Mechanochemical synthesis of fluoride-free Ti_3C_2

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Intruduction

MXenes, a family of two-dimensional (2D) layered early transition metal carbides and carbonitrides, have rapidly drawn intensive research attention due to their high metallic conductivity, large theoretical specific surface area, excellent mechanical properties, and high hydrophilicity. Their general chemical formula is $M_{n+1}X_nT_x$ (n=2-4), where M represents a transition metal, X is carbon and/or nitrogen, and T stands for surface termination groups (–OH, –F, –O).

$Ti_3C_2T_x$ was the first MXene reported in 2011, and more than 25 different MXene compositions have been synthesised since then. To date, most MXenes have been prepared through the wet chemical etching methods where A-element atomic layers (e.g., aluminum) are etched from the $M_{n+1}AX_n$ phase (e.g., Ti_3AlC_2) using highly hazardous HF or LiF/HCl solutions. Therefore, there is an urgent need to explore safe, reliable, and fluorine-free synthetic methods to prepare MXene.

In this work, we describe fluoride-free mechanochemical route for the preparation of the Ti_3C_2 MXene from the Ti_3AlC_2 MAX phase. It consists of a ball-milling of the MAX phase with LiCl or $ZnCl_2$, followed by washing and ultrasonication in order to completely exfoliate the MXene sheets. The prepared MXene was studied by powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and dynamic light scattering (DLS). The results reported here pave the way for new preparation methods for various fluoride-free Mxenes.

Experimental

High energy ball milling was utilized to prepare $Ti_3C_2T_x$ MXene from the Ti_3AlC_2 MAX phase. 300 mg MAX phase powder was placed in a plastic jar with 120 mg $ZnCl_2$ or LiCl (40 %) and a stainless steel balls 2xØ7 mm. The product was a black powder that could be easily collected from the jar using a spatula. After milling, the material was ultrasonically treated with HCl (10 %) and ethanol (96 %) for 30 to 120 min. Then, washing was carried out using centrifuge (2500 rpm, 5 min), with all material placed in a 50 ml plastic bottle and topped with deionized (DI) water. Cascading washing cycles (with replacement of DI water and sonicating between each cycle) were necessary to bring the pH up to ~6. When the MX3 solution acidity had been optimised a portion of supernatant was carefully separated from the sediment and collected for characterization (MX3_S).

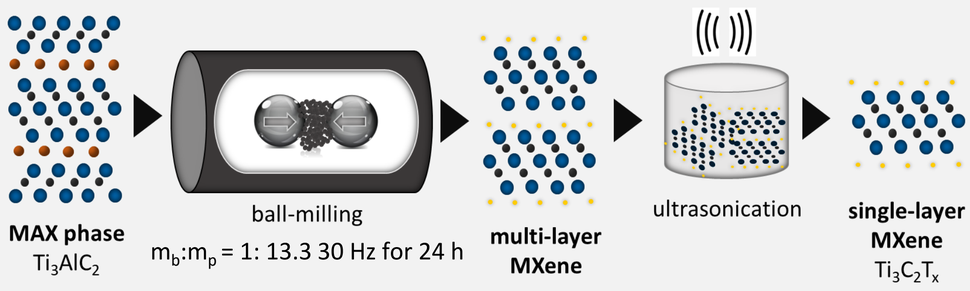

Table 1. Synthesis conditions employed to obtain $Ti_3C_2T_x$ powders.

MXene	MAX phase	Etching agent	Milling parameters	Ultrasonication parameters
MX1	Ti_3AlC_2	$ZnCl_2$	30 Hz, 24 h	Ethanol, 96 %, 40 min
MX2	Ti_3AlC_2	$ZnCl_2$	30 Hz, 24 h	Ethanol, 96 %, 120 min
MX3	Ti_3AlC_2	LiCl	30 Hz, 24 h	HCl, 10 %, 30 min

Analysis

- ✓ XRD
- ✓ SEM
- ✓ DLS

Results and discussion

X-ray diffraction (XRD) pattern is used to characterise the structure of the samples. Fig. 1 shows the X-ray diffractograms of the Ti_3AlC_2, MX1, MX2 and MX3_S respectively. For the MX1 and MX2 (Fig. 1a) the almost completely eradication of the (104) peak at 2θ ~39° indicates the conversion of Ti_3AlC_2 to $Ti_3C_2T_x$. Furthermore, the (002) peak at 2θ = 9.51°, which corresponds to the (002) crystal plane that is related to interlayer space between Ti_3C_2 planes bound by Al^{3+} ions, decrease in intensity and shifts towards lower value of 9.28°. An increase in the interlayers spacing is responsible for this shift in the (002) angle, providing further evidence that there have been changes in the main structure of MAX phase. For the MX3_S sample (Fig.1 b) the (002) peak disappeared completely from the XRD spectrum indicating the total oxidation of crystalline MXene to an amorphous structure. The XRD results are in accordance with the DLS analsis. Smaller particle sizes were obtain in the HCl and they oxidize faster then the larger flakes obtained in ethanol (Fig. 2.). Because $Ti_3C_2T_x$ is oxidized in the presence of water and oxygen, dispersions in ethanol could provide a better way to mitigate or prevent oxidation and extend the shelf life of $Ti_3C_2T_x$ in solution.

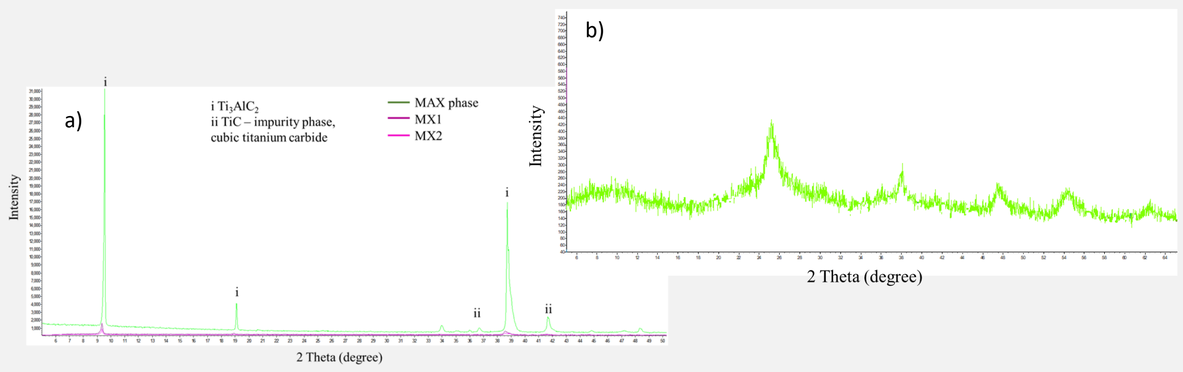

Figure 1. Diffractograms of a) MAX, MX1, MX2 and b) MX3_S samples

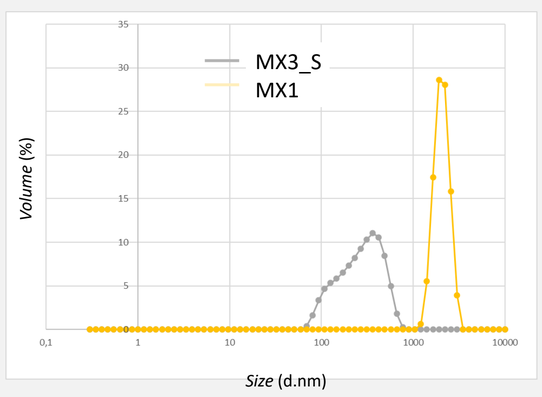

Figure 2. Particle size determination by dynamic light scattering (DLS).

Fig. 3 shows the morphology and elemental composition of the MAX powder and raw MX1, MX1 and MX3_S samples. Raw MX1 is obtained after MC treatment of the MAX phase without the ultrasonication step. Fig. 3a illustrates the typical compact layered structure of the Ti_3AlC_2, while the morphology of the materials obtained after MC treatment (Fig 3b,c,d) shows a smaller particle size with vaguely defined edges. After grinding the MAX phase with the $ZnCl_2$, the presence of the holes in the material are visible (Fig. 3b). The size of the holes ranged between 100 and 500 nm. It may be concluded that presence of the $ZnCl_2$ during the ball-milling process is responsible for the formation of the holes. After the ultrasonication treatment with ethanol the holes on the MXene surface have evidently disappeared indicating damaging and tearing of the material (Fig. 3c). Morphology of the MX3_s is more aggregated but consist of small particle. The elemental distribution in the MXene were determined using EDX analysis. It is clearly that the best etching of the Al is obtained in the MX3_S with only 1.36 at% Al, compared to 9.02 and 17.90 at% in the raw MX1 and MX1, respectively. It is worth mentioning that only in the MX1 there was no O terminal groups or other impurities.

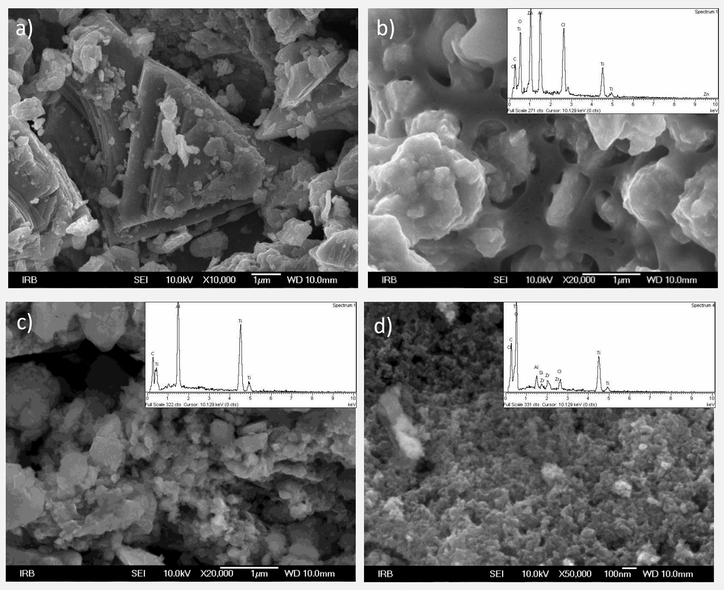

Figure 3. SEM images of the a) MAX , b) raw MX1, c) MX1 and d) MX3_S. Insert shows EDX analysis.

Conclusions

- ✓ MC method is simple and safe route to obtain Mxene material.
- ✓ Introducing $ZnCl_2$ into the etching process generated macropores into the surface of the material.
- ✓ Using ethanol can effectively prevent MXene oxidation.