Homoepitaxial growth of 2D titanium carbide MXenes

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MXenes[1] are two-dimensional (2D) transition metal carbides and/or nitrides that are produced by selective etching of the 'A' element (Al, Ga, etc.) from the parent MAX phase(s) or related layered ceramics,[2,3] where 'M' is an early transition metal and 'X' is either carbon or nitrogen. MXenes have recently gained interest for applications that are geared towards electromagnetic interference shielding,[4] energy storage applications,[3,5,6] catalysis,[7] optoelectronics,[8] sensors,[9] and medicine.[10] Although bottom-up synthesis methods for 2D materials such as graphene and transition metal dichalcogenides (TMD) are well developed, until now, bottom-up synthesis of MXenes has not been reported. Understanding the bottom-up growth mechanism for MXenes will enable growth of large-scale, high-quality MXenes, while also providing increased opportunities to tailor properties for electronic and optoelectronic applications.

In this work, *in situ* aberration-corrected scanning transmission electron microscopy (STEM) was used to directly determine that the Frank van der Merwe growth mode is operative, as a hexagonal TiC (*h*-TiC) single adlayer forms on both surfaces of free-standing 2D MXene (Ti_3C_2) monolayer flakes, thereby forming new 2D MXenes, Ti_4C_3 and Ti_5C_4, at temperatures above 500 °C (Figure 1). After the functional groups are removed, the Ti and C atoms in Ti_3C_2 monolayer flakes migrate to the two surfaces then diffuse to form triangular islands of a single *h*-TiC adlayer (Figure 1a). Local Ti_4C_3 and Ti_5C_4 structures are confirmed by excellent agreement between experimental and simulated STEM images (Figure 1b). The growth of single-layer *h*-TiC is controlled by a small diffusion barrier and a large step-edge barrier, as confirmed by density functional theory (DFT) and ReaxFF molecular dynamics simulations. The *in situ* heating experiments also reveal how the edge structure of the MXene and the *h*-TiC adlayer evolve during transformation. The findings presented here provide insights into new, controlled growth methods to fabricate MXenes with controlled morphologies for tailored functionality.

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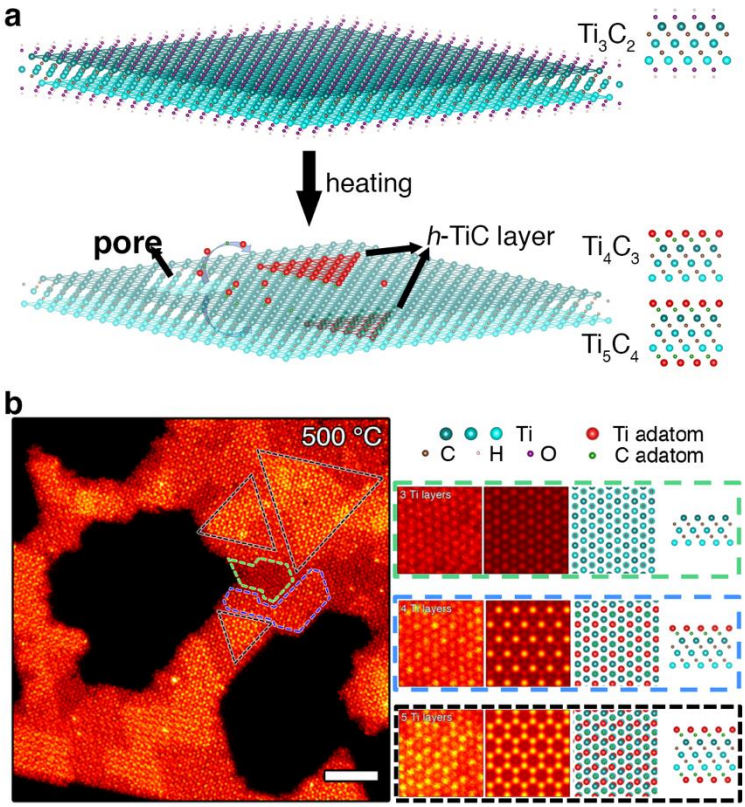

Figure 1. (a) Schematic of the homoepitaxial growth process to form new MXene phases (Ti_4C_3 and Ti_5C_4) from a monolayer $Ti_3C_2T_x$ substrate through electron beam irradiation and heating. Ti atoms from different layers are plotted using different shades of blue. (b) Typical STEM image acquired after heating the MXene flakes inside the microscope at 500 °C. The black areas are holes while areas framed by green, blue, and black dashed lines are new MXene layers of Ti_3C_2, Ti_4C_3, and Ti_5C_4, respectively. The comparison between experimental STEM image, simulated STEM image, and crystal structure models are shown on the left.