Multilayers of two-dimensional (2D) $Ti_2B_2Cl_x$, obtained from selective etching of 3D Ti_2InB_2

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With the rapid expansion of two-dimensional (2D) MXenes [1] efforts have been made to find other families of nanolaminated materials in both 3D and 2D. One such group is boron-containing compounds, known as MAB and MBene phases, where metal (M) and boron (B) layers are separated by layers of A-elements (A=Al, In, etc.) in the MAB precursor. Due to their similarities with MAX phases, experimental attempts to etch these 3D materials into its 2D counterpart have primarily involved selective etching of the A-layers using hydrochloric [2–5] and hydrofluoric acids [6,7] and, more recently, Lewis acids/molten salts have also been attempted [7–10].

Despite, the 2D $Mo_{4/3}B_{2-x}$ boridene synthesized in 2021 [6], the subsequent experimental research, has demonstrated that 2D metal borides are significantly more challenging to obtain than MXenes (metal carbides/nitrides) [11]. For instance, MoAlB phase was only partially etched to Mo_2AlB_2, regardless of of whether molten salt [8] or acid etching [2,4] was used. Molten salt etching of Hf_2InB_2 has resulted in complete oxidation to HfBO [7], rather than forming a halogenated MBene. Additionally, unsuccessful acid etching trials have been reported for Fe_2AlB_2 [6], Mo_5SiB_2 [6], Ti_2InB_2 [12] and Hf_2InB_2 [7]. Further, while In atoms from Ti_2InB_2 have been removed through a dealloying reaction [12], TEM images and the *Cmcm* space group found suggests that the resulting TiB is a 3D material, instead of a 2D counterpart.

Here, we present the synthesis of 2D multilayer $Ti_2B_2Cl_x$, obtained from molten salt ($ZnCl_2$) etching of Ti_2InB_2. Energy Dispersive (EDS) and Electron Energy Loss Spectroscopies (EELS) confirm that indium is fully removed and replaced by chlorine atoms from the salt, leading to an increased c-lattice parameter and a corresponding shift in X-ray diffraction (XRD) peaks to lower angles. Furthermore, transmission electron microscopy (TEM) shows the laminated atomic structure, with chlorine terminations of the stacked 2D sheets. These XRD and TEM results are consistent with density functional theory (DFT) calculations. *In situ* XRD experiments further reveal that the 3D to multilayer (ml) 2D transformation occurs without any intermediate phase. Furthermore, our DFT results provide insights into the reaction mechanism governing this transformation.

This work not only establishes the 3D MAB phases as 2D MBene precursors but also unlocks new possibilities for engineering of 2D multilayer metal borides using molten salt etching, facilitating controlled surface chemistry. This work paves the way for a new class of functional nanomaterials with tunable properties.

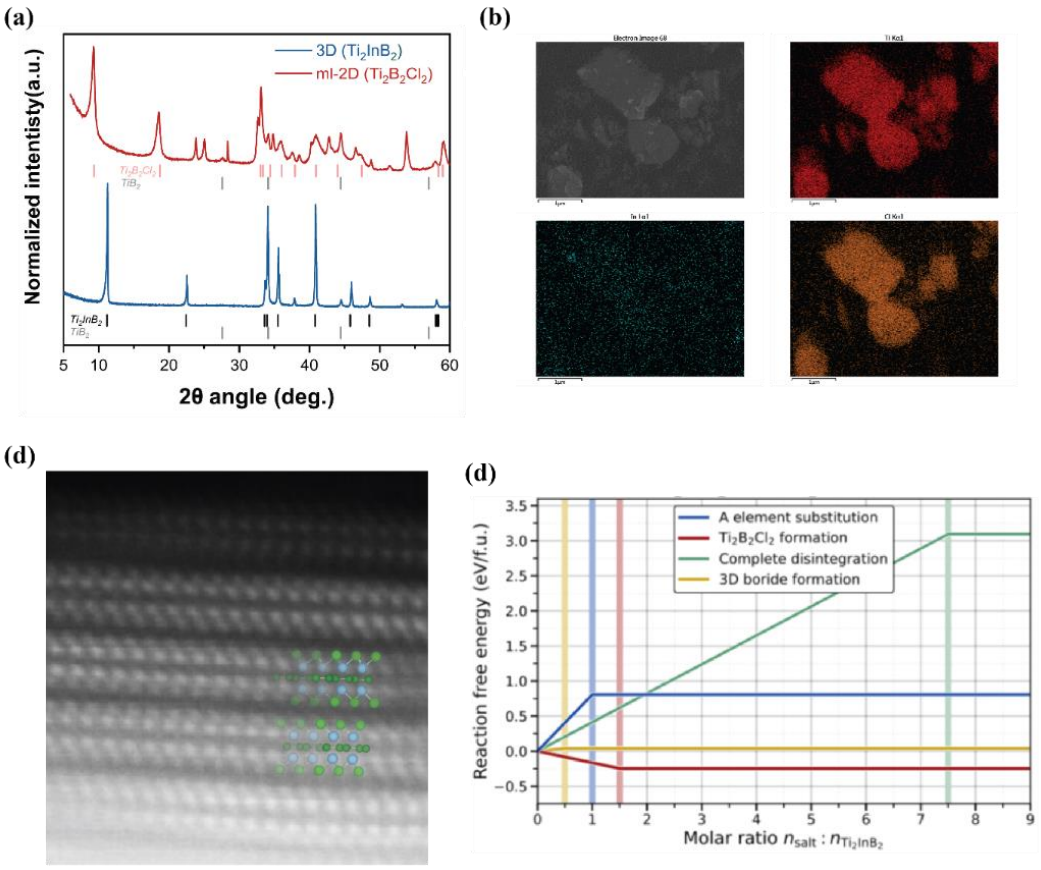

Figure 1: (a) XRD comparing the 3D MAB Ti_2InB_2 and the ml-MBene $Ti_2B_2Cl_x$ structure. (b) EDS maps showing the complete removal of In and replacement by Cl. (c) HRTEM image with the proposed DFT structure and (d) DFT calculations of different paths, showing that the formation of the MBene is preferred.

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