g^{-1})			d-$V_4C_3T_x$ (F g^{-1})		
0°C	255.6	250.6	260	70.0	79.6	80	270.0	274.9	279.0
20°C	260.0	263.5	270	79.6	83.1	85	288.1	290.5	310.3
40°C	268.0	286.6	290	90.4	105.7	103	300.4	320.5	333.8

References

1. Hu M, Zhang H, Hu T, et al. Emerging 2D MXenes for supercapacitors: status, challenges and prospects[J]. Chem Soc Rev, 2020, 49(18): 6666-6693.
2. S. Zhao, C. Chen, X. Zhao, X. Chu, F. Du, G. Chen, Y. Gogotsi, Y. Gao and Y. Dall'Agnese, *Advanced Functional Materials*, 2020, **30**, 2000815.