Chinese Chemical Letters 34 (2023) 106898

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

MBenes: Two-dimensional transition-metal borides with ordered metal vacancies

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ARTICLE INFO

Article history:
Received 11 September 2021
Revised 4 October 2021
Accepted 26 October 2021
Available online 29 October 2021

Keywords:
Transition-metal borides
i-MAB phases
MBenes
Monolayer
Ordered metal vacancies

ABSTRACT

2D MBenes have been theoretically predicted to possess unique electronic structures and physicochemical properties, and thus shown great promise in various applications. However, the synthesis of individual single-layer MBene remains a grand challenge due to its orthorhombic structure of MAB phases. Recently, scientists from Linköping University have fabricated 2D monolayer $Mo_{4/3}B_{2-x}T_z$ with ordered metal vacancies. Their results demonstrated the feasibility of top-down approach by chemical exfoliation of laminated compounds and provided the principle for further preparation of a wealth of MBenes.

Ternary layered transition metal nitrides/carbides/carbonitrides (MAX phases, M is a transition metal, A is an A-group element, and X is either carbon or nitrogen) and the derived two-dimensional (2D) MXenes have attracted extensive attention since 2011, due to the abundance of their forms, unique electronic structures and physicochemical properties, and thus shown great promise in applications. Recently, Ade and Hillebrecht successfully fabricated a series of single-crystalline ternary transition metal borides (MAB phases) as analogs of MAX by introducing B as the X element [1]. Therefore, boron-based 2D materials, referred to as MBenes, have correspondingly emerged and theoretically predicted to possess diverse applications in electronic, optoelectronic, and energy devices.

Motivated by chemical exfoliation of MAX to obtain 2D MXene, the Al-containing MAB phases are as promising candidates for obtaining new 2D MBenes. Experimentally, there are mainly three methods for synthesizing 2D MBenes. 2D MoB [2] was first reported to obtain by partially etching of Mo_2AlB_2 phases through the deintercalation of Al layers from ordered stacking faults region. Selectively HCl-etching Al layers from Cr_2AlB_2 yielded the bulk layered CrB nanosheets [3]. Removal of the indium layer through a high-temperature dealloying of Ti_2InB_2 also obtained a bulk layered TiB structure [4]. However, the synthesis of individual single-layer MBene, to date, has not been realized. Because single-layer MBene was quite difficult to synthesize due to its orthorhombic structure of MAB phases which has much higher static exfoliation energy of Al removal than that of MAX phase [5]. To enhance the exfoliation possibility for MAB phases, ternary laminated $M_xM'_{1-x}AlB$ phases (called i-MAB phases) formed by alloying MAB with other transition metals were naturally developed. In this way, obtaining single-layer 2D MBenes with complete Al removal from the i-MAB phases which possess lower static exfoliation energy can become easier.

Recently, single-layer $Mo_{4/3}B_{2-x}T_z$ derived by selective etching of laminated i-MAB phases was successfully fabricated in aqueous hydrofluoric (HF) acid (Fig. 1A) [6]. First, the target material $(Mo_{2/3}Y_{1/3})_2AlB$ i-MAB phase was with close-packed hexagonal structure along [0001] direction (Fig. 1B) with Mo and Y partially overlapped along $[1\bar{1}00]$ direction (Fig. 1C). Furthermore, Mo and Y atoms in the M layer are laminated ordering with Y atoms extending toward the Al layer along the $[11\bar{2}0]$ axis, which can form a Kagomé lattice and was confirmed to be i-MAB structure (Fig. 1D). Thus, after the removal of Al layers, ordered metal vacancies can appear in the 2D $Mo_{4/3}B_{2-x}$ layers due to the additional removal of Y etching. Theoretically, the Y-B bond strength is only 1.3 times as strong as that of Y-Al interaction, so chemical exfoliation to remove Al can also induce the lack of Y atoms. The structure of $Mo_{4/3}B_{2-x}T_z$ layers with XRD (000l) peak at a low angle of 9.35° corresponded to the d-spacing value of 9.23 Å (Fig. 1E) and can increase to 20.37 Å after the intercalation by tetrabutylammoniumhydroxide (TBAOH) with multilayer sheets delaminating

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https://doi.org/10.1016/j.cclet.2021.10.078
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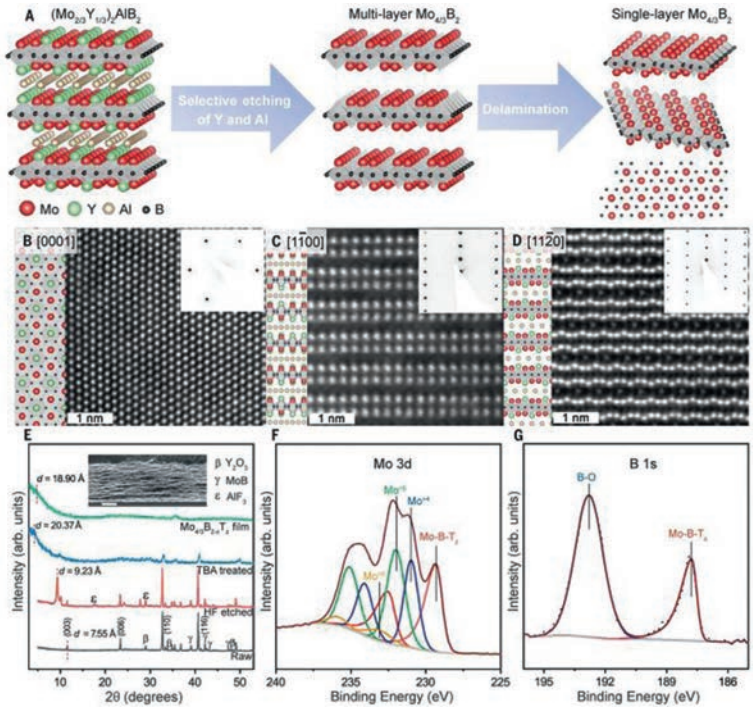

Fig. 1. Synthesis and characterization of 3D $(Mo_{2/3}Y_{1/3})_2AlB_2$ and its 2D derivative $Mo_{4/3}B_{2-x}T_z$ (boridene). (A) Schematic of the transformation process from 3D i-MAB to 2D boridene, (B to D) In-plane chemical ordering of the $(Mo_{2/3}Y_{1/3})_2AlB_2$ i-MAB phase evident from STEM images along the (B) [0001], (C) [1$\bar{1}$00], (D) [11$\bar{2}$0] with corresponding SAED patterns. (E) XRD pattern of $(Mo_{2/3}Y_{1/3})_2AlB_2$ before (black) and after (red) HF etching and after TBAOH intercalation (blue) and delamination (green). (Inset) SEM image showing the cross-section of a $Mo_{4/3}B_{2-x}T_z$ film (scale bar, 2 mm). High-resolution XPS spectra of a filtered film of boridene with peak fittings for the (F) Mo 3d and (G) B 1s regions. Reprinted with permission [6]. Copyright 2021, Science.

in water. The composition in the delaminated layers revealed the presence of Mo, B, O and F, and cross-sectional SEM images and corresponding XPS analysis confirmed the complete conversion from 3D $(Mo_{2/3}Y_{1/3})_2AlB$ to 2D $Mo_{4/3}B_{2-x}$ during the etching process. This work indicates that single-layer 2D MBenes can be prepared from i-MAB phases and also provide a powerful strategy for a wealth of MBenes preparation.

2D MBenes have been theoretically predicted to possess many potential applications in various fields such as Li- and Na-ion batteries, electrocatalysis, and magnetic devices. 2D MnB MBene [7] exhibits robust metallic ferromagnetism (3.2 μ_B per Mn atom) and high Curie temperature (345 K), which can increase to 405 K and 600 K after the functionalization with -F and -OH groups, respectively. W_2B_2 monolayer [8] has an excellent catalytic activity to reduce N_2 to NH_3 under ambient conditions with a low limiting potential of −0.24 eV, as well as Nb_3B_4 (0.50 eV), Ta_3B_4 (0.39 eV), and Ti_2B_2 (0.37 eV). The improved catalytic activity of nitrogen reduction reactions was attributed from strong backdonation between the hybridized d orbital of metal atoms and the 2p orbital in N_2. The theoretical results also confirm that monolayer MBenes are promising electrode materials for hydrogen evolution [9], lithium/sodium ion batteries (LIBs/NIBs) [10] with low diffusion energy barriers (0.22/0.13, 0.28/0.17 and 0.29/0.17 eV for V_2B_2, Cr_2B_2, and Mn_2B_2, respectively) and high Li/Na atomic storage capacities (969/614, 696/492 and 679/483 mAh/g). In addition, 2D MBenes was also attempted and considered to apply in biotechnological fields [11] such as biological recognition, response, and potential impact to living organisms by connecting their biological properties with structural and chemical features.

In summary, boron-based 2D materials as MBenes have been emerged and theoretically predicted to possess diverse applications in Li- and Na-ion batteries, electrocatalysis, and magnetic devices. The synthesis of individual single-layer $Mo_{4/3}B_{2-x}T_z$ derived by selective etching of laminated i-MAB phases have been successfully realized. The top-down approach provides principles and guidance for further preparation of a wealth of MBenes for the common electronic, optoelectronic, and energy devices applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 52172205, 11804166) and the China Postdoctoral Science Foundation (No. 2018M630587) and Tianjin Natural Science Foundation (No. 18JCQNJC77100).

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