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Research Article

Structural, Morphological and Elemental Analysis of Selectively Etched and Exfoliated Ti_3AlC_2 MAX Phase

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Abstract

In the present research major focus is on the synthesis of materials that can be easily used in small portable devices and as energy storage devices. Here we focused on a new family of 2D materials Ti_3C_2 (MXenes). Ti_3AlC_2 (MAX phase) was intercalated using selective etching of aluminium present in the MAX phase. The etching was done using HF in combination with HCl followed by delaminated in DMSO medium using ultrasonication. The synthesized samples were physically characterized via XRD, SEM and EDX. The XRD diffractogram confirms the formation of MXene through its characteristic plane (002) arising at 2θ~9°. The morphological study revealed the stacked layered sheet like structure obtained through SEM. The elemental confirmation of removal of aluminium was done as indicated by EDX spectroscopy.

Keywords: delamination, intercalation, MAX phase, MXene

1. INTRODUCTION

The 2D materials like graphene are widely known for their distinctive properties that are not found in their bulk counterparts, thus making them ideal for a vast range of applications extending from electronic and optoelectronic devices to electrochemical catalysis [1-3]. Generally, 2D materials are produced by exfoliating layered 3D materials with weak van der Waals-like coupling between layers [4]. Recent technological advancements have allowed the synthesis of various 2D materials by chemical exfoliation or mechanical cleavage of layered 3D precursors.

MXene are newly discovered 2D ceramic materials belonging to the family of transition metal carbides, carbonitrides and nitrides [5]. Naguib et al. [6] was the pioneer in synthesizing a 2D nanocrystalline material by exfoliation of layered solids in 2011. MAX phases are the precursors of MXene, they are a large family of ternary carbides or nitrides with a general chemical formula of $M_{n+1}AX_n$, where M stands for early transition metal, A is an element generally from group IIIA or IVA, X is either carbon or nitrogen and n =1,2,3 and so on [4][6].

MAX phases have layered structure in which M-X units and A layers are alternately stacked. Because the M-X bonds are much stronger than M-A bonds, the A layer can be selectively removed from MAX phases by HF etching, thus creating MXenes [7]. The MXene made by HF etching are attached with functional groups like oxygen (=O), hydroxyl (-OH) or fluorine (-F) or a combination of these, due to its high surface energi [4][7-8]. Thus, the general formula of MXenes can be summarized as $M_{n+1}X_nT_x$, where T represents surface termination groups and x is the number of termination groups per formula unit [1]. MXenes exist in a multi-layered structure, which appears as planar sheets stacked in flakes. These multi-layered structures can be delaminated into single-layer flakes by sonication [8]. MXenes have hydrophilic surfaces, good chemical stability, fabulous electrical conductivity, and environment friendly. They have plenty of exciting mechanical, electronic, magnetic, and electrochemical properties which have drawn a huge research interest in this area [5][9]. MXene have a flexible and layered structure. Owning to their 2D morphology, they can easily form composites with other materials, so they can integrate the properties of different materials in a complementary way.

Due to their low vapour pressure, excellent conductivity, non-flammability, and outstanding electrochemical activity, MXene and its composites can operate at very high voltages compared to the other electrolytes. Therefore, they can find use as high-performance electrodes in energy storage devices, catalysis, supercapacitors, and pseudocapacitors [2][5][10]. They have cations intercalation capability so they can also work as anode material for Li-Ion batteries [8][11]. Researchers are also looking to use MXene as reinforcement for other composites, to increase their mechanical properties.

Recently MXenes and MXene-based composites find prominent use in the environment related fields. They have been used as efficient catalysts or co-catalysts for electro/photocatalytic water splitting and photocatalytic reduction of carbon dioxide (CO_2). They can remove contaminants in water including heavy metal ions, organic dyes, eutrophic substances, and nuclear waste. They have also been applied to biosensors and gas sensors, and exhibiting excellent performances. Many theoretical papers have synthesized and MXene and predicted their properties and applications.

Herein, we have analyzed the MXene Ti_3C_2 which was selectively etched and exfoliated from Ti_3AlC_2 MAX Phase. A complete analysis on its structural, morphological, and elemental properties has been done. The reports suggest that the synthesized MXene samples could be used for various sensing, electromagnetic shielding and energy harvesting, and storage applications.

2. MATERIALS AND METHODS

2.1. Materials

For the synthesis of MXenes, MAX phase Ti_3AlC_2 powder (Sigma Aldrich), the etchants which include hydrofluoric acid (HF) and hydrochloric acid (HCl), and dimethyl sulfoxide (DMSO) for delamination were used. All chemicals are analytical grade and used directly without further purification. Prior to the experiment, teflon and glass beakers were cleaned with aqua regia for 3 hours, soap solution, and de-ionized water, respectively.

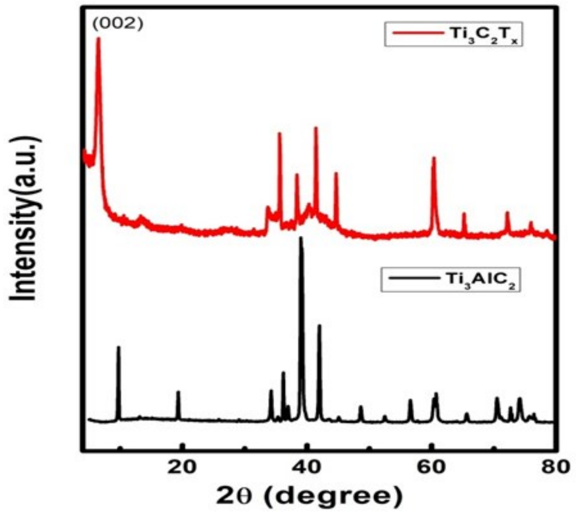

Figure 1. X-ray diffraction spectra of Ti_3AlC_2 (MAX phase) and $Ti_3C_2T_x$ (MXene).

2.2. Synthesis of $Ti_3C_2T_x$

MXenes synthesis was done through selective etching of aluminium layers from the bulk MAX phase at room temperature. With a combination of HF and HCl of different concentrations of etchant is used to etch out of the MAX phase powder. $Ti_3C_2T_x$ was synthesized by etching Al from Ti_3AlC_2 of 1 gram appropriated from teflon beaker and 20 mL of etchant in which 30%wt HF and 9M HCl is further blend for 48 hours. As the etching is concluded, the

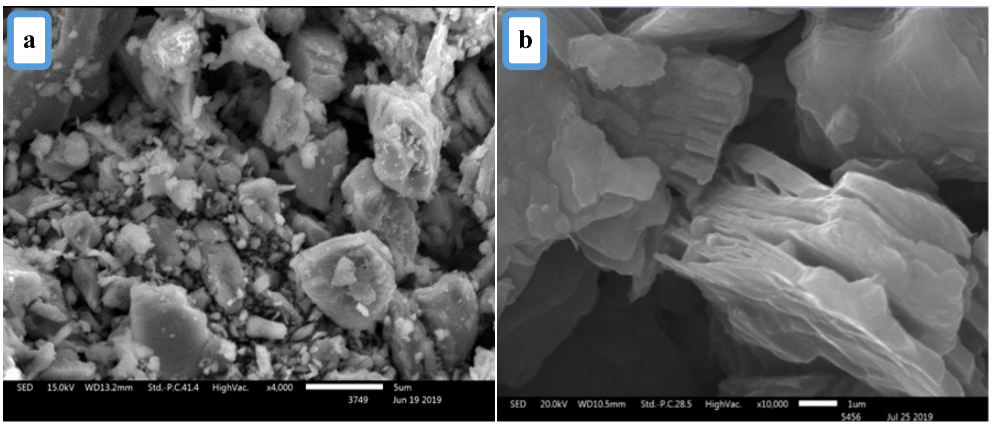

Figure 2. (a) Represents the SEM pictograph of Ti_3AlC_2 (MAX Phase) and (b) represents the exfoliated accordion type morphology of stacked layers of $Ti_3C_2T_x$ (MXene) flakes.

solution is cleaned numerous times via centrifugation at 7,000 rpm for 10 minutes for the respective cycle until the pH value reached approx 6. The etching is not sufficient for complete removal of aluminium, so for further exfoliation, the above-exfoliated powder is intercalated with DMSO for 8 hours. Then, the intercalated sample is sonicated in deionized followed by washing several times at 7000 rpm to remove the residual. Then, the obtained powder sample is treated with 1 M NaOH and further washed away. After washing, the obtained sample is dried in an oven at 60 °C for 48 hours for obtaining flakes MXenes powder.

Table 1. Average crystallite size and Interplanar spacing of MAX phase and MXene.

Parameters	Ti_3AlC_2 (MAXphase)	$Ti_3C_2T_x$ (MXene)
Avg. Crystallite size (nm)	37.56	14.68
Interlayer spacing (Å)	9.07	8.03

2.3. Material Characterization Techniques

X-ray diffraction (XRD) analysis was carried out for structure characterization with a powder diffractometer (BRUKER, ecoD8 ADVANCE) with Cu K_α radiation (wavelength=1.5418 Å). A scanning electron microscope, SEM, (JEOL JSM - 7600F) equipped with an energy dispersive spectrometer, EXS was cast-off for getting surface morphological and elemental confirmation.

3. RESULTS AND DISCUSSIONS

3.1. Structural Analysis

Figure 1 shows the X-ray diffraction plot of the prepared Ti_3AlC_2 MAX phase and $Ti_3C_2T_x$ MXene. In this plot, the dominant peak of Ti_3AlC_2 MAX phase appears at 2θ~9° while for the $Ti_3C_2T_x$ Mxene appears at 2θ ~11°. Those peaks correspond to the (002) planes of hexagonal crystal structure. The multiple peaks show that the MAX phase powder and MXene powder were polycrystalline in nature. The MAX phase powder had excellent crystallinity compared to MXene powder. The crystallite size of MAX phase powder and MXene powder were calculated by using the Debye-Scherrer formula:

$$D=\frac{0.9\lambda}{\beta\cos\theta} \quad (1)$$

Where λ is the wavelength of X-ray, θ is the Bragg's angle, and β is the full width at half maxima (FWHM) of the dominating peak corresponding to the (002) plane.

The average crystallite size of Ti_3AlC_2 MAX phase was 37.56 nm and $Ti_3C_2T_x$ MXene was 14.68 nm as shown in table 1. It is observed that the crystallite size decreases after etching. In comparison of Ti_3AlC_2 MAX phase and $Ti_3C_2T_x$ MXene, most of the diffraction peaks disappeared in $Ti_3C_2T_x$ MXene. It shows the depletion of Ti_3AlC_2 MAX phase into $Ti_3C_2T_x$ MXene phase (i.e. removal of Al). The intensity of the peak at 39° almost decreased, which shows the removal of Al [12]. In addition, the shift of $Ti_3C_2T_x$ MXene peaks from 9.74° to 11.11° shows the compression of the interlayer distance from 9.07Å to 8.03Å.

3.2. Morphological study through SEM

The surface topography image analysis of obtained synthesize MXenes flakes were carried-

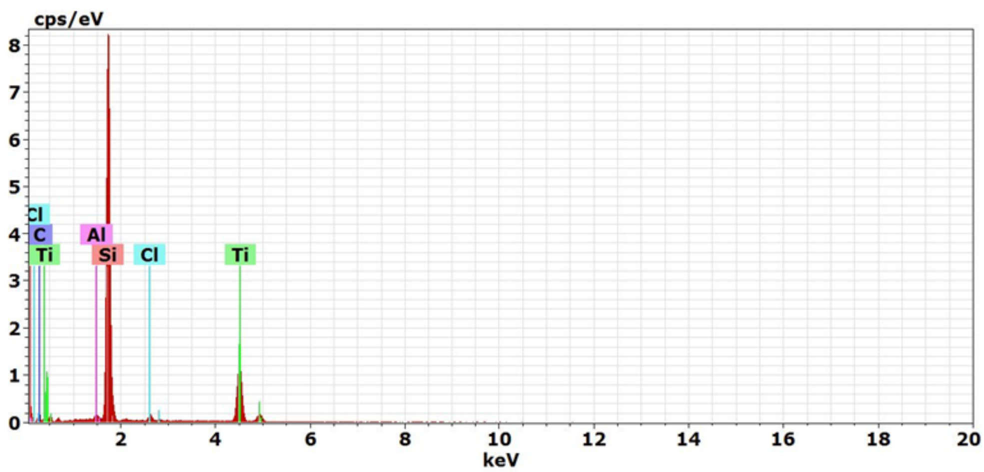

Figure 3. Typical EDX spectra of $Ti_3C_2T_X$ after the selective etching of aluminium layers from the MAX Phase.

out via SEM. The tightly bonded layer of the MAX phase flakes are found be exfoliated following HF and HCl etchings. In general, the stacked layers of MXene resemble to the shape of accordion with irregular profile bounded by weak Van der Waals force. The layers could be more exfoliated via the delamination process. Figure 2 shows the SEM image of Ti_3AlC_2 (MAX phase) and $Ti_3C_2T_x$ (MXene).

Table 2. The percentage of elements present in the sample after the formation of MXene.

Element	Series	Atomic %
Silicon	K-Series	36.48
Titanium	K-Series	13.69
Carbon	K-Series	48.49
Chlorine	K-Series	0.85
Aluminium	K-Series	0.49
	Total	100

3.3. Elemental Analysis from EDX spectroscopy

The information about the elemental composition in the exfoliated MXene sample is given by the energy-dispersive X-ray (EDX) spectroscopy in figure 3. It is evident from the plot that the traces of aluminium in the sample are negligible, i.e. below 0.5%. The presence of chlorine is in small amount but it is assumed to be as a result of HCl used in the process of etching of the sample and is proportionately higher than aluminium. A greater intensity peak of silicon is noticed because of the silicon substrate upon which the MXene sample is drop casted for various analyses. Carbon is present in large quantity whereas titanium is comparatively low in concentration. Table 2 gives a tabular representation of the concentration in weight percentage of each element present in the sample.

4. CONCLUSIONS

2D materials like MXene are newly discovered ceramic materials, which have the features to incorporate the properties of different materials. This paper highlights the MXene synthesis with a fusion of etchants like HF in combination with HCl that precisely etched the aluminium layer. The XRD demonstration of phase represents the excellent crystallinity and the most prominent peak arises in the range of 9-11° representing the (002) plane. SEM displays non-uniform profile of MXene having accordion like structure after further delamination process. The EDX plot reveals that most of the aluminium are easily etched from the MAX phase, although the negligible traces of aluminium < 0.5% is still present. MXene synthesized by the selectively etching process can be best suited for applications in energy storage devices where the high voltage operation of its composites can swiftly carry out the Faradaic reactions.

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