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The fabrication of Ti_3C_2 and Ti_3CN MXenes by electrochemical etching†

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2D MXenes are well-known for their outstanding performance in electrochemical energy storage and many other applications owing to their high conductivity and specific surface area. An obstacle to the wider synthesis of MXenes for research and industrial applications is the use of hazardous hydrofluoric acid (HF) during their synthesis. Herein, we developed the electrochemical etching process for the synthesis of Ti_3C_2 and Ti_3CN MXenes by using aqueous tetrafluoroboric acid as the electrolyte, thus only involving a very low concentration of HF. The effect of electrical potential and temperature on the etching rate is studied and compared to chemical etching with HBF_4 . A mechanism based on the selective anodic dissolution of aluminium from Ti_3AlC_2 and Ti_3AlCN with the tetrafluoroborate ion is proposed. The MXene formation was confirmed by Raman spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction and electron microscopy. The MXene flakes from the electrochemical etching process have larger lateral dimensions compared to chemically etched MXene flakes as a result of the suppression of the HF decomposition and rapid etching rate. The electrodes of lithium-ion supercapacitors made from electrochemically etched Ti_3C_2 and Ti_3CN exhibited cycle performance and rate capabilities comparable to HF-etched MXenes.

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1. Introduction

MXenes, two-dimensional transition metal carbides, nitrides, and carbonitrides, have received a tremendous amount of research attention since its discovery in 2011.¹ The high specific surface area, hydrophilicity, conductivity, and mechanical strength of MXenes make them promising for applications including energy storage,^{2–7} electromagnetic interference shielding,^{8–10} and catalysis.¹¹ MXenes can be described as a hexagonal close packed structure with the composition $\text{M}_{n+1}\text{X}_n\text{T}_x$ ($n = 1$ to 4; where M is an early d block transition metal; X is carbon or nitrogen; T is surface terminal groups such as =O, –OH, –Cl, and –F, depending on the chemical etchant).¹² Terminal group free MXenes ($\text{M}_{n+1}\text{X}_n\text{T}_0$) are determined to have D_{3d} symmetry.¹³ However, the presence of the terminal groups distorts the symmetry of the unit cell. Hence, the literature generally refers to the unit cell of $\text{M}_{n+1}\text{X}_n\text{T}_0$ as pseudo- $P6_3/mmc$.¹⁴

MXenes are fabricated from corresponding MAX phases with the chemical composition of $\text{M}_{n+1}\text{AX}_n$, where A is either group 3 or 4 elements (*e.g.*, Al, Ga, Si) lying between the MXene layers.^{15–18} MXenes have very diverse chemical compositions due to the different combinations of M, A, and X elements. To date, more than 50 MXenes have been reported to be successfully synthesised.¹² The family of MXenes is further expanded when two transition metals are mixed in an MXene structure, in which the transition metal atoms may either be arranged randomly across all the M layers, or they may form ordered structures.^{19–21} Given that the ratio of M and X in these double transition metal MAX precursors can be controlled as needed, the number of possible MXenes can be limitless.

Conventionally, the synthesis of MXene requires the use of hydrofluoric acid, either on its own or mixed with other acids (*e.g.*, HCl, H_2SO_4),^{1,17,18,22,23} or the use of reagents that release HF *in situ* (*e.g.*, LiF + HCl, known as the MILD approach, and NH_4HF_2) to remove the A layer from the MAX precursor.^{24–26} However, HF is extremely hazardous to humans and the environment. Furthermore, the aggressiveness of HF causes unavoidable damage to the basal plane of the MXene layer, resulting in a small flake size of the delaminated MXenes. A few hydrothermal approaches have been reported to etch the MAX phase to MXene. Gentile *et al.* reported the hydrothermal etching of Ti_3C_2 using HBF_4 as an etchant.²⁷ Yet, the etching mechanism was still based on the decomposition of HBF_4 to HF upon heating to 60 °C. Another example, inspired by the Bayer process used in bauxite refining for the isolation of aluminium

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oxide,²⁸ is a fluorine-free synthesis of $\text{Ti}_3\text{C}_2\text{T}_x$ *via* alkali treatment reported by Li *et al.*, which involves the use of 27.5 M of NaOH at 270 °C for 12 hours.²⁹ Peng *et al.* reported a hydrothermal etching of MAX phases (Ti_3AlC_2 and Nb_2AlC) by 12 M HCl and 0.5 M NaBF_4 for up to 32 hours at 180 °C.³⁰ Alternatively, non-aqueous approaches such as molten salt and halogen etching have also been reported.^{31–36} However, the abovementioned approaches require harsh reaction conditions, making them costly and difficult to scale up. They may also damage, oxidise or hydrolyse MXene nanosheets.

Amongst all other approaches, electrochemical etching of MAX phases is particularly promising. Electrochemical fabrication of 2D materials is well studied for graphene, 2D- MoS_2 , and mono-elemental Xenes.^{37,38} In van der Waals solids, upon applying electrical potential, the ion intercalation or gas evolution between the 2D material layers causes the interlayer spacing to expand, overcoming the van der Waals forces and ultimately exfoliating the bulk layered material into its 2D form. The major advantage of electrochemical exfoliation is its environmental friendliness. Using graphene as the example, electrochemical exfoliation involves milder chemicals as the electrolyte (*e.g.*, Na_2SO_4 or other sulfate salts) in contrast to the Hummers' method (concentrated H_2SO_4 and H_3PO_4 in combination with KMnO_4).^{39,40} Despite the success of electrochemical exfoliation in the synthesis of graphene and other 2D materials, there are very few reports on the electrochemical fabrication of MXenes. The main obstacle originates from the unique interlayer interaction of the MXene layer in the MAX phase precursor. Unlike other bulk laminated materials, the M–A–M chemical bonding between the MXene layers in the bulk MAX phase precursor is significantly stronger than the physical van der Waals force between the layers in graphite. Thus, the electrochemical exfoliation processes need to chemically selectively etch the A layer in addition to expanding the interlayer distance. Furthermore, unlike the carbon in the strong sp^2 -hybridised framework in graphene, the transition metal in MXenes is prone to oxidize if the voltage applied is over its oxidation potential (*c.f.* for the anodic exfoliation of graphite, a voltage of up to +10 V can be applied).³⁹ Nonetheless, since the semi-covalent M–X bond is more thermodynamically stable than the weakly metallic M–A and A–A bonds, the selective oxidation of the A element is feasible under suitable conditions. The electrochemical etching of MAX phases has been reported using various types of HCl, NaCl, LiTFSI, and $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ electrolytes.^{41–46} However, the MXenes synthesised in those studies were mixed with carbide-derived carbon. This suggests that those electrolytes do not entirely remove the carbide generated during etching. Furthermore, the reaction setups reported in the literature are not scalable; working electrodes comprise MAX phases of ceramic pieces produced by cutting the ceramic or pressing the MAX phase powders into pellets.^{43,45,46} However, the rate of the reaction would unavoidably be hindered by the limited surface area of the electrode. There are also reports of depositing MAX phase powders onto conductive material (*e.g.*, carbon fiber clothes).^{42,44} However, a binder is needed to ensure good contact. Furthermore, the use of CFC and the MXene produced *via* this method is always

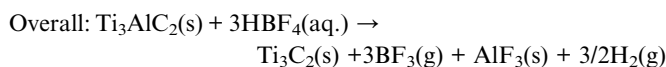
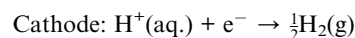
mixed with the fiber residues caused by carbon fiber destruction during the washing process.

Herein, we report a low-HF synthesis of Ti_3C_2 and Ti_3CN MXenes *via* electrochemical etching, using HBF_4 as the electrolyte. The proposed mechanism allows the Ti_3AlC_2 and Ti_3AlCN precursors to undergo selective anodic dissolution of aluminium with the tetrafluoroborate ion. With the addition of the etching pathway provided by the presence of electrical potential, the etching of MXene is quicker and occurs at a lower temperature, minimising the release of HF. The role of electrical potential in accelerating the etching was studied. Furthermore, the influence of temperature for both electrochemical and chemical etching with HBF_4 was studied. As a result of the suppression of HF decomposition and etching time, the electrochemically etched MXene exhibits a larger lateral size compared to the MXene produced by chemically etching in HF or HBF_4 . The energy storage performance of the electrochemically etched Ti_3C_2 and Ti_3CN in lithium-ion batteries is tested and mimics the superior cycle performance and rate capabilities of chemically etched MXene. The electrochemically etched Ti_3C_2 and Ti_3CN anodes exhibit superior cycle performance and rate reversibility for lithium-ion supercapacitors. For clarification, the electrochemically etched Ti_3C_2 , Ti_3CN and MXene will be labeled EE- Ti_3C_2 , EE- Ti_3CN , and EE-MXene, respectively. MXenes that are chemically etched by HBF_4 will be labeled CE-MXene. MXene etched by HF and HCl will be labeled HF/HCl-MXene.

2. Results and discussion

2.1 Mechanism

Fig. 1a schematically shows the setup of the reaction. A graphite crucible was used as the reaction container and the current collector for the MAX phase powder. This approach allowed the etching of the MAX phase in its powder form without using a binder, as all MAX phase particles settled at the bottom of the graphite crucible during the etching process. Pt wire was used as the cathode. However, it is worth mentioning that the etching can also be carried out with graphite as the counter electrode, which suggests that the hydrogen evolution does not have to occur on the surface of platinum. For the electrochemical etching, the mechanism was proposed as follows:



The anodic polarisation of the MAX phase triggers the dissolution of aluminium accompanied by the release of BF_3 gas, whilst a proton is reduced to hydrogen gas on the surface of the cathode. Note that +1 V was applied to all electrochemical etching to minimize the oxidation of the MXene. The initial concentration of HBF_4 in both electrochemical and chemical etching was 24%.



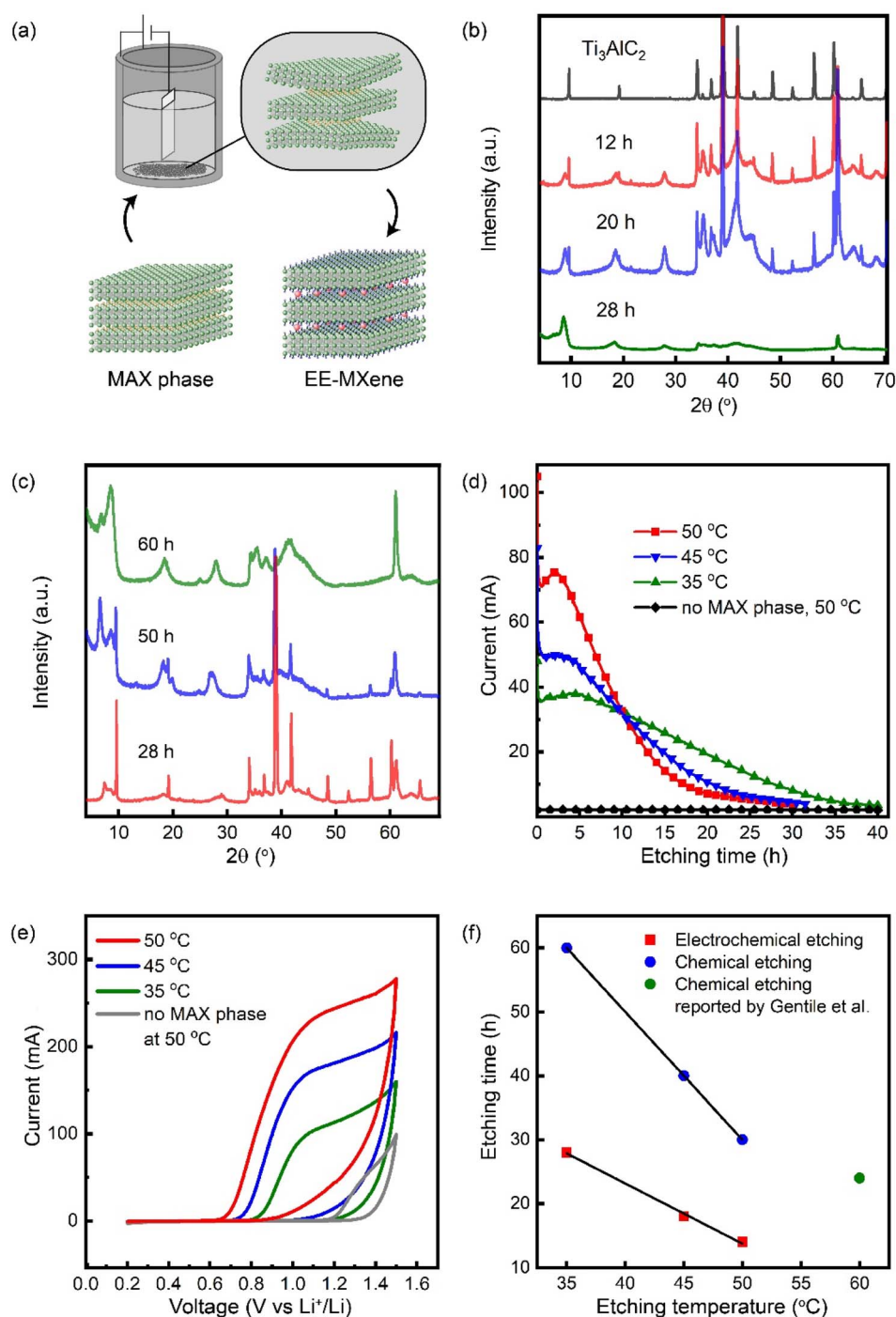


Fig. 1 (a) Schematic illustration of the setup. (b) XRD of EE- Ti_3C_2 etched with an applied voltage of +1 V at 35 °C with different etching times. (c) XRD pattern of CE- Ti_3C_2 at 35 °C with different etching times. (d) Amperometric monitoring of the electrochemical etching of EE- Ti_3C_2 at various temperatures. (e) Cyclic voltammogram of 1 g of Ti_3AlC_2 at various temperatures. Scan rate: 10 mV s^{-1} . (f) Etching time required to completely etch Ti_3AlC_2 to Ti_3C_2 by electrochemical etching and electrochemical etching at various temperatures.

2.2 XRD analysis

Fig. 1b gives the XRD pattern of the electrochemically etched Ti_3C_2 and shows the change of the crystal lattice upon etching the MAX phases to give MXene. Upon electrochemically etching with HBF_4 for 28 hours at 35 °C, the (002) peak of the Ti_3AlC_2 precursor at 9.52° was shifted to 8.63° . According to Bragg's law

and the reciprocal-space metric tensor equation of hexagonal crystal lattices, this corresponds to a change of d -spacing from 9.31 Å to 10.26 Å, equivalent to a change of c -LP from 18.62 Å to 20.52 Å. The increased interlayer spacing was also accompanied by an increase of FWHM from 0.10 to approximately 0.6, which is attributed to the decrease of crystallinity upon the removal of

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HF. Compared to solely chemical etching with HBF_4 , the extra reaction pathway provided by the electrochemical etching is concluded to be the main reason for the increased efficiency of etching at low temperatures. In addition, the electrolyte residue after electrochemical etching was dried by heating in a PTFE beaker. A white precipitate was formed after all the HBF_4 residue was evaporated. The FTIR spectrum of the white precipitate corresponded to aluminium oxide, further confirming the anodic dissolution of aluminium during the etching (Fig. S2†).

Fig. 2a shows the Raman spectra of the EE- Ti_3C_2 and EE- Ti_3CN and their MAX phase precursors. For EE- Ti_3C_2 that has undergone completed etching, peaks at 202 and 661 cm^{-1} originating from the A_{1g} (Ti, Al, C, O, F) and C (A_{1g}) modes of Ti_3AlC_2 MAX phases are no longer observable. Conversely, new peaks were detected at 210 and 727 cm^{-1} corresponding to the A_{1g} (Ti, C, O, F) and C (A_{1g}) modes of EE- Ti_3C_2 . A broad peak was detected from 230 to 470 and 580 to 730 cm^{-1} , the literature attributes the region of this peak to the in-plane vibration of the terminal group on the MXene surface.¹³ The peak at around

123 cm^{-1} is the resonant peak which is only detected when an excitation wavelength of 785 nm is used. For EE- Ti_3CN , the A_{1g} (C, N) peak appeared at 714 cm^{-1} . However, the A_{1g} (Ti, C, N, O, F) and A_{1g} (Ti, C, Al, N) peaks were not observed. This might be attributed to the peak broadening induced by the random arrangement of carbon and nitrogen atoms in the X plane. No peak was observed in the carbon region, suggesting that the EE-MXene is free from carbide-derived carbon.

X-ray photoelectron spectroscopy was performed to probe the composition and the oxidation state of the element. The wide scan of the EE-MXene can be found in Fig. 2b. High-resolution core-level scans were performed to get an insight into the oxidation state of each element. Upon successful etching, no Al_{2p} signal was detected for the EE-MXene. In terms of the termination group introduced during the etching, both fluorine and oxygen were detected. No boron was detected in all the etched samples, indicating that no Ti-O- BF_3 terminal groups were introduced. EE-MXene has a higher binding energy for the Ti 2p signal compared to its MAX phase precursor, as the aluminium in the MAX phases is substituted by O and F atoms,

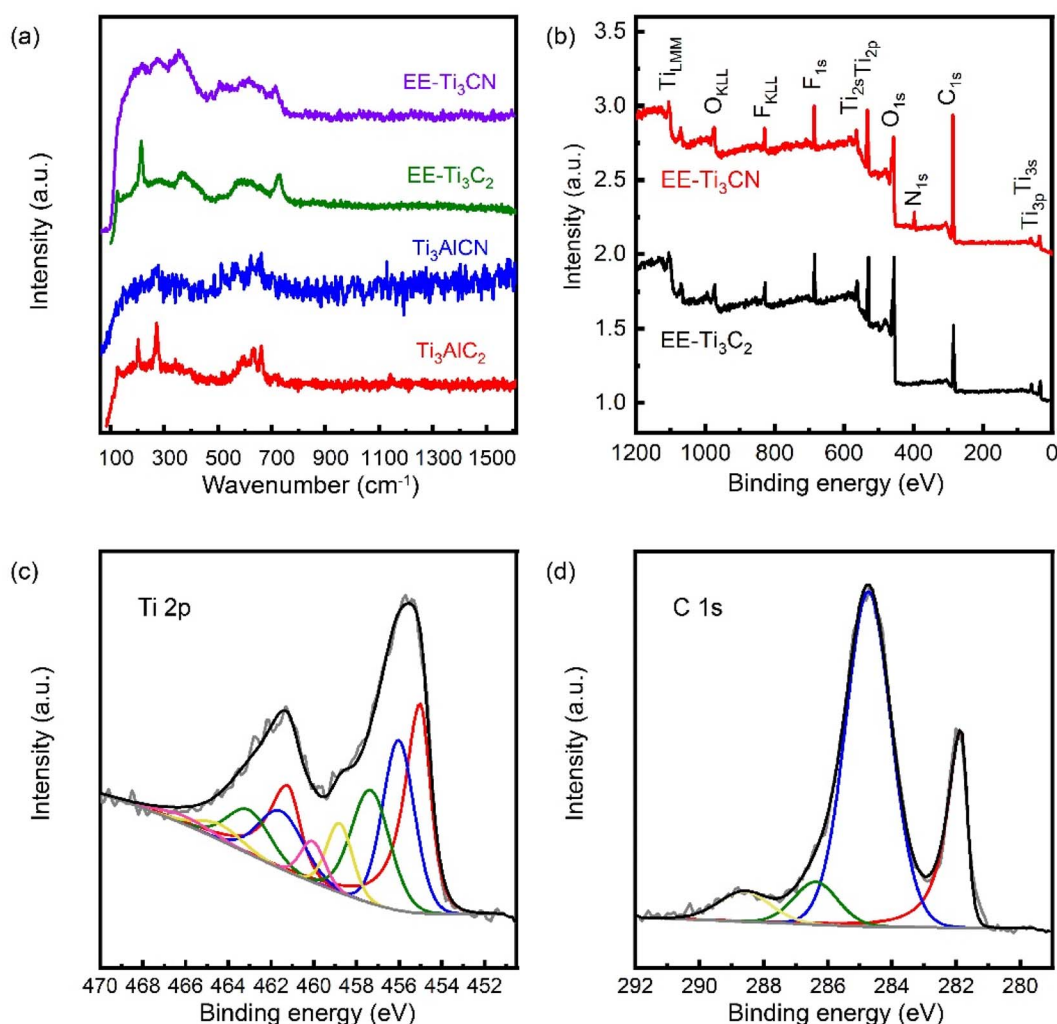


Fig. 2 (a) Raman spectrum of the EE- Ti_3C_2 , EE- Ti_3CN , Ti_3AlC_2 , and Ti_3AlCN . Excitation wavelength: 785 nm. (b) XPS survey spectrum of EE- Ti_3C_2 and EE- Ti_3CN . (c) XPS Ti 2p spectrum of EE- Ti_3C_2 . (d) XPS C 1s spectrum of EE- Ti_3C_2 .



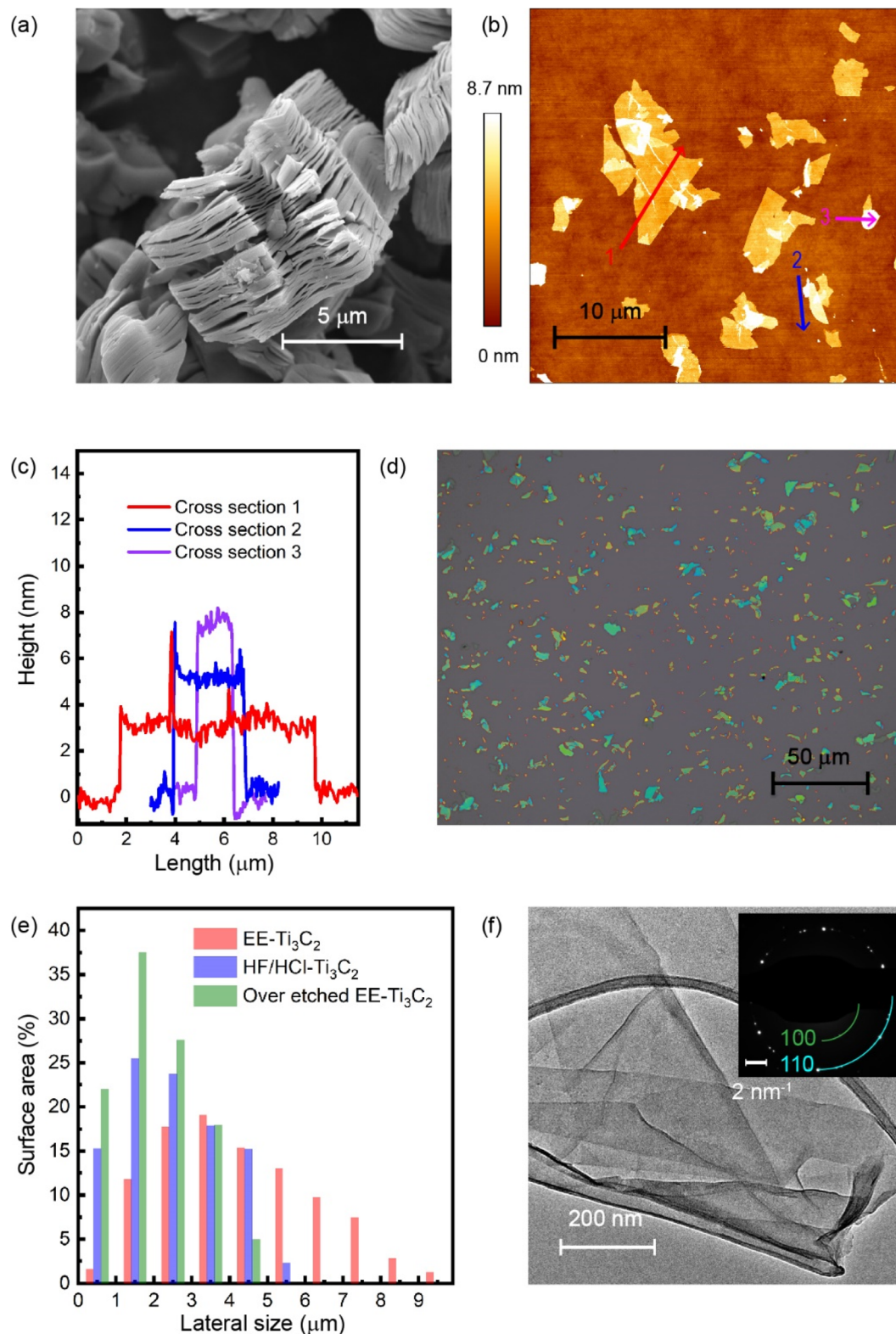


Fig. 3 (a) SEM image of EE-Ti₃C₂ multilayer powder. (b and c) AFM images and the cross-section of the delaminated EE-Ti₃C₂ flake. (d and e) Optical images of delaminated EE-Ti₃C₂. (d and e) Lateral size distribution of delaminated EE-Ti₃C₂ and HF/HCl-Ti₃C₂ flake. Overlapped flakes were excluded to avoid incorrect estimations. (f) TEM image of delaminated EE-Ti₃C₂ flake.

observed as follows: EE-Ti₃C₂ = 140 mA h g⁻¹, EE-Ti₃CN = 165 mA h g⁻¹, HF/HCl-Ti₃C₂ = 142 mA h g⁻¹, HF/HCl-Ti₃CN = 166 mA h g⁻¹. All MXenes exhibit superior cyclic performance,

with a capacity retention of approximately 80% after 2000 cycles. The trend of increase in the capacity of MXene during cycling may be attributed to that of the irreversible expansion of



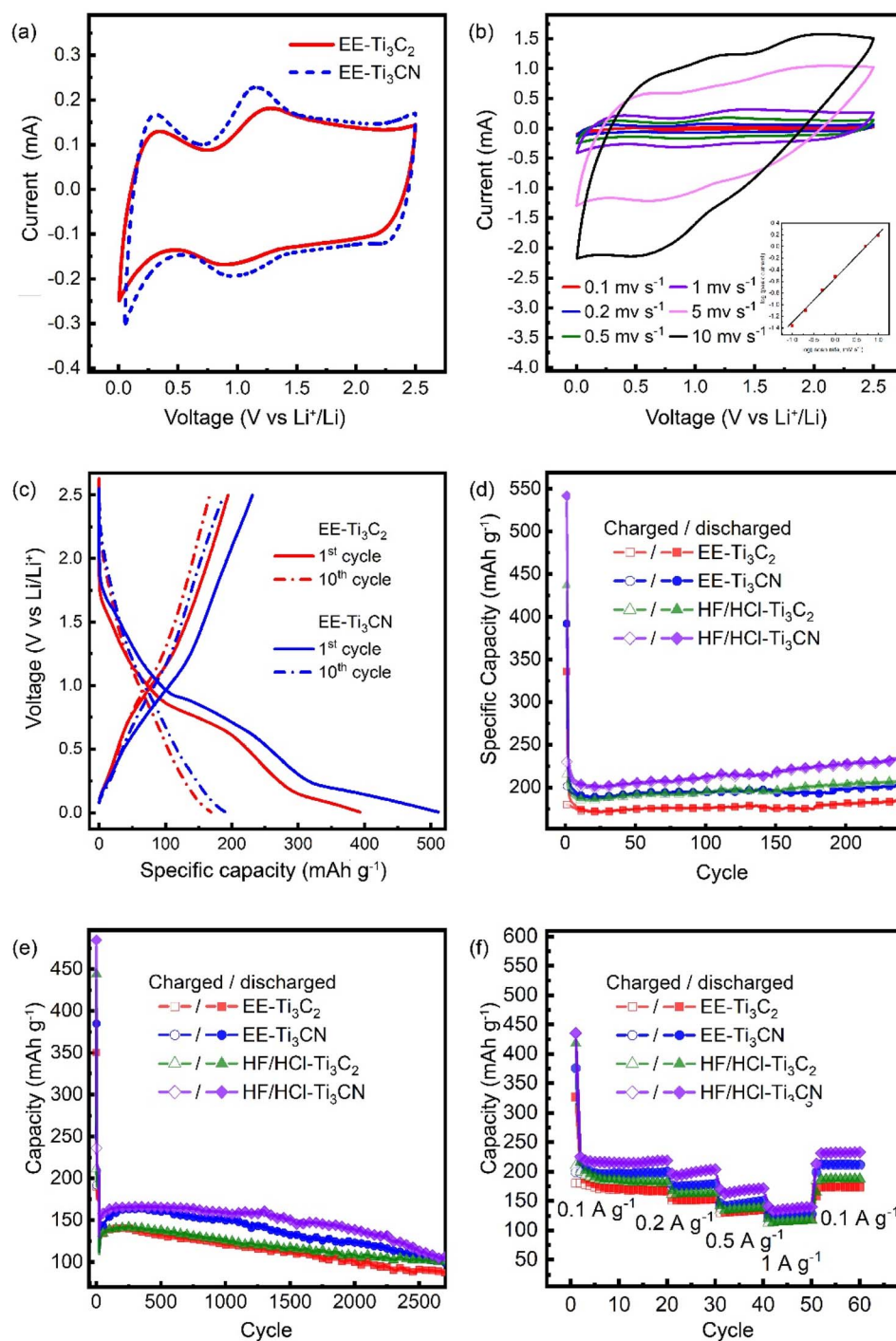


Fig. 4 (a) CV curves of EE-Ti₃C₂ and EE-Ti₃CN from 2.5 V to 0.05 V vs. Li⁺/Li, obtained at a scan rate of 0.5 mV s⁻¹. (b) CV curves of EE-Ti₃C₂ at various scan rates. (c) Galvanostatic charge–discharge profiles of EE-Ti₃C₂ and EE-Ti₃CN at a current density of 0.1 A g⁻¹. (d) Cycle performance of EE-Ti₃C₂, EE-Ti₃CN, HF/HCl-Ti₃C₂, and HF/HCl-Ti₃CN at a current density of 0.1 and (e) 1 A g⁻¹. (f) Rate capability test of EE-Ti₃C₂ and EE-Ti₃CN and their HF/HCl etched analogs at 0.1, 0.2, 0.5, and 1 A g⁻¹.

the interlayer spacing caused by lithiation. Thus, more lithium can be accommodated between the MXene layers. This trend was also observed for other MXene energy storage systems.^{31,52–54}

Both, EE-Ti₃C₂ and EE-Ti₃CN, showed slightly lower capacity than their HF/HCl etched analogues. Such difference is

attributed to the small amount of chloride termination in the HF/HCl-MXene, which is bulkier than the hydroxide and fluoride functional groups, creating wider spaces for the accumulation of lithium ions.⁵⁵ Furthermore, the differences in flake size are important; smaller flakes should increase the ionic conductivity (more pathways) while reducing the electronic



conductivity (higher ohmic resistance). The delaminated EE-MXene flakes showed a slightly larger lateral size in contrast to HF/HCl-MXene, making the latter more accessible to lithium deposition.⁵⁶ All MXenes exhibited good rate capability; the capacity decreased by approximately 60% when the rate increased from 0.1 to 1 A g⁻¹. The capacity was then recovered when the rate decreased back to 0.1 A g⁻¹ without any loss of capacity, indicating good rate reversibility (Fig. 4d). The difference in capacity of all MXenes became smaller at high current capacity. This is because the current density is so high that the redox-active components were not able to undergo complete lithiation and delithiation. Therefore, at high current density, the redox contribution becomes less dominant and the electrode exhibits EDL-like behaviour, which is more dependent on the specific surface area.

3. Conclusions

This work has demonstrated that applying voltage can significantly increase the efficiency of the etching of MAX phases to produce MXene sheets with a large lateral size. The applied voltage allows the aluminium in both the Ti₃AlC₂ and Ti₃AlCN MAX phases precursor to undergo anodic dissolution. This extra reaction pathway significantly reduces the etching time and the etching temperature required for etching in HBF₄, and reduces the release of HF during the etching. Temperature accelerated both chemical and electrochemical etching but also may lead to over-etching and nanosheet damage. Compared to the conventional chemical approaches which use HF-based etchants, the electrochemical etching with HBF₄ is milder, faster, and safer to handle, with a high yield of 85%. Furthermore, unlike conventional HF approaches, in which temperature and concentration of the etchant are the only variables that control the reaction kinetics, voltage can provide further driving force to the reaction. This process may eventually be used to fabricate MXenes that cannot be etched by using HF. The simple experimental setup and mild reaction conditions of the electrochemical etching allow scale up for large-volume manufacturing. As the result of reduced etching time and HF exposure, the EE-MXene exhibits a bigger aspect ratio and less halide termination compared to HF-etched MXene. For energy storage applications, EE-MXene demonstrated the pseudocapacitive nature of energy storage in lithium-ion supercapacitors and exhibited superior cyclability and rate performance.

4. Experimental section

4.1 Electrochemical etching of MAX phases

MAX phase powder (1 g, 500 mesh, Nanoplexus) and HBF₄ (250 mL, 24% in H₂O) were added to a graphite crucible. A platinum wire was used as the counter electrode. The suspension was rested for 30 minutes until the electrolytes reached the desired temperature and all the MAX phase powders settled at the bottom of the crucible. +1 V was applied for 28 hours at 35 °C. After electrochemical etching, the MXene was washed with deionized water *via* vacuum filtration. The MXene was dried at 80 °C under vacuum for 15 hours. The dried EE-MXene was

stored at 3 °C until further characterization application. The average yield of EE-Ti₃C₂ and EE-Ti₃CN obtained was between 85% and 75%.

4.2 Chemical etching of MAX phases with HBF₄

The chemical etching with HBF₄ was carried out similar to the electrochemical etching, but without applying voltage.

4.3 Chemical etching of Ti₃AlC₂ with HF and HCl

The chemical etching of Ti₃AlC₂ with HF and HCl was carried out as reported elsewhere.⁵⁷ In brief, 1 g of Ti₃AlC₂ was slowly added to the chemical etchant and stirred at 300 rpm for 24 hours at 35 °C. The chemical etchant was a mixture of HF (48%, 2 mL) and HCl (37%, 12 mL), diluted with deionized water (volumetric ratio of HCl:H₂O:HF = 6:3:1). The resulting suspension was washed with deionized water several times *via* centrifugation until the pH of the suspension became neutral. The solid was collected *via* vacuum filtration and stored at 3 °C until further analysis.

4.4 Delamination

100 mg of EE-MXene was added to 10 mL of TMAOH (0.15 M) and stirred for 15 hours at 35 °C. The dispersion was washed with DI water until the pH of the dispersion became neutral. The suspension was sonicated for 1 hour to facilitate further delamination. The suspension was submerged in an ice bath with N₂ flow during the sonication to suppress the rate of oxidation. The dispersion was allowed to settle overnight at 3 °C, the supernatant was collected for further analysis.

4.5 Materials characterisation

Raman spectroscopy was carried out to study the vibrational mode of the MAX phase and MXene using an inVia confocal Raman microscope (Renishaw, Wotton-under-Edge, Gloucestershire, UK). X-ray diffraction patterns were obtained using a D8 autochanger (Bruker, Brighton, Sussex, UK) using Cu K_α radiation with a step size of 0.02° in the range of 3–90°. Atomic force microscopy was carried out to measure the thickness of the delaminated MXene flakes using a Nanowizard 4 XP Nanoscience atomic force microscope (Bruker, Brighton, Sussex, UK). SEM and TEM images were obtained to study the morphology using a Tescan Mira scanning electron microscope (Tescan, Kohoutovice, Czech Republic) and Talos transmission electron microscope (ThermoFisher, Loughborough, UK), respectively. X-ray photoelectron microscopy was carried out to obtain the elemental composition and oxidation state of the MAX phase and MXene using an ESCA2SR spectrometer (ScientaOmicron GmbH) using monochromated Al K_α radiation (1486.6 eV, 20 mA emission at 300 W, 1 mm spot size) with a base vacuum pressure of ~1 × 10⁻⁹ mbar. Charge neutralisation was achieved using a low-energy electron flood source (FS40A, PreVac). Binding energy scale calibration was performed by defaulting the C–C in the C 1s photoelectron peak to be 284.7 eV. Analysis and curve fitting were performed using Voigt-approximation peaks using CasaXPS.



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