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Inherent Electrochemistry and Charge Transfer Properties of Few-Layer Two Dimensional Ti$_2$C$_2$T$_x$ MXene

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We report the effect of Ti$_2$C$_2$T$_x$ MXene flake thickness on its inherent electrochemistry and heterogeneous charge transfer characteristics. It is shown that the Ti$_2$C$_2$T$_x$ undergoes irreversible oxidation in the positive potential window, which strongly depends on the flake thickness and pH of the electrolyte. Few-layer Ti$_2$C$_2$T$_x$ exhibits faster electron transfer kinetics ($k^+=0.09533$ cm/s) with [Fe(CN)$_3$]$^{4+/3+}$ redox mediator compared to multi-layer Ti$_2$C$_2$T$_x$ ($k^+=0.00503$ cm/s). In addition, few-layer free standing Ti$_2$C$_2$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 MXenes, was discovered in 2011.1 Allied with layered graphitic structure, MXene are stacks of 2D early transition metal carbides, nitrides and carbonitrides of general formula M$_n$X$_n$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 (-OH, -O, and/or -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 M$_n$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.6,8 Amongst, Ti$_2$C$_2$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 Ti$_2$C$_2$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.9 However, there is limited understanding of inherent electrochemistry of Ti$_2$C$_2$T$_x$ MXene in aqueous solution, i.e. how Ti$_2$C$_2$T$_x$ MXene 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 Ti$_2$C$_2$T$_x$ MXene, leading to important conclusions for the application of Ti$_2$C$_2$T$_x$ MXene in various electrochemical applications in an aqueous medium. Our study shows that the Ti$_2$C$_2$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 Ti$_2$C$_2$T$_x$.10 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.11

Results and discussion

The MXenes reported in this study were prepared by selective etching of Al layer from Ti$_2$AlC$_2$ MAX phase. The detailed synthesis protocol is outlined in Scheme 1. The
characterizations of parent MAX phase and Ti$_3$C$_2$T$_x$ MXene are discussed in the supporting information (ESI, Fig. S1). The Ti$_3$C$_2$T$_x$ MXene consists of 2D Ti$_2$C$_2$T$_x$ layers stacked in 3D bulk form with large interlayer spacing due to the removal of ‘Al’ lattice plane from parent Ti$_3$AlC$_2$ MAX phase and hereafter will be named as bulk-Ti$_3$C$_2$T$_x$ for our convenience. We attempted to decrease the layer thickness of bulk-Ti$_3$C$_2$T$_x$ by simple clay method followed by ultrasonication (multi-layer MXene, ML-Ti$_3$C$_2$T$_x$) and minimum intensive layer delamination root (MILD method, few-layer MXene, FL-Ti$_3$C$_2$T$_x$). Unlike the parent MAX phase, the bulk-Ti$_3$C$_2$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. S2a), 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-Ti$_3$C$_2$T$_x$ (the thickness of an individual MXene flake is reported to be 0.98 nm based on HRTEM study and DFT calculations). 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-Ti$_3$C$_2$T$_x$ flake. In contrast, the ML-Ti$_3$C$_2$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-Ti$_3$C$_2$T$_x$ and ML-Ti$_3$C$_2$T$_x$ is discussed in Fig. S3, ESI.

Next, we investigated inherent electrochemistry of both ML-Ti$_3$C$_2$T$_x$ and FL-Ti$_3$C$_2$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-Ti$_3$C$_2$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-Ti$_3$C$_2$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 Ti$_3$C$_2$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 Ti$_3$C$_2$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-Ti$_3$C$_2$T$_x$ MXene (Fig. S4 a, b) and parent Ti$_3$AlC$_2$ MAX phases (Fig. S4 c, d) under similar experimental conditions. Very similar CV features, but with lower current were observed for bulk-Ti$_3$C$_2$T$_x$. However, interestingly, no prominent oxidation/reduction is observed 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
attributed to the removal of surface termination groups (mainly -OH, -O)\(^{17,18}\). The absence of oxidation peak at MAX phase modified electrode, its appearance in bulk-Ti\(_3\)C\(_2\)T\(_x\) and more prominent oxidation after slicing bulk-Ti\(_3\)C\(_2\)T\(_x\) into ML-Ti\(_3\)C\(_2\)T\(_x\) and FL-Ti\(_3\)C\(_2\)T\(_x\) can be due to the introduction of surface defects in the synthesis process.\(^1\) In addition, a large specific surface area in FL-Ti\(_3\)C\(_2\)T\(_x\) could be the reason for visibly larger redox current compared to ML- and bulk-Ti\(_3\)C\(_2\)T\(_x\).

We also investigated the pH dependence of the redox peaks during the anodic scan of ML-Ti\(_3\)C\(_2\)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 Ti\(_3\)C\(_2\)T\(_x\) MXene is highly prone to oxidation in alkaline medium.

Since the anodic scan results in prominent oxidation and FL-Ti\(_3\)C\(_2\)T\(_x\) liberates more oxidation current, we characterized all-Ti\(_3\)C\(_2\)T\(_x\) after conducting the anodic scan. The HRTEM and STEM micrographs for FL-Ti\(_3\)C\(_2\)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-Ti\(_3\)C\(_2\)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 Ti\(_3\)C\(_2\)T\(_x\) and diffraction rings of amorphous regions. Again, the elemental maps for FL-Ti\(_3\)C\(_2\)T\(_x\) (Fig. 3c) confirm the composition (Ti, C, and O), distributions and the overlapped map indicates homogeneous structural feature in FL-Ti\(_3\)C\(_2\)T\(_x\). In contrast, the map for anodized FL-Ti\(_3\)C\(_2\)T\(_x\) (Fig. 3d) displays oxygen-rich fragments, confirmed by a non-uniform structural feature on anodized FL-Ti\(_3\)C\(_2\)T\(_x\).


\(\text{Fig. 2} \) Inherent electrochemical properties of Ti\(_3\)C\(_2\)T\(_x\) MXene. Cyclic voltammmograms showing anodic and cathodic scans of (a and b) FL-Ti\(_3\)C\(_2\)T\(_x\) and (c and d) ML-Ti\(_3\)C\(_2\)T\(_x\). (e) CVs of ML-Ti\(_3\)C\(_2\)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.

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/reduced in subsequent scans. Despite this, the inherent processes are highly dependent on the flake thickness of Ti\(_3\)C\(_2\)T\(_x\) as evident from Fig. 2. In the anodic scan of FL-Ti\(_3\)C\(_2\)T\(_x\) (Fig. 2a), the oxidation peak intensity is 1200 μA during the first scan, which falls to 220 and 35 μA for ML-Ti\(_3\)C\(_2\)T\(_x\) and bulk-Ti\(_3\)C\(_2\)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-Ti\(_3\)C\(_2\)T\(_x\)) in the initial scan to 67 and 35 μA for ML-Ti\(_3\)C\(_2\)T\(_x\) and bulk-Ti\(_3\)C\(_2\)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

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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). 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 TiO2-xFx. The concentration of TiO2 appears to be 3.9% and 4.32% before and after subjecting to anodic scan, whereas the concentration of TiO2-xFx 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 TiC2Tx surface.

To understand the trends in heterogeneous charge transfer kinetics in TiC2Tx 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-TiC2Tx (Fig. 4) and ML-TiC2Tx (Fig. S6). As reflected in Fig. 4a, for FL-TiC2Tx, 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 TiC2Tx 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 different scan rates from 50-500 mV/s after recording (d); (f) again at varying scan rates from 50-500 mV/s. Corresponding Klingler-Kochi and Nicholson analyses and calculated HET rate (k0) are shown in (c)and insets of (d and f) (g) Summary of peak-to-peak separations (ΔE) and HET rate (k0) of ML-TiC2Tx and FL-TiC2Tx 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 concentration of TiO2, x, after and before anodic scan for both inner and outer sphere redox couples, [Fe(CN)6]4-/3- resulted in a stable TiO2-xFx, x changes from 6.6% to 15.5%. After recording three consecutive scans, we recorded CVs at different scan rates from 50-500 mV/s after recording (d); (f) again at varying scan rates from 50-500 mV/s. Corresponding Klingler-Kochi and Nicholson analyses and calculated HET rate (k0) are shown in (c)and insets of (d and f) (g) Summary of peak-to-peak separations (ΔE) and HET rate (k0) of ML-TiC2Tx and FL-TiC2Tx after and before anodic scan for both inner and outer sphere redox couples, [Fe(CN)6]4-/3- and [Ru(NH3)6]3+/2+.

Fig. 4 Cyclic voltammograms of FL-TiC2Tx 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 rom 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 Klingler-Kochi and Nicholson analyses and calculated HET rate (k0) are shown in (c)and insets of (d and f) (g) Summary of peak-to-peak separations (ΔE) and HET rate (k0) of ML-TiC2Tx and FL-TiC2Tx after and before anodic scan for both inner and outer sphere redox couples, [Fe(CN)6]4-/3- and [Ru(NH3)6]3+/2+.

Fig. 5 (a) Digital photographs showing a flexible FL-TiC2Tx MXene free-standing film. Top view FESEM image of FL-TiC2Tx MXene film electrode (b) before and (c) after anodic CV; (d) and (f) after recording anodic CV; (e and g) show the corresponding high resolution FESEM images, (h) X-ray diffractogram and (i) Raman spectra of FL-TiC2Tx 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') (discussed briefly in ESI).\textsuperscript{21,23} The calculated k' values and peak-to-peak separations (ΔE) are summarized in Fig. 4g. As observed, the k' value for [Fe(CN)]\textsubscript{6}\textsuperscript{4-}/3- is increases by going from ML-Ti\textsubscript{2}C\textsubscript{1-x}T\textsubscript{x} to FL-Ti\textsubscript{2}C\textsubscript{1-x}T\textsubscript{x} which agrees well with the literature on other 2D materials like graphene and TMDCs (compared in Table S2 and S3).\textsuperscript{14,16} It is seen that the k' value for [Ru(NH\textsubscript{3})\textsubscript{6}]\textsuperscript{3+}/2+ does not vary much in going from ML-Ti\textsubscript{2}C\textsubscript{1-x}T\textsubscript{x} to FL-Ti\textsubscript{2}C\textsubscript{1-x}T\textsubscript{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).\textsuperscript{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-Ti\textsubscript{2}C\textsubscript{1-x}T\textsubscript{x} and ML-Ti\textsubscript{2}C\textsubscript{1-x}T\textsubscript{x} flakes, we extended our investigation on FL-Ti\textsubscript{2}C\textsubscript{1-x}T\textsubscript{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-Ti\textsubscript{2}C\textsubscript{1-x}T\textsubscript{x} flakes and the electrode preparation scheme is discussed in materials and methods section. We performed surface, morphological and structural characterization of FL-Ti\textsubscript{2}C\textsubscript{1-x}T\textsubscript{x} MXene free-standing film electrode before and after conducting the anodic scan. A digital photograph (Fig. 5a) shows an as-fabricated freestanding FL-Ti\textsubscript{2}C\textsubscript{1-x}T\textsubscript{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 freestanding 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. S1i represents the Raman spectra recorded on FL-Ti\textsubscript{2}C\textsubscript{1-x}T\textsubscript{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-O, and C-C 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\textsubscript{2} and strengthens the out-of-plane vibration of C atoms.\textsuperscript{36,37} It is observed that the peak associated with doubly degenerated E\textsubscript{g} modes at 156 cm\textsuperscript{-1} corresponding to in-plane vibrations of Ti\textsubscript{2} and C atoms in the as-prepared FL-Ti\textsubscript{2}C\textsubscript{1-x}T\textsubscript{x} film shifts to lower wavenumber 125 cm\textsuperscript{-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 Ti\textsubscript{2}C\textsubscript{1-x}O\textsubscript{2} (631.4 and 725 cm\textsuperscript{-1}) is observed, which indicates attachment of O functionalities after the anodic scan.\textsuperscript{38} Hence it is clearly understood that anodic scan develops amorphous oxidized fragments over Ti\textsubscript{2}C\textsubscript{1-x}T\textsubscript{x} MXene surface without any substantial alteration of properties, indicating stability of MXene freestanding electrode for various applications.

Ti\textsubscript{2}C\textsubscript{1-x}T\textsubscript{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.\textsuperscript{39} This study is the first step toward understanding fundamental inherent electrochemistry of Ti\textsubscript{2}C\textsubscript{1-x}T\textsubscript{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.\textsuperscript{9}

Conclusions

In summary, we have studied the inherent electrochemistry of Ti\textsubscript{2}C\textsubscript{1-x}T\textsubscript{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 Ti\textsubscript{2}C\textsubscript{1-x}T\textsubscript{x} exhibits faster electron transfer kinetics (k' = 0.09533 cm/s) with Fe(CN)\textsubscript{6}\textsuperscript{4-}/3- redox mediator compared to multi-layer Ti\textsubscript{2}C\textsubscript{1-x}T\textsubscript{x} (k' = 0.00503 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.

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

Experimental

Materials and methods

Materials

Potassium ferrocyanide [K\textsubscript{4}[Fe(CN)\textsubscript{6}] 99.9%), hexaaminruthenium(III) chloride [Ru(NH\textsubscript{3})\textsubscript{6}]Cl\textsubscript{3}, 98%), potassium chloride (KCl, 99%) were purchased from Sigma-Aldrich. Layered ternary carbide (Ti\textsubscript{3}AlC\textsubscript{2}) MAX phase powder was procured from (Carbon-Ukraine ltd. particle size < 40 μm). Dimethylformamide ((CH\textsubscript{3})\textsubscript{2}NC(O)H, DMF)
was purchased from Sigma Aldrich. Concentrated hydrochloric acid (HCl, technical grade, 35-38%) was procured from Fisher Scientific. Lithium fluoride (LiF, 98+ %) was purchased from Alfa Aesar. Polypropylene (3501 coated PP) and cellulose nitrate (0.22 μm pore size) filter papers 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 MΩ cm, Milli-Q Direct 8, Merck Millipore, and Billerica, MA) without further purification.

Preparation of Ti$_3$C$_2$T$_x$, MXene

All chemicals were used as received without further purification. Ti$_3$C$_2$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$_3$AlC$_2$ powder was slowly added to the etchant at 35 °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 °C overnight and referred to as bulk-Ti$_3$C$_2$T$_x$, MXene.

Preparation of 2D Ti$_3$C$_2$T$_x$, MXene flakes

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

**ML-Ti$_3$C$_2$T$_x$**

To obtain a dispersion of ML-Ti$_3$C$_2$T$_x$ flakes, about 300 mg of freshly synthesized bulk-Ti$_3$C$_2$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-Ti$_3$C$_2$T$_x$**

FL-Ti$_3$C$_2$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$_3$AlC$_2$ powder was slowly added to the MILD etchant at 35 °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-Ti$_3$C$_2$T$_x$ was observed and then collected after 30 min centrifugation at 3500 rpm. The concentration of the FL-Ti$_3$C$_2$T$_x$ solution was measured by filtering specific amounts of colloidal solution followed by drying under vacuum at 70 °C overnight and measuring the weight.

Preparation of free-standing Ti$_3$C$_2$T$_x$, MXene film electrode

The FL-Ti$_3$C$_2$T$_x$ free-standing film was prepared using vacuum filtration using polypropylene filter paper followed by drying under vacuum at 70 °C overnight. The free-standing film electrode was prepared by cutting a piece of required dimension and making electrical 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 Ka radiation) with a scanning rate of 0.02°/step and 0.5 s/step in the range 20angles of 5°-50°. 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×50 objective lens. XPS studies were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Ka X-ray source (hv = 1486.6 eV) operating at 150 W, a multi-channel plate and delay line detector under a vacuum of ~10$^{-6}$ mbar. All spectra were recorded using an aperture slot of 110 μm x 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-Ti$_3$C$_2$T$_x$ and FL-Ti$_3$C$_2$T$_x$

Fundamental electrochemical studies of MXene samples were performed in 0.1 M PBS of pH 7 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$_3$AlC$_2$ MAX phase, bulk-Ti$_3$C$_2$T$_x$, ML-Ti$_3$C$_2$T$_x$, and FL-Ti$_3$C$_2$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-cast 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 mV/s$^{-1}$. 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 mVs\(^{-1}\) for both inner-sphere and outer sphere redox probes: 5mM of K\(_2[Fe(CN)_6]_2\) and K\(_2[Fe(ClO_4)_6]\) in KCl (0.1 M) as supporting electrolyte. The \(k_r\) values were calculated from the Nicholson method and Klinger-Kochi methods. The roughness of the electrode was not factored into the calculation of \(R_s\). The diffusion coefficient \(D = 7.26 \times 10^{-6}\) cm\(^2\) s\(^{-1}\) and 8.43 \(\times 10^{-7}\) cm\(^2\) s\(^{-1}\) was used to compute the \(k_r^0\) value for [Fe(CN)\(_6\)]\(^{3-}\)\(^{2-}\) and [Ru(NH\(_3\))\(_6\)]\(^{3+}\)\(^{2+}\) respectively.

References


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Inherent Electrochemistry and Charge Transfer Properties of Few-Layer Two Dimensional Ti$_3$C$_2$Tx MXene

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