Comment on ‘Multilayered stable 2D nano-sheets of Ti_2NT_x MXene: synthesis, characterization, and anticancer activity’

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Abstract

A recent article entitled “Multilayered stable 2D nano-sheets of Ti_2NT_x MXene: synthesis, characterization, and anticancer activity” published in Journal of Nanobiotechnology, claimed that two-dimensional Ti_2NT_x MXene could be synthesized by selectively etching Ti_2AlN in concentrated hydrofluoric acid at room temperature. However, the X-ray diffraction pattern of Ti_2NT_x MXene reported in that paper is completely different with those of other MXenes. In this comment, it is argued that the samples synthesized in that paper were NOT Ti_2NT_x MXene at all. Although carbide MXenes can be made by selectively etching A layers from MAX phase, it is very difficult or impossible to make nitride MXenes (Ti_2NT_x) by the same way.

Keywords: MXene, Ti_2NT_x, Selectively etching

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Background

The recent paper by Szuplewska et al. published in Journal of Nanobiotechnology [1] is on the synthesis of Ti_2NT_x MXene. MXenes are novel two-dimensional (2D) materials, which are prepared by selectively etching away A-site element from MAX ($M_{n+1}AX_n$) phase with hydrofluoric acid (HF) or fluoride salts solutions[2, 3], where M is an early transition metal, A usually belongs to groups IIIA and IVA, X is carbon and/or nitrogen. In general, MXenes are made from carbide MAX phases (e.g. Ti_3AlC_2)[4] or carbonitride MAX phases (e.g. Ti_3AlCN)[5]. It is very difficult to make MXene from nitride MAX. Ti_2AlN is the most common nitride MAX phase. If Ti_2AlN can be selectively etching, Ti_2NT_x MXene can be made and it is predicted to have excellent properties. However, there is only one report on the experimental synthesis of Ti_2NT_x MXene by Soundiraraju et al. at 2017[6]. In that report[6], it was claimed that Ti_2NT_x MXene was successfully made from Ti_2AlN by KF/HCl etching. However, as the authors know, there are no reports to repeat that work.

The commented paper published in 2019[1] is the second paper to claim the successful synthesis of Ti_2NT_x MXene from Ti_2AlN. The etching solution is HF. However, the X-ray diffraction (XRD) patterns of Ti_2NT_x MXene in the paper are completely different with that in the first paper in 2017[6]. Although the experiment in 2017 paper[6] has not been repeated, the XRD pattern of Ti_2NT_x MXene in that paper was similar with those of other MXenes ($Ti_3C_2T_x$[7] or Ti_2CT_x[8]). The feature of MXenes’ XRD patterns is that there is a very strong (002) peak and other peaks are very weak. However, the XRD pattern in the commented paper[1] is completely different with that in Ref. [6] and does not have the feature of MXenes’ patterns. In addition, it was acknowledged in the paper [1] that the structure of Ti_2NT_x MXene was far from ideal. Moreover, in a recent work[9], it is theoretically indicated that Ti_2NT_x MXene cannot be successfully synthesized in HF solution from Ti_2AlN, due to the fact that single layered nitride MXenes possess poor stability in the solution. Thus, we think that Ti_2NT_x MXene was not successfully synthesized in the commented paper.

Experiment and discussion

In order to prove this thought, the following experiment was carried out. 2 g Ti_2AlN (< 25 μm, lab made) was immersed in two etching solutions with magnetic stirring. One solution was 20 ml hydrofluoric acid (HF, ≥ 40.0 wt.%; Yantai Far Eastern Fine Chemical Company, China). The other was 2 g KF (>99 wt.%; Aladdin, China) + 40 ml 6 M HCl (36 ~ 38 wt.%; Yantai Shuangshuang Chemical Company, China). The suspension after etching was further ultrasonically treated at room temperature for 1 h. Thereafter etched powders were separated from the suspensions by centrifuge. The powders were dried under vacuum at 60 °C for 8 h.

The composition of samples were detected by an X-ray diffractometer (XRD; Rigaku, Samart-lab, Tokyo, Japan) with Cu K_{α} radiation, λ = 1.5406 Å.

The XRD patterns are shown in Figure 1. Figure 1(a) is the XRD pattern of Ti_3C_2 MXene in Reference [4]. Figure 1(b) is the XRD pattern of the sample etched in HF solution at 30 °C for 1 h. Figure 1(c) is the XRD patterns of the sample treated in KF+HCl solution at 60 °C for 24 h. Figure 1(d) is XRD pattern of commercial TiN powders (TiN, >99 wt.%; Macklin, China). The diffraction peaks of TiN from PDF card No. 65-0715 is shown in Figure 1(e). Figure 1(f) is the XRD pattern of Ti_2AlN powders before etching.

Figure 1(a) is a typical XRD pattern of MXene. All MXenes have similar XRD pattern with one strong peak at 2θ = ~7°, corresponds the (002) plane. Figure 1(b) and Figure 1(c) are completely different with Figure 1(a), and are consistent with the XRD pattern of etched sample obtained by Szuplewska et al[1] (red line pattern in Figure 2(I) in that paper). Thus those etched samples cannot be Ti_2NT_x MXene. The XRD patterns of those samples in Figure 1(b-c) agree well with the pattern of commercial TiN in Figure 1(d). All the three patterns can be perfectly indexed by PDF card No. 65-0715 in Figure 1(e). Therefore, the etched samples in this paper and those in the commented paper [1] are TiN powders with cubic crystal structure. They are NOT Ti_2NT_x MXene.

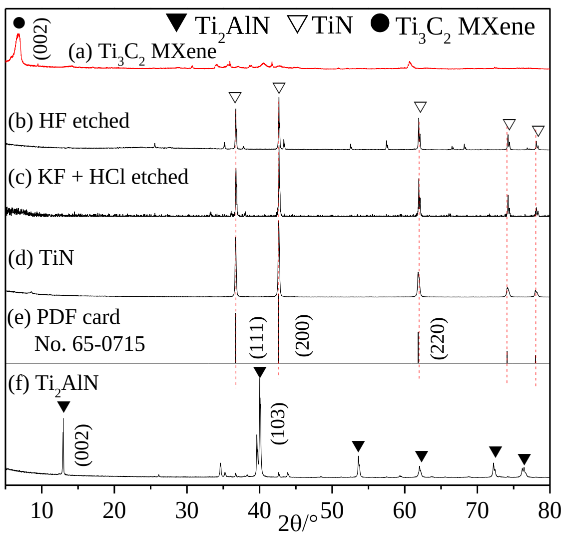

Fig. 1 XRD patterns of different samples

Conclusion

In summary, it is very difficult or impossible to make Ti_2NT_x MXene from Ti_2AlN by selective etching of HF solution or KF + HCl solution. The obtained products in the commented paper was cubic TiN compounds rather than the claimed Ti_2NT_x with 2D structure.

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Authors' Contribution

YG performed the experiments of the work concerning this manuscript and wrote the manuscript. QH analyzed the XRD data. LW guided the experiments and provided critical review. AZ designed the experiments and revised the manuscript. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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