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Effect of Etching Method on the Morphology and Stability of Ti_2CT_x MXene

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For the last decade, two-dimensional early-transition metal carbides and nitrides, known as MXenes, have garnered much research interest because of their unique mechanical, optoelectronic, and chemical properties that are ideal for potential applications in electronics, biosensors, energy storage, carbon capture, and photocatalysis [1-5]. MXenes are formed from selectively etching the A-layer from the three-dimensional ceramic MAX phase, which have the general formula, $M_{n+1}AX_n$, [6] where *M* is an early transition metal, *A* is a Group IIIA or IVA element, *X* is carbide, nitride, or carbonitride, and *n* is an integer (1- 4). Surface termination groups (T_x) form on the MXene surface during the etching procedure, and are usually -O, -OH, and -F if the etching is performed using a harsher direct hydrofluoric acid (HF) or milder *in situ* lithium fluoride salt/hydrochloric acid (LiF/HCl) procedure. While most published research has been on the first discovered MXene, the 3-2 titanium carbide $Ti_3C_2T_x$ MXene [5], the 2-1 titanium carbide Ti_2CT_x MXene has been much less experimentally studied, likely due to its relative instability [7]. In this paper, we present the effect of the etching method on the morphology of the Ti_2CT_x MXene, as observed by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM).

A sample of commercially available MAX phase Ti_2AlC powder (>99%, 375 mesh, Luoyang Tongrun Info Technology Co. Ltd., Luoyang, Henan, China) was obtained and used without any further purification or milling. Batch 1 Ti_2CT_x MXene was prepared by etching Al from Ti_2AlC powder in a HF aqueous solution (>48%, Sigma Aldrich, St. Louis, MO, USA). First, 5.05g of Ti_2AlC powder was slowly added into a polyethylene bottle containing 45-mL of HF solution. Next 15 mL of deionized (DI) water was slowly added to flush all the powder into the solution, and the resulting solution was magnetically stirred at 300 rpm for about 46 hours at ambient temperature (21 °C). The crude Ti_2CT_x product was collected and centrifuged at 4500 rpm for 20 minutes and further washed three times with 40 mL of 6 M HCl followed by seven times with DI water. The pH of the decantate for each cycle of the DI water wash was monitored until a pH>6 was reached. The Ti_2CT_x product was transferred in a 100-mL beaker and placed inside an oven at 75°C for about 24 hours to get the solid product (0.482 g). Batch 2 Ti_2CT_x MXene was prepared by etching Al from Ti_2AlC powder in a solution prepared by dissolving 4.81 g LiF in 100 mL of 6 M HCl. First, 5.00 g Ti_2AlC powder was slowly added into a polyethylene bottle containing 100 mL LiF/HCl solution and magnetically stirred at 300 rpm for 144 hr at room temperature (21 °C). A 5:1 mole ratio of LiF to Ti_2AlC was used during the etching. The crude Ti_2CT_x product was collected and centrifuged at 4500 rpm for 20 minutes and further washed three times with 6 M HCl followed by 17 times with DI water until the decantate reached a pH>6. The product was transferred in a 100-mL beaker and placed inside an oven at 75°C for about 24 hours for the solid product (3.60 g).

XRD measurements of the Ti_2CT_x powder were conducted on a Rigaku Miniflex 600 X-ray diffractometer, operating at a 20 kV voltage and a 2 mA current, and collected over a scan range of 5-90° at a rate of 0.075°/min. **Figure 1** shows the XRD patterns of HF and LiF-etched Ti_2CT_x samples. The typical peaks of HF-etched Ti_2CT_x sample are within this range and are consistent with the

previously published results [8]. The XRD patterns of LiF-etched Ti_2CT_x sample has several additional peaks suggesting incomplete etching of Ti_2AlC. The peaks at 25° and 54° are assigned to AlF_3, and the peaks at 13°, 39° and 48° are attributed to unetched Ti_2AlC [7].

For morphological characterization, a solution of Ti_2CT_x in DMSO was drop casted on glass, dried, sputter-coated with gold and imaged in a JEOL JSM-6510LV SEM. **Figure 2** shows the SEM images of HF and LiF-etched Ti_2CT_x thin films prepared under similar conditions. We observed a discrete layered/sheet structure with well-crystallized feature in both films. However, the LiF-etched Ti_2CT_x has a more layered structure with larger grain size compared to the HF-etched Ti_2CT_x (**Figure 2**). This suggests that the 2D-layered structure can be disrupted by the harsh HF etching as also indicated by the lack of the low angle peak (8°) in the XRD yet present in the LiF-etched Ti_2CT_x (**Figure 1**). The smaller grain size is also supported by the decreased yield (0.482 g) of processed Ti_2CT_x from the HF-etched method compared to that (3.60 g) from the LiF-etched method, even though nearly identical amounts of Ti_2AlC were used.

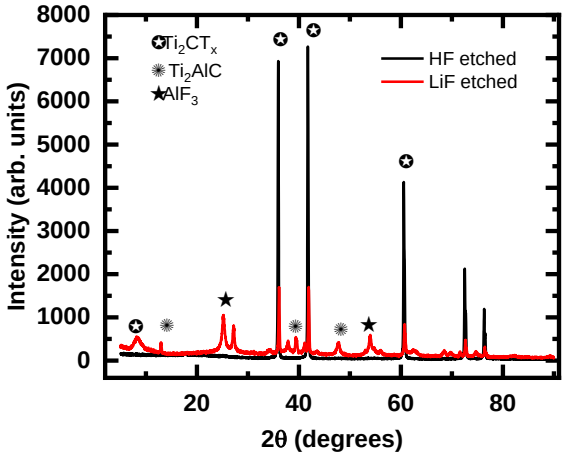

Figure 1. XRD patterns of HF and LiF etched Ti_2CT_x MXenes

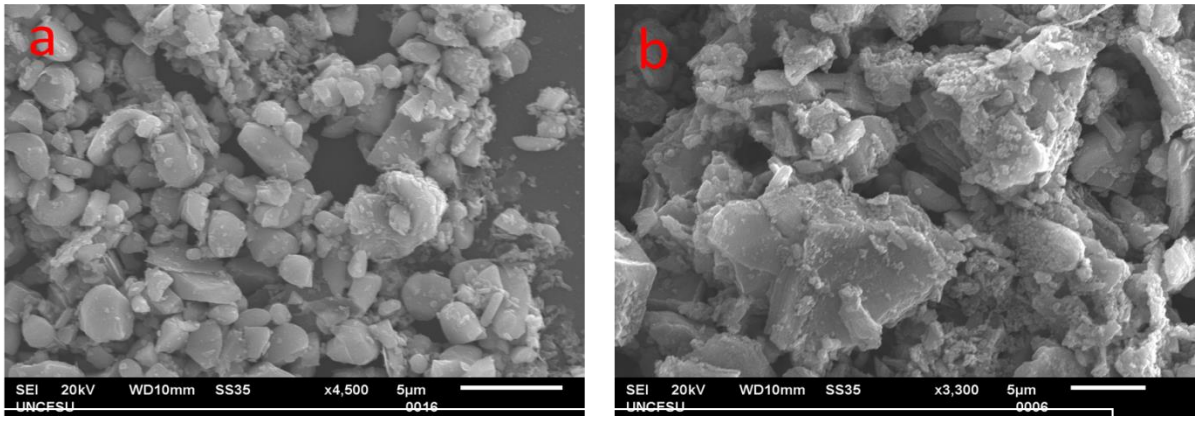

Figure 2. XRD patterns of HF (a) and LiF (b) etched Ti_2CT_x MXenes.

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