Nanoscale

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: P. Nayak, Q. Jiang, R. Mohanraman, D. H. Anjum, M. N. Hedhili and H. N. Alshareef, *Nanoscale*, 2018, DOI: 10.1039/C8NR01883A.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

Journal Name

ARTICLE

Inherent Electrochemistry and Charge Transfer Properties of Few-Layer Two Dimensional $\text{Ti}_3\text{C}_2\text{T}_x$ MXeneReceived 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Pranati Nayak,^{a,b,†} Qiu Jiang,^{a,†} Rajeshkumar Mohanraman,^{a,†} Dalaver Anjum,^c Mohamed Nejib Hedhili,^c and Husam N. Alshareef^{a*}

We report the effect of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flake thickness on its inherent electrochemistry and heterogeneous charge transfer characteristics. It is shown that the $\text{Ti}_3\text{C}_2\text{T}_x$ undergoes irreversible oxidation in the positive potential window, which strongly depends on the flake thickness and pH of the electrolyte. Few-layer $\text{Ti}_3\text{C}_2\text{T}_x$ exhibits faster electron transfer kinetics ($k^0=0.09533$ cm/s) with $[\text{Fe}(\text{CN})_6]^{4-/3-}$ redox mediator compared to multi-layer $\text{Ti}_3\text{C}_2\text{T}_x$ ($k^0=0.00503$ cm/s). In addition, few-layer free standing $\text{Ti}_3\text{C}_2\text{T}_x$ film electrode remains intact after enduring irreversible oxidation.

Introduction

The successful isolation of graphene and realization of its remarkable electronic, mechanical, thermal, optical, and electrochemical properties spurred investigation of fundamental properties of other two-dimensional (2D) materials. Amidst a new family of 2D materials, known as MXene, was discovered in 2011.¹ Allied with layered graphitic structure, MXenes are stacks of 2D early transition metal carbides, nitrides and carbonitrides of general formula $\text{M}_n\text{X}_n\text{T}_x$, where M stands for metal atom, X stands for C and/or N, $n = 1, 2$, or 3 , and T_x represents various surface terminations ($-\text{OH}$, $-\text{O}$, and/or $-\text{F}$ groups).² MXenes are composed of conductive carbon core with outer transition metal oxide/hydroxide like surface produced by selective etching of the A layers from ternary $\text{M}_{n+1}\text{AX}_n$ phases, where A is mainly a group IIIA or IVA (i.e., group 13 or 14) element. The atoms are held by strong mixed covalent/metallic/ionic bonds within the layers, whereas stacked layers after "A" removal are weakly bonded with hydrogen bonds.³

The past few years have witnessed an exponential increase in research on 2D MXenes, which has elucidated many of its promising properties such as good hydrophilic nature, mechanical strength, and superior ion interaction capacity.^{4,5} The unique combination of

excellent metallic conductivity with solution processability could potentially make MXene as an outstanding electrode material for many applications such as electrochemical capacitors, mobile ion batteries, and electromagnetic interference shielding.^{6,7} Though relatively new to many other fields, some members of the MXene family have also been studied for electronic, energy harvesting and storage device fabrication.^{8,9} Amongst, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene has been well investigated and etching recipes were optimized to control the quality of MXenes layers. Recently, it has been shown that $\text{Ti}_3\text{C}_2\text{T}_x$ MXene exhibits proton induced pseudocapacitance in acidic electrolytes, which can be attributed to reversible redox reactions of transition metal in non-aqueous medium.¹⁰ However, there is limited understanding of inherent electrochemistry of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in aqueous solution, i.e. how $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes behave under oxidative/reductive potential irrespective of analyte in aqueous solution. Yes, many electrochemical applications such as a biosensor, a chemical sensor, and catalysis require catalytic properties and good stability of the electrode material in an aqueous solution of different pH.

Herein, we report a systematic investigation of the inherent electrochemistry and heterogeneous electron transfer (HET) characteristics of few and multi-layer $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, leading to important conclusions for the application of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in various electrochemical applications in an aqueous medium. Our study shows that the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene exhibits strong inherent electrochemical properties, which enhances when multi-layer MXene is sliced to few-layer flakes. This behavior possibly stems from the more accessible electrochemical surface area in few-layer flakes of $\text{Ti}_3\text{C}_2\text{T}_x$.¹¹ Such large surface area in delaminated few-layer flakes carries defects and high density of edge plane sites, which are potentially active sites for electrochemical sensing and energy-related applications.¹²

Results and discussion

The MXenes reported in this study were prepared by selective etching of Al layer from Ti_3AlC_2 MAX phase. The detailed synthesis protocol is outlined in Scheme 1. The

^a Qiu Jiang, Rajeshkumar Mohanraman, and Prof. Husam N. Alshareef
Materials Science and Engineering, Physical Sciences & Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

E-mail: husam.alshareef@kaust.edu.sa

^b Pranati Nayak

Electrodes and Electrocatalysis (EEC) Biosensor Division, CSIR- Central Electrochemical Research Institute (CSIR-CECRI), Karaikudi, Tamilnadu, 630006, India

^c Dalaver Anjum, Mohamed Nejib Hedhili

Core Labs, King Abdullah University of Science and Technology (KAUST)
Thuwal 23955-6900, Saudi Arabia

[†] Contributed equally

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

ARTICLE

Journal Name

characterizations of parent MAX phase and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene are discussed in the supporting information (ESI, Fig. S1). The $\text{Ti}_3\text{C}_2\text{T}_x$ MXene consists of 2D $\text{Ti}_3\text{C}_2\text{T}_x$

towards cathodic potential resulted in mild oxidation peaks at +0.3 V and reduction peak at -1.1 V respectively (Fig. 2d). It is understood that the origin of the redox peaks in any

Scheme 1. Scheme representing the synthesis route to prepare bulk, ML- and FL- $\text{Ti}_3\text{C}_2\text{T}_x$ from parent Ti_3AlC_2 MAX phase.

layers stacked in 3D bulk form with large interlayer spacing due to the removal of 'Al' lattice plane from parent Ti_3AlC_2 MAX phase and hereafter will be named as bulk- $\text{Ti}_3\text{C}_2\text{T}_x$ for our convenience. We attempted to decrease the layer thickness of bulk- $\text{Ti}_3\text{C}_2\text{T}_x$ by simple clay method followed by ultrasonication (multi-layer MXene, ML- $\text{Ti}_3\text{C}_2\text{T}_x$) and minimum intensive layer delamination root (MILD method, few-layer MXene, FL- $\text{Ti}_3\text{C}_2\text{T}_x$).^{13, 14} Unlike the parent MAX phase, the bulk- $\text{Ti}_3\text{C}_2\text{T}_x$ consists of a stack of a large number of 2D layers as shown in the FESEM and high-resolution transmission electron microscopy (HRTEM) images in Fig. S1. It is clear that larger and thinner MXene flakes can be achieved using the MILD method (Fig. 1a) compared to clay method (Fig. 1b). The AFM images (Fig. 1c), corresponding height profiles (Fig. S2 a), and the statistical distribution of thickness (Fig. 1e) shows significantly thinner flakes (1 nm to ~2 nm thick), which indicates 1 to 2 number of layers in FL- $\text{Ti}_3\text{C}_2\text{T}_x$ (the thickness of an individual MXene flake is reported to be 0.98 nm based on HRTEM study and DFT calculations).^{15, 16} The spikes in thickness shown in the line scan of Fig. S2a compared to the reported single-layer MXene thickness is likely due to the presence of surface adsorbents, such as water molecules trapped under the FL- $\text{Ti}_3\text{C}_2\text{T}_x$ flake. In contrast, the ML- $\text{Ti}_3\text{C}_2\text{T}_x$ in Fig. 1(d) shows a height of ca. 10 nm to ~13 nm (Fig. 1f and Fig. S2b), which validates its multi-layer nature. The XPS analysis of the FL- $\text{Ti}_3\text{C}_2\text{T}_x$ and ML- $\text{Ti}_3\text{C}_2\text{T}_x$ is discussed in Fig. S3, ESI.

Next, we investigated inherent electrochemistry of both ML- $\text{Ti}_3\text{C}_2\text{T}_x$ and FL- $\text{Ti}_3\text{C}_2\text{T}_x$ under anodic and cathodic current-voltage (CV) scans in the potential window of -1.8 to +1.8 V (electrolyte: pH7 phosphate buffer solution, all the potentials stated in this paper are versus Ag/AgCl reference electrode). The electrode fabrication technique is discussed in experimental section. Fig. 2 shows the measured CVs in both anodic and cathodic directions. Three consecutive scans were recorded for each MXene electrode. The first anodic scan of FL- $\text{Ti}_3\text{C}_2\text{T}_x$ resulted in a prominent oxidation peak at +0.7 V with a shoulder peak overlapped at nearly 0.37 V (Fig. 2a). The cathodic CV scan indicates an oxidation peak at 0.43 V with mild reduction peak at -1.1 V (Fig. 2b). For ML- $\text{Ti}_3\text{C}_2\text{T}_x$ the oxidation peak in anodic scan occurs distinctly at 0.34 V with a mild reduction peak at -1.4 V (Fig. 2c). While the first scan

voltammogram is either from the electrochemical reaction of redox moieties present in the electrode material itself or the redox active probe in the electrolyte. As the electrolyte is free from any redox-active probe, it is clear that the measured redox current is due to the redox reaction of $\text{Ti}_3\text{C}_2\text{T}_x$ itself. Also, it is observed that the reduction peak is less prominent during the anodic scan, which indicates the initial oxidation renders the redox active moieties on $\text{Ti}_3\text{C}_2\text{T}_x$ flakes less prone to reduction. In parallel, the initial cathodic scan resulted in a less prominent oxidation peak compared to initial anodic scan. CVs were also recorded for bulk- $\text{Ti}_3\text{C}_2\text{T}_x$ MXene (Fig. S4 a, b) and parent Ti_3AlC_2 MAX phases (Fig. S4 c, d) under similar experimental conditions. Very similar CV features, but with lower current were observed for bulk- $\text{Ti}_3\text{C}_2\text{T}_x$. However,

interestingly, no prominent oxidation/reduction is observed

Fig. 2 Inherent electrochemical properties of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. Cyclic voltammograms showing anodic and cathodic scans of (a and b) FL- $\text{Ti}_3\text{C}_2\text{T}_x$ and (c and d) ML- $\text{Ti}_3\text{C}_2\text{T}_x$, (e) CVs of ML- $\text{Ti}_3\text{C}_2\text{T}_x$ during anodic scan in PBS (0.1 M) at pH starting from 2–12. Conditions: back ground electrolyte, PBS (0.1 M, pH 7.0); scan rate, 100 mV/s; (f) summary of peak potential (E_p) and peak current (I_p) at different pH of the electrolyte medium. The mass loading was maintained same for all the modified electrodes to carry out a comparative analysis.

for both scan directions in the parent Ti_3AlC_2 MAX phase, indicating absence of redox active moieties.

A key feature observed in the above study is the complete disappearance of redox peaks in subsequent scans in both cathodic and anodic direction for all MXene electrodes, indicating the complete stabilization of the surface redox active moieties in first scan itself. We may proclaim that the redox processes are largely chemically irreversible as the respective redox moieties were not re-oxidized/re-reduced in subsequent scans. Despite this, the inherent processes are highly dependent on the flake thickness of $\text{Ti}_3\text{C}_2\text{T}_x$, as evident from Fig. 2. In the anodic scan of FL- $\text{Ti}_3\text{C}_2\text{T}_x$ (Fig. 2a), the oxidation peak intensity is 1200 μA during the first scan, which falls to 220 and 35 μA for ML- $\text{Ti}_3\text{C}_2\text{T}_x$ and bulk- $\text{Ti}_3\text{C}_2\text{T}_x$, respectively (Fig. 2c and Fig. S4a). The oxidation peak in cathodic scan also exhibits a drop in current intensity from 234 μA (for FL- $\text{Ti}_3\text{C}_2\text{T}_x$) in the initial scan to 67 and 35 μA for ML- $\text{Ti}_3\text{C}_2\text{T}_x$ and bulk- $\text{Ti}_3\text{C}_2\text{T}_x$, respectively (Fig. 2b, d, and Fig. S4b). These changes in the current values are also replicated for other redox peaks in both cathodic and anodic sweeps.

The irreversible oxidation in the positive potential window in all MXene electrodes is deemed due to the anodization of surface Ti atoms, possibly at the defect sites and edges, which are more prone to oxidation. The reduction peak can be

attributed to the removal of surface termination groups (mainly $-\text{OH}$, $-\text{O}$).^{17, 18} The absence of oxidation peak at MAX phase modified electrode, its appearance in bulk- $\text{Ti}_3\text{C}_2\text{T}_x$ and more prominent oxidation after slicing bulk- $\text{Ti}_3\text{C}_2\text{T}_x$ into ML- $\text{Ti}_3\text{C}_2\text{T}_x$ and FL- $\text{Ti}_3\text{C}_2\text{T}_x$ can be due to the introduction of surface defects in the synthesis process.¹⁵ In addition, a large specific surface area in FL- $\text{Ti}_3\text{C}_2\text{T}_x$ could be the reason for visibly larger redox current compared to ML- and bulk- $\text{Ti}_3\text{C}_2\text{T}_x$.

We also investigated the pH dependence of the redox peaks during the anodic scan of ML- $\text{Ti}_3\text{C}_2\text{T}_x$ in various pHs ranging from 2 to 12. Since the subsequent scans result in no further oxidation, only the first scans of each electrode were compared. All CVs and the variation of the oxidation peak potential (E_p) and peak current (I_p) with pH are shown in Fig. 2 (e, f). The anodic peak at pH 7 appears at +0.39 V vs Ag/AgCl, which progressively shift toward lower values with a declined oxidation current as the pH decreases towards acidic. Surprisingly at pH 2, no oxidation is observed with highly liberated oxygen evolution reaction (OER) current. In contrast, for alkaline pHs, a shifted oxidation potential towards more positive value is observed with progressive enhancement in oxidation current. Hence $\text{Ti}_3\text{C}_2\text{T}_x$ MXene is highly prone to oxidation in alkaline medium.

Since the anodic scan results in prominent oxidation and FL- $\text{Ti}_3\text{C}_2\text{T}_x$ liberates more oxidation current, we characterized FL- $\text{Ti}_3\text{C}_2\text{T}_x$ after conducting the anodic scan. The HRTEM and STEM micrographs for FL- $\text{Ti}_3\text{C}_2\text{T}_x$ (Fig. 3a) depicts 2D layer structure with the hexagonal atomic arrangement (see selected area electron diffraction (SAED) pattern in upper and HRTEM image in lower inset).^{16, 19} In contrast, the anodized FL- $\text{Ti}_3\text{C}_2\text{T}_x$ (Fig. 3b) depicts un-oxidized fragments (region p1) and partially oxidized surface (region p2). This is supported by the corresponding SAED pattern, which indicates the hexagonal phase of $\text{Ti}_3\text{C}_2\text{T}_x$ and diffraction rings of amorphous regions. Again, the elemental maps for FL- $\text{Ti}_3\text{C}_2\text{T}_x$ (Fig. 3c) confirm the composition (Ti, C, and O), distributions and the overlapped map indicates homogeneous structural feature in FL- $\text{Ti}_3\text{C}_2\text{T}_x$. In contrast, the map for anodized FL- $\text{Ti}_3\text{C}_2\text{T}_x$ (Fig. 3d) displays oxygen-rich fragments, confirmed by a non-uniform structural feature on anodized FL- $\text{Ti}_3\text{C}_2\text{T}_x$.

Fig. 3 HRTEM image of (a) FL- $\text{Ti}_3\text{C}_2\text{T}_x$ flakes; Inset shows SAED pattern (upper) and lattice resolved HRTEM image (lower) of FL- $\text{Ti}_3\text{C}_2\text{T}_x$, (b) STEM image of FL- $\text{Ti}_3\text{C}_2\text{T}_x$ resulting from anodic scan, insets shows SAED pattern at selected area p1 and p2, elemental mapping and mixed elemental mapping (c) before and (d) after anodic scan.

Fig. 4 Cyclic voltammograms of FL-Ti₃C₂T_x MXene flakes recorded for 5 mM [Fe(CN)₆]⁴⁻ in 0.1 M KCl as supporting electrolyte; (a) initial three consecutive scans at 50 mV/s scan rate, (b) CVs at varying scan rates from 50-500 mV/s after recording 1st three scans. CVs recorded for 5 mM [Ru(NH₃)₆]^{3+/2+} in 0.1 M KCl as supporting electrolyte at (d) scan rates from 50-500 mV/s; (e) three consecutive scans recorded at 50 mV/s scan rate after recording (d); (f) again at varying scan rates from 50-500 mV/s. Corresponding Klinger-Kochi and Nicholson analyses and calculated HET rate (k^0) are shown in (c) and insets of (d) and (f), (g) Summary of peak-to-peak separations (ΔE) and HET rate (k^0) of ML-Ti₃C₂T_x and FL-Ti₃C₂T_x after and before anodic scan for both inner and outer sphere redox couples, [Fe(CN)₆]^{4-/3-} and [Ru(NH₃)₆]^{3+/2+}.

The quantitative evaluation of the extent of oxidation after the anodic scan was done by X-ray photoelectron spectroscopy (XPS), shown in Fig. S5. The deconvoluted Ti 2p spectra reveal different valence/charged state of Ti (listed in Table S1).²⁰ The peak with a formal valence of 4⁺ located at 458.5 eV corresponds to TiO₂. The peak located at 459.3 eV corresponds to TiO_{2-x}F_x. The concentration of TiO₂ appears to be 3.9% and 4.32% before and after subjecting to anodic scan, whereas the concentration of TiO_{2-x}F_x changes from 6.6% to 15.5% (Fig. S5 b and d, Table S1). This confirms the electrochemical anodic scan does not completely oxidize MXene, rather makes it more stable by the introduction of oxidation debris on Ti₃C₂T_x surface.

To understand the trends in heterogeneous charge transfer kinetics in Ti₃C₂T_x MXene, we conducted CVs using both inner- and outer-sphere electrochemical redox probes such as [Fe(CN)₆]^{4-/3-} and [Ru(NH₃)₆]^{3+/2+} respectively for both FL-Ti₃C₂T_x (Fig. 4) and ML-Ti₃C₂T_x (Fig. S6). As reflected in Fig. 4a, for FL-Ti₃C₂T_x, the initial scan in presence of [Fe(CN)₆]^{4-/3-} resulted in a clear observation of the ferro/ferricyanide redox peaks (zoomed in insets) along with a predominant oxidation peak due to the inherent oxidation of Ti₃C₂T_x MXene. But the successive scans resulted in only redox peaks corresponding to [Fe(CN)₆]^{4-/3-}. After recording three consecutive scans, we recorded CVs at different scan rate (Fig. 4 b). In contrast, in presence of [Ru(NH₃)₆]^{3+/2+} redox probe, the initial scans don't display any oxidation peak except the redox peaks of the probe (Fig. 4d). This validates the inherent electrochemistry of MXene that it undergoes irreversible oxidation in the positive potential window only. After recording the CVs at different scan rates, we again changed the potential range from -0.6 to 1 V, which resulted in the redox peaks corresponding to [Ru(NH₃)₆]^{3+/2+} redox probe along with the irreversible oxidation

peak corresponding to MXene surface oxidation (Fig. 4e). Again, in sequence with our previous claims, the follow-up scans resulted in no oxidation of MXene and displays only redox peaks of the probe. After recording three consecutive scans, we recorded CVs at

Fig. 5 (a) Digital photographs showing a flexible FL-Ti₃C₂T_x MXene free-standing film. Top view FESEM image of FL-Ti₃C₂T_x MXene film electrode (b) before and (c) after anodic CV; insets: digital photograph of corresponding electrode design; Cross-sectional FESEM image of MXene free-standing electrode (d) before and (f) after recording anodic CV; projections (e and g) show the corresponding high resolution FESEM images, (h) X-ray diffractogram and (i) Raman spectra of FL-Ti₃C₂T_x MXene film electrode before (black plot) and after

different scan rate as shown in Fig. 4f. We employed both classical Nicholson method (limited to ΔE_p below 220 mV) and method developed by Klingler and Kochi (when ΔE_p exceeds 220 mV) to calculate the heterogeneous charge transfer coefficient (k^0) (discussed briefly in ESI).^{21–23} The calculated k^0 values and peak-to-peak separations (ΔE) are summarized in Fig. 4g. As observed, the k^0 value for $[\text{Fe}(\text{CN})_6]^{4-/3-}$ is increases by going from ML- $\text{Ti}_3\text{C}_2\text{T}_x$ to FL- $\text{Ti}_3\text{C}_2\text{T}_x$, which agrees well with the literature on other 2D materials like graphene and TMDs (compared in Table S2 and S3).^{24–34} It is seen that the k^0 value for $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$ does not vary much in going from ML- $\text{Ti}_3\text{C}_2\text{T}_x$ to FL- $\text{Ti}_3\text{C}_2\text{T}_x$ MXene or before and after the anodic scan. This could be due to the inert nature of outer-sphere redox probe towards a number of layers and surface moieties (oxidation debris, functional groups).^{30, 35} This behavior highly piqued our curiosity to compare the charge transfer behavior of the MXene before and after the anodic scan. An in-depth analysis is desired to identify the role of oxidation debris in charge transfer.

After examining the inherent electrochemistry and charge transfer studies of FL- $\text{Ti}_3\text{C}_2\text{T}_x$ and ML- $\text{Ti}_3\text{C}_2\text{T}_x$ flakes, we extended our investigation on FL- $\text{Ti}_3\text{C}_2\text{T}_x$ MXene free-standing film electrode. Such study can reveal interesting insights into the stability of the MXene free-standing film electrode against irreversible oxidation in the positive potential window and justify our findings in favor of using it for biosensing and many analytical applications. The free-standing electrodes were prepared from FL- $\text{Ti}_3\text{C}_2\text{T}_x$ flakes and the electrode preparation scheme is discussed in materials and methods section. We performed surface, morphological and structural characterization of FL- $\text{Ti}_3\text{C}_2\text{T}_x$ MXene free-standing film electrode before and after conducting the anodic scan. A digital photograph (Fig. 5a) shows an as-fabricated freestanding FL- $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film. Fig. 5b–g shows the top-view and cross-sectional FESEM micrographs of free-standing film electrode before and after conducting the anodic scan. Insets of Fig. 5b and 5c show the digital image of the free-standing film electrode before and after conducting the anodic scan. As evinced, no structural incongruity is observed before and after recording anodic CV. Including this, the XRD analysis (Fig. 5 h) of free-standing film electrode suggests no obliteration in structure and confirms that the oxidation debris formed on MXene surface are of very thin amorphous oxidized fragments, which is supported by our previous HRTEM and STEM mapping analysis. Fig. 5(i) represents the Raman spectra recorded on FL- $\text{Ti}_3\text{C}_2\text{T}_x$ MXene free-standing film electrode before and after conducting anodic CV. The Raman peaks corresponding to different vibration modes of Ti–C, Ti–C– T_x are present in as prepared film electrode. Since the MXene is chemically etched and delaminated, usually it is terminated with OH, O and F functionalities, which weakens the out-of-plane vibration of surface Ti_2 and strengthens the out-of-plane vibration of C atoms.^{36, 37} It is observed that the peak associated with doubly degenerated E_g modes at 156 cm^{-1} corresponding to in-plane vibrations of Ti_2 and C atoms in the as-prepared FL- $\text{Ti}_3\text{C}_2\text{T}_x$ film shifts to lower wavenumber 125 cm^{-1} after anodic scan, which indicates termination by surface –OH functional groups. Similarly, a shift toward lower wavenumber and simultaneous strengthening of the peaks assigned to out-of-plane vibrations of C atoms in $\text{Ti}_3\text{C}_2\text{O}_2$ (631.4 and 725 cm^{-1}) is observed, which indicates attachment

of O functionalities after the anodic scan.³⁸ Hence it is clearly understood that anodic scan develops amorphous oxidized fragments over $\text{Ti}_3\text{C}_2\text{T}_x$ MXene surface without any substantial alteration of properties, indicating stability of MXene freestanding electrode for various applications.

$\text{Ti}_3\text{C}_2\text{T}_x$ is the most representative member of MXene family, which has shown its novelty in many applications due to its unique physicochemical properties. However, the electrochemical behavior is highly dependent on many factors such as defects, surface terminations (–OH, –O, –F, etc) and degree of delamination, which are altered vastly by its processing protocols that determine the quality of the 2D flakes produced.³⁹ This study is the first step toward understanding fundamental inherent electrochemistry of $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes with different flake thickness and open a wide window for its use as an electrode material for various electrochemical applications in an aqueous medium. Also, there are now close to 25 members of MXene family with different transition metals, such as Nb, Mo, V, and so forth, which should be similarly investigated and explored to understand their potential use in different applications in an aqueous medium.⁹

Conclusions

In summary, we have studied the inherent electrochemistry of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene and found it undergoes irreversible oxidation in the positive potential window in an aqueous medium, which is due to Ti anodization. It is highly dependent on flake thickness and pH of the electrolyte. Also, it is shown that the few-layer $\text{Ti}_3\text{C}_2\text{T}_x$ exhibits faster electron transfer kinetics ($k^0 = 0.09533\text{ cm/s}$) with $[\text{Fe}(\text{CN})_6]^{4-/3-}$ redox mediator compared to multi-layer $\text{Ti}_3\text{C}_2\text{T}_x$ ($k^0 = 0.00503\text{ cm/s}$). In spite of this, no ample alternation of properties was observed even in MXene free-standing film electrode in aqueous medium and positive potential window.

Acknowledgments

Research reported in this publication is supported by funding from King Abdullah University of Science and Technology (KAUST), Saudi Arabia. Authors would like to thank Dr. Narendra Kurra for helpful discussions. Dr. P. Nayak would like to thank DST (Government of India) for the Inspire Faculty Award (Grant No. 04/2015/002660).

Keywords: MXene, charge transfer, oxidation, reduction, few-layer, multi-layer

Experimental

Materials and methods

Materials

Potassium ferrocyanide [$\text{K}_4[\text{Fe}(\text{CN})_6]$, 99.9%], hexaaminruthenium(III) chloride [$[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$, 98%], potassium chloride (KCl, 99%) were purchased from Sigma-Aldrich. Layered ternary carbide (Ti_3AlC_2) MAX phase powder was procured from (Carbon-Ukraine Ltd. particle size $< 40\text{ }\mu\text{m}$). Dimethylformamide ($(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$, DMF)

was purchased from Sigma Aldrich. Concentrated hydrochloric acid (HCl, technical grade, 35–38%) was procured from Fischer Scientific. Lithium fluoride (LiF, 98+ %) was purchased from Alfa Aesar. Polypropylene (3501 coated PP) and cellulose nitrate (0.22 μm pore size) filter paper were procured from Celgard LLC, NC. Pt wire counter electrode, Ag/AgCl (1M KCl) reference electrode and glassy carbon (GC) working electrode were purchased from CH Instruments, Texas, USA. PBS was purchased from Fisher Scientific-US. All the reagents were of analytical grade and were used as received. All stock solutions were prepared using deionized (DI) water (18.2 M Ω cm, Milli-Q Direct 8, Merck Millipore, and Billerica, MA) without further purification.

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

All chemicals were used as received without further purification. $\text{Ti}_3\text{C}_2\text{T}_x$ MXene was synthesized following LiF/HCl clay method reported elsewhere. The etching solution was prepared by adding 1.33 g of LiF to 20 ml 6 M HCl followed by stirring for 5 min. 2 g of Ti_3AlC_2 powder was slowly added to the etchant at 35 $^\circ\text{C}$ and stirred for 24 h. The acidic suspension was washed with deionized (DI) water until pH ≥ 6 via centrifugation at 3500 rpm (5 min per cycle) and decanting the supernatant after each cycle. The final product, with a small amount of water, was filtered on cellulose nitrate filter paper followed by drying under vacuum at 70 $^\circ\text{C}$ overnight and referred to as bulk- $\text{Ti}_3\text{C}_2\text{T}_x$ MXene.

Preparation of 2D $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes

The previously prepared clay was used to prepare ML- $\text{Ti}_3\text{C}_2\text{T}_x$ flakes. To obtain FL- $\text{Ti}_3\text{C}_2\text{T}_x$, we followed minimum intensive layer delamination (MILD) technique. The synthesis protocol is described as follows.

ML- $\text{Ti}_3\text{C}_2\text{T}_x$

To obtain a dispersion of ML- $\text{Ti}_3\text{C}_2\text{T}_x$ flakes, about 300 mg of freshly synthesized bulk- $\text{Ti}_3\text{C}_2\text{T}_x$ MXene powder was dispersed in 30 ml of DMF and stirred with a magnetic Teflon coated bar for 10 minutes at 500 rpm. The dispersion was sonicated for 30 minutes under ice bath conditions under Ar in order to prevent oxidation. After sonication, the suspension was centrifuged at 3500 rpm for 5 minutes and then decanted to separate the supernatant dispersion from sediment MXene particles. The supernatant suspension was named ML-MXene hereafter and was stored in Teflon sealed glass vial by purging N_2 gas. The material concentration in the supernatant was calculated roughly by filtering a calculated amount of supernatant by vacuum filtration, drying the filtrate under vacuum and finally measuring the weight difference of the filter paper and dried ML-MXene on filter paper.

FL- $\text{Ti}_3\text{C}_2\text{T}_x$

FL- $\text{Ti}_3\text{C}_2\text{T}_x$ was prepared by MILD technique. In brief, the etching solution was prepared by adding 1 g LiF to 20 ml 9 M HCl followed by stirring for 5 min. 1 g of Ti_3AlC_2 powder was slowly added to the MILD etchant at 35 $^\circ\text{C}$ and stirred for 24 h. The acidic suspension was washed with deionized (DI) water until pH 6 via centrifugation at 3500 rpm (5 min per cycle) and decanting the supernatant after each cycle. Around pH ≥ 6 , the stable dark green supernatant of FL- $\text{Ti}_3\text{C}_2\text{T}_x$ was observed and then collected after 30 min centrifugation at 3500 rpm. The concentration of the FL- $\text{Ti}_3\text{C}_2\text{T}_x$ solution was measured by filtering specific amounts of colloidal solution followed by drying under vacuum at 70 $^\circ\text{C}$ overnight and measuring the weight.

Preparation of free-standing $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film electrode

The FL- $\text{Ti}_3\text{C}_2\text{T}_x$ free-standing film was prepared using vacuum filtration using polypropylene filter paper followed by drying under vacuum at 70 $^\circ\text{C}$ overnight. The free-standing film electrode was prepared by cutting a piece of required dimension and making contacts using conducting copper tape and silver paste. The fabricated electrode was used to do an anodic scan and further characterized to confirm the viability of the electrode for various applications.

Characterization Methods

XRD patterns were collected by a Bruker diffractometer (D8 Advance) with Cu K α radiation) with a scanning rate of 0.02 $^\circ$ /step and 0.5 s/step in the range 2 θ angles of 5 $^\circ$ –50 $^\circ$. The morphology and microstructure of the samples were characterized by high-resolution field emission scanning electron microscopy (Nova Nano 630, FEI) and high-resolution transmission electron microscopy (Titan 80–300 kV). Cross-sectional SEM was employed to measure the thickness of freestanding MXene films. Raman spectroscopy measurements were carried out on the samples using a micro-Raman spectrometer (LabRAM Aramis, Horiba, Japan) equipped with a 473-nm wavelength cobalt blue laser and an Olympus $\times 50$ objective lens. XPS studies were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K α X-ray source ($h\nu = 1486.6$ eV) operating at 150 W, a multi-channel plate and delay line detector under a vacuum of $\sim 10^{-9}$ mbar. All spectra were recorded using an aperture slot of 110 $\mu\text{m} \times 110$ μm . The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 and 20 eV, respectively. The spectral deconvolution was done using CASA XPS software.

Inherent electrochemistry studies on ML- $\text{Ti}_3\text{C}_2\text{T}_x$ and FL- $\text{Ti}_3\text{C}_2\text{T}_x$

Fundamental electrochemical studies of MXene samples were performed in 0.1 M PBS of pH7 as the background electrolyte. All the electrochemical measurements were performed using a CHI 608D workstation (Austin, USA). Cyclic voltammetry was used as the main technique to characterize the MXene modified electrodes. Prior to each new electrochemical measurement, GCE was cleaned by polishing with a 0.05 μm alumina slurry on a polishing pad, thoroughly washed with deionized water and dried by purging N_2 gas. The Ti_3AlC_2 MAX phase, bulk- $\text{Ti}_3\text{C}_2\text{T}_x$, ML- $\text{Ti}_3\text{C}_2\text{T}_x$ and FL- $\text{Ti}_3\text{C}_2\text{T}_x$ MXene dispersion (1 mg/ml concentration) were ultrasonicated for a period of 5 min to maintain the well-dispersed suspension. Aliquots of 2 μL of the suspension inks were drop-casted on GCE and were left to dry under the lamp with the N_2 flow. The above step was repeated 2 times in order to yield an electrode surface homogeneously modified with 4.0 μg film of the desired material. All cyclic voltammetry experiments were conducted at a scan rate of 100 mVs $^{-1}$. Both anodic and cathodic scans were started from 0 V; the potential at which no redox process is predicted to occur. In a typical anodic CV, voltammetry scan began at 0 V and scanned toward 1.8 V followed by a reverse sweep to -1.8 V and for the cathodic study, first toward -1.8 V followed by a reverse sweep to 1.8 V before returning to 0 V. All of the measurements were conducted under ambient conditions.

Heterogeneous electron transfer (HET) rate

The modified electrodes were tested for heterogeneous electron transfer (HET) studies using cyclic voltammetry at a scan rate from

50–500 mV⁻¹ for both inner-sphere and outer sphere redox probes: 5mM of K₄[Fe(CN)₆] and [Ru(NH₃)₆Cl₃] in KCl (0.1 M) as supporting electrolyte. The k^0 values were calculated from the Nicholson method and Klinger-Kochi methods. The roughness of the electrode was not factored into the calculation of k^0 . The diffusion coefficient $D = 7.26 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $8.43 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was used to compute the k^0 value for [Fe(CN)₆]^{4-/3-} and [Ru(NH₃)₆]^{3+/2+} respectively.

References

1. M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi and M. W. Barsoum, *Adv. Mater.*, 2011, **23**, 4248–4253.
2. M. Naguib, O. Mashtalir, J. Carle, V. Presser, J. Lu, L. Hultman, Y. Gogotsi and M. W. Barsoum, *ACS Nano*, 2012, **6**, 1322–1331.
3. M. Naguib, V. N. Mochalin, M. W. Barsoum and Y. Gogotsi, *Adv. Mater.*, 2014, **26**, 992–1005.
4. K. Maleski, V. N. Mochalin, and Y. Gogotsi, *Chem. Mater.*, 2017, **29**, 1632–1640.
5. F. M. R'omer, U. Wiedwald, T. Strusch, J. Halim, E. Mayerberger, M. W. Barsoum and M. Farle, *RSC Adv.*, 2017, **7**, 13097–13103.
6. Y. Peng, B. Akuzum, N. Kurra, M-Q. Zhao, M. Alhabeb, B. Anasori, E. C. Kumbur, H. N. Alshareef, M-D. Gerc and Y. Gogotsi, *Energy Environ. Sci.*, 2016, **9**, 2847–2854.
7. N. Kurra, B. Ahmed, Y. Gogotsi, H. N. Alshareef, *Adv. Energy Mater.*, 2016, **6**, 1601372.
8. H. Kim, B. Anasori, Y. Gogotsi, and H. N. Alshareef. *Chem. Mater.* 2017, **29**, 6472–6479.
9. B. Anasori, M. R. Lukatskaya and Y. Gogotsi, *Nature Materials*, 2017, **2**, 16098.
10. X. Wang, S. Kajiyama, H. Iinuma, E. Hosono, S. Oro, I. Moriguchi, M. Okubo & A. Yamada, *Nature Commun.*, 2015, **6**, 6544.
11. K. Rasool, M. Helal, A. Ali, C. E. Ren, Y. Gogotsi and K. A. Mahmoud, *ACS Nano*, 2016, **10**, 3674–3684.
12. S. Kajiyama, L. Szabova, H. Iinuma, A. Sugahara, K. Gotoh, K. Sodeyama, Y. Tateyama, M. Okubo and A. Yamada, *Adv. Energy Mater.*, 2017, **7**, 1601873.
13. M. Ghidui, M. R. Lukatskaya, M-Q Zhao, Y. Gogotsi & M. W. Barsoum, *Nature*, 2014, **516**, 78–81.
14. M. Alhabeb, K. Maleski, B. Anasori, P. Lelyukh, L. Clark, S. Sin and Y. Gogotsi, *Chem. Mater.*, 2017, **29**, 7633–7644.
15. X. Sang, Y. Xie, M-W. Lin, M. Alhabeb, K.L. Van Aken, Y. Gogotsi, Paul R. C. Kent, Kai Xiao, and R. R. Unocic, *ACS Nano*, 2016, **10**, 9193–9200.
16. X. Wang, X. Shen, Y. Gao, Z. Wang, R. Yu and L. Chen, *J. Am. Chem. Soc.*, 2015, **137**, 2715–2721.
17. M. E. Sibert, *J. Electrochem. Soc.*, 1963, **110**, 65–72.
18. C. J. Zhang, S. Pinilla, N. McEvoy, C. P. Cullen, B. Anasori, E. Long, S-H. Park, A. S-Ascaso, A. Shmeliov, D. Krishnan, C. Morant, X. Liu, G. S. Duesberg, Y. Gogotsi, and V. Nicolosi, *Chem. Mater.*, 2017, **29**, 4848–4856.
19. X. Li, X. Yin, M. Han, C. Song, X. Sun, H. Xu, L. Cheng and L. Zhang, *J. Mater. Chem. C*, 2017, **5**, 7621–7628.
20. J. Halim, K. M. Cook, M. Naguib, P. Eklund, Y. Gogotsi, J. Rosen, M. W. Barsoum, *Appl. Surf. Sci.*, 2016, **362**, 406–417.
21. R. S. Nicholson, *Anal. Chem.*, 1965, **37**, 1351–1355.
22. R. J. Klinger, J. K. Kochl, *J. Phys. Chem.*, 1981, **85**, 1731–1741.
23. A. N. Patel, M. G. Collignon, M. A. O'Connell, W. O. Y. Hung, K. McKelvey, J. V. Macpherson, and P. R. Unwin, *J. Am. Chem. Soc.*, 2012, **134**, 20117–20130.
24. T. J. Davies, R. R. Moore, C. E. Banks, and R. G. Compton, *J. Electroanal. Chem.*, 2004, **574**, 123–152.
25. D. A. C. Brownson, S. A. Varey, F. Hussain, S. J. Haigh and C. E. Banks, *Nanoscale*, 2014, **6**, 1607–1621.
26. M. Velick, D. F. Bradley, A. J. Cooper, E. W. Hill, I. A. Kinloch, A. Mishchenko, K. S. Novoselov, H. V. Patten, P. S. Toth, A. T. Valota, S. D. Worrall, and R. A. W. Dryfe, *ACS Nano*, 2014, **8**, 10089–10100.
27. K. Griffiths, C. Dale, J. Hedley, M. D. Kowal, R. B. Kaner and N. Keegan. *Nanoscale*, 2014, **6**, 13613–13622.
28. C. B. Navarro, Z. P. L. Laker, J. P. Rourke, and N. R. Wilson, *Phys. Chem. Chem. Phys.*, 2015, **17**, 29628–29636.
29. E. P. Randviir, D. A. C. Brownson, M. G. Mingot, D. K. Kampouris, J. Iniesta and C. E. Banks, *Nanoscale*, 2012, **4**, 6470–6480.
30. P. Nayak, N. Kurra, C. Xia and H. N. Alshareef. *Adv. Electron. Mater.* 2016, **2**, 1600185.
31. A. Yong, S. Eng, A. Ambrosi, Z. Sofer, P. Šimek, M. Pumera, *ACS Nano*, 2014, **8**, 12185–12198.
32. X. Chia, A. Ambrosi, Z. Sofer, J. Luxa, D. Sedmidubský and M. Pumera, *ACS Nano*, 2016, **10**, 112–123.
33. X. Chia, Z. Sofer, J. Luxa and M. Pumera, *ACS Appl. Mater. Interfaces*, 2017, **9**, 25587–25599.
34. X. Chia, A. Ambrosi, D. Sedmidubsky, Z. Sofer and M. Pumera. *Chem. Eur. J.*, 2014, **20**, 17426–1743.
35. P. Nayak, B. Anbarasan, S. Ramaprabhu, *J. Phys. Chem. C*, 2013, **117**, 13202–13209.
36. T. Hu, J. Wang, H. Zhang, Z. Li, M. Hu and X. Wang, *Phys. Chem. Chem. Phys.*, 2015, **17**, 9997–10003.
37. M. Hu, Z. Li, T. Hu, S. Zhu, C. Zhang, and X. Wang, *ACS Nano* 2016, **10**, 11344–11350.
38. M. Naguib, O. Mashtalir, M. R. Lukatskaya, B. Dyatkin, C. Zhang, V. Presser, Y. Gogotsi and M. W. Barsoum, *Chem. Commun.*, 2014, **50**, 7420–7423.
39. M. D. Levi, M. R. Lukatskaya, S. Sigalov, M. Beidaghi, N. Shpigel, L. Daikhin, D. Aurbach, M. W. Barsoum, and Y. Gogotsi, *Adv. Energy Mater.*, 2015, **5**, 1400815.

Table of Contents

Inherent Electrochemistry and Charge Transfer Properties of Few-Layer Two Dimensional $\text{Ti}_3\text{C}_2\text{T}_x$ MXene

Pranati Nayak,^{a,b,†} Qiu Jiang,^{a,†} Rajeshkumar Mohanraman,^{a,†} Dalaver Anjum,^c Mohamed Nejib Hedhili,^c and Husam N. Alshareef^{a*}

^aMaterials Science and Engineering, Physical Sciences & Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia

^bElectrodics and Electrocatalysis (EEC) Biosensor Division, CSIR- Central Electrochemical Research Institute (CSIR-CECRI), Karaikudi, Tamilnadu, 630006, India

[†]These authors contributed equally to the work

*E-mail: husam.alshareef@kaust.edu.sa

TOC

Few-layered $\text{Ti}_3\text{C}_2\text{T}_x$ MXene undergoes more electro oxidation in positive potential window and aqueous medium compared to multi-layered and bulk 3D stack of $\text{Ti}_3\text{C}_2\text{T}_x$ layers.