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Synthesis and thermal stability of two-dimensional carbide MXene Ti_3C_2

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ABSTRACT

We investigated the synthesis of quasi-two-dimensional carbide (Ti_3C_2), with the name of MXene, by immersing Ti_3AlC_2 in 40% or 49% hydrofluoric acid (HF) at 0 °C, 15 °C or 60 °C. The influences of time, temperature, and source of Ti_3AlC_2 on the synthesis were researched. It was found that Ti_3C_2 synthesized from pressureless synthesized Ti_3AlC_2 was highly oriented compared to that from hot-pressed Ti_3AlC_2. As-synthesized Ti_3C_2 could be further exfoliated by intercalation with urea, dimethylsulfoxide or ammonia. From the results of thermogravimetry and differential scanning calorimetry, Ti_3C_2 MXene with F/OH termination was found to be stable in argon atmosphere at temperature up to 800 °C. In oxygen atmosphere, at 200 °C, parts of MXene layers were oxidized to obtain an interesting structure: anatase nano-crystals were evenly distributed on 2D Ti_3C_2 layers. At 1000 °C, MXene layers were completely oxidized and anatase phase fully transformed to rutile in oxygen atmosphere.

1. Introduction

Two-dimensional (2D) materials, such as graphene [1], are well known to have unique properties and important applications. In general, 2D materials are produced by exfoliating layered 3D materials with weak van der Waals-like coupling between layers. During the last decade, some 2D materials such as hexagonal boron nitride [2], metal oxides [3], and chalcogenides [4] have been synthesized by chemical exfoliation or mechanical cleavage of layered 3D precursors.

However, there was no report on the synthesis of 2D nanocrystalline materials by exfoliation of layered solids with strong primary bonds until Naguib et al. [5,6] synthesized two-dimensional transition metal carbides by HF exfoliating from MAX phases: Ti_3AlC_2, Ti_2AlC, etc. These 2D materials were made by removing "A" element from MAX phase and named as MXenes to emphasize their graphene-like morphology. MXenes are conductive and hydrophilic 2D materials. From experiments [7–9] and theoretic computation [10], MXenes are very promising electrode materials for lithium-ion batteries and supercapacitors. Additionally, we found that MXene are promising hydrogen storage medium [11], lead adsorption medium [12], and catalyst [13]. The research on MXenes opened a door for the synthesis of a large number of 2D $M_{n+1}X_n$ structures and attracted the attention of many scientists [14–16].

MAX phases, the precursors of MXenes, are ternary carbides or nitrides with the general formula of $M_{n+1}AX_n$, where M is an early transition metal; A is an A-group element (mostly group IIIA or IVA); X is either carbon or nitrogen and the value of n can be 1, 2, or 3 [17–20]. A typical MAX compound consists of metallic A layers and ceramic $M_{n+1}X_n$ layers. A layers are chemically more active than $M_{n+1}X_n$ layers [21]. 2D MXenes were made by removing A layers from MAX phases by HF etching [5,6]. The surfaces of MXene made in HF solution are usually terminated by F and/or OH groups due to its high surface energy. Fig. 1 shows the chemical structures of a typical MAX phase (Ti_3AlC_2) and MXene (Ti_3C_2) with OH termination. The later can be made from the former by HF etching and sonication.

Thereafter, many theoretic papers predicted the properties and applications of these novel 2D materials [10,11,16,22–25]. However, there are only a few reports on the experimental synthesis and characterization of MXenes.

In this paper, for fully understanding MXene synthesis process, Ti_3C_2 MXene was made by exfoliating Ti_3AlC_2 with HF acid at different temperature for different time. In order to further exfoliate 2D MXene, as-synthesized MXenes were intercalated with urea, dimethylsulfoxide or $NH_3{\cdot}H_2O$.

Besides the synthesis procedure, we studied the thermal stability of Ti_3C_2 2D sheets in oxygen or argon atmosphere. This property

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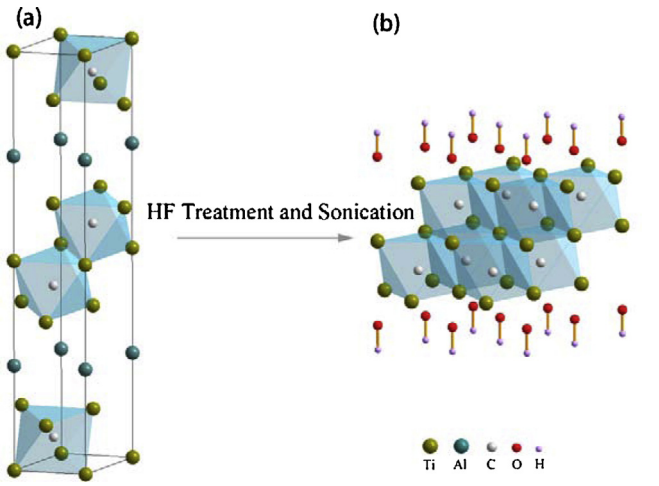

Fig. 1. Chemical structures of (a) Ti_3AlC_2 (a typical MAX phase), and (b) Ti_3C_2 (a typical MXene) with OH termination. Ti_3C_2 is made from Ti_3AlC_2 by HF etching and sonication.

is very important for the application of these materials at high temperature. As far as the authors know, this is the first report on the experimental measurement of MXenes' thermal stability. Additionally, the thermal process of MXenes in oxygen atmosphere obtained an interesting structure, that anatase nano-crystals were evenly distributed on conductive 2D Ti_3C_2 layers.

2. Experimental

Two kinds of Ti_3AlC_2 powders were used in this paper. One (HP-Ti_3AlC_2, 98 wt.% pure) was obtained by grinding hot-pressed (HP) Ti_3AlC_2, which was made from 3Ti/Al/2C mixture by hot-press at 1400 °C under 25 MPa for 2 h with a heating rate of 20 °C/min. The other (PLS-Ti_3AlC, 98 wt.% pure) was pressureless synthesized powders from TiH_2/Al/2TiC by a tube furnace with flowing Ar atmosphere at 1450 °C for 2 h with a heating rate of 15 °C/min [26]. Both HP-Ti_3AlC_2 powders and PLS-Ti_3AlC_2 powders passed through a 325-mesh screen. Ten grams of Ti_3AlC_2 were immersed in 100 ml 40% or 49% HF solutions (Aladdin Reagent, Shanghai, China). The solution was stirred for 1 min, and then kept at different temperature (0 °C, 15 °C, or 60 °C). After some time, the samples were washed by deionized water and MXene powders were centrifugally separated from supernatant. The powders were washed by deionized water until the pH value ≈ 7, then washed by ethanol twice. Thereafter, they were dried in a vacuum oven at 80 °C for 24 h.

The intercalation experiment was carried out with dimethyl sulfoxide (DMSO), urea, or $NH_3{\cdot}H_2O$, respectively. The intercalation procedure was: (1) 0.5 g MXene powders were mixed with 10 ml DMSO and then magnetically stirred for 18 h at room temperature; (2) 0.5 g MXene powders were mixed with 6 ml $NH_3{\cdot}H_2O$ (25–28%) and then magnetically stirred for 2 h at room temperature; (3) 0.5 g powders were mixed with 3 g urea and 10 ml water, then magnetically stirred for 24 h at 60 °C. Thereafter, the samples were washed several times by deionized water and then dried in a vacuum oven at 80 °C.

X-ray diffraction (XRD) patterns were obtained from powders directly without further treatment with a diffractometer (Brukeraxs Co., Germany) using Cu K_α radiation. A scanning electron microscopy (FESEM, S4800, Hitachi, Japan) with an accelerating voltage of 3 kV, and equipped with an energy dispersive spectrometer (EDS, EMAX ENERGY EX-250, Horiba, Japan), was used to obtain microstructure images. Transmission electron microscope (TEM, JEOL JEM-2100, Japan) with an accelerating voltage of 200 kV, was used to investigate the structure of some 2D MXene powders.

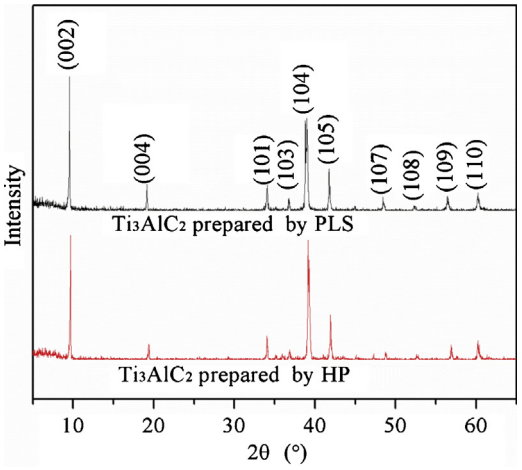

Fig. 2. XRD patterns of Ti_3AlC_2 as starting material.

Thermal stability of obtained MXene was measured by using a Setaram Evolution 2400 thermal analyzer with α-Al_2O_3 pans under argon/oxygen flow of 20 ml/min with a heating rate of 15 °C/min from room temperature (RT) to 1000 °C.

3. Results

3.1. XRD analysis of exfoliation process to synthesize MXene

The XRD patterns of two Ti_3AlC_2 powders as starting materials are shown in Fig. 2. The two patterns are very similar and both show peaks corresponding to quite pure Ti_3AlC_2. Fig. 3 shows the XRD patterns of samples exfoliated by 40% HF or 49% HF at 0 °C for 2 h, 24 h or 72 h, respectively. For either 2 h or 24 h etching, the etched samples still mainly consisted of Ti_3AlC_2 without Ti_3C_2 MXene. If etching time was extended to 72 h, the strongest peak of Ti_3AlC_2, (1 0 4) peak at 39.2°, obviously decreases. Therefore, part of Ti_3AlC_2 reacted with HF to form Ti_3C_2. In the figure, (0 0 2) peak at 9.7° and (0 0 4) peak at 19.4° are bifurcated into two minor peaks. One minor peak keeps in the original position, which belongs to Ti_3AlC_2. The other minor peak shifts to low angle, which belongs to newly formed Ti_3C_2 MXene. A conclusion can be drawn that, at 0 °C, no matter what the concentration of HF acid was, at least 72 h was required for the beginning of Ti_3AlC_2 exfoliation.

Fig. 4 shows the XRD patterns of samples processed at 15 °C. Similar with the 0 °C results shown in Fig. 3, at least 72 h was required for the exfoliation of Ti_3AlC_2. As shown in Fig. 4b, for 72 h sample, a new peak at 9.1° appeared near the (0 0 2) peak of Ti_3AlC_2 at 9.7°. The 9.1° peak belonged to Ti_3C_2 MXene. A long exfoliating time, 168 h, resulted extensive generation of MXene as shown in the figure. However, there was a little residual Ti_3AlC_2 in 40% HF sample and some TiC was formed in 49% HF sample. Therefore, at 15 °C, 168 h was not long enough to make pure MXene by 40% HF exfoliation while it was too long for the process of 49% HF exfoliation.

Theoretically, high temperature and high concentration of HF are favorable for the synthesis of MXene. Fig. 5 shows the XRD patterns of sample exfoliated at 60 °C by 49% HF. Different from literature reports [5,27], 2 h was not enough for the fully exfoliation of Ti_3AlC_2. As processing time increased, Ti_3AlC_2 peaks decrease and MXene peaks appear obviously only if the time >8 h. Weak peaks of Ti_3AlC_2 are still detectable at 12 h sample. However, for 24 h sample, all Ti_3AlC_2 was exfoliated and transformed to MXene with some TiC impurity.

To understand the influence of Ti_3AlC_2 source on the exfoliating process, MXene was made from PLS-Ti_3AlC_2 or HP-Ti_3AlC_2, by 49%