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Atomic Defects and Edge Structure in Single-layer $Ti_3C_2T_x$ MXene

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MXene phases have emerged as a promising group of 2D materials, finding applications in energy storage and conversion, catalysis, and electronic devices [1]. Most MXene phases are electrically conductive and are excellent candidates for supercapacitors. MXenes are fabricated from parent MAX phases, where M is an early transition metal, A is an A-group element, and X denotes C or N. The specific Ti_3AlC_2 (MAX) to Ti_3C_2 (MXene) conversion generally involves etching out the Al layer from MAX, leaving behind 2D flakes with the MXene structure [2]. The crystal structure of the typical and most-investigated MXene phase, $Ti_3C_2T_x$, is shown in Figure 1a, where T_x designates surface terminal groups. MXenes exhibit interesting defect structures that could be exploited to tune the functional properties.

Atomic-resolution scanning transmission electron microscopy (STEM) images (Figure 1b and 1c) were acquired to reveal point defects in single-layer MXene using a Nion UltraSTEM 60-100 equipped with a probe aberration corrector and operated at 60 kV. Figure 1c shows the typical defect configurations in a single-layer $Ti_3C_2T_x$ flake: a Ti vacancy (V_{Ti})and Ti vacancy clusters, with clusters ranging from 2-17 V_{Ti}. The defect concentration was tuned by using an HF etchant with different concentrations, which influences the Ti vacancies on the surface functional groups, thereby tuning the electronic conductivity. The ability to tune the defect concentration is critical to control the functional properties of the MXene phases.

The edge structure of 2D materials are also important defects that can influence electronic properties. At room temperature, investigating the edge structure in single-layer $Ti_3C_2T_x$ MXene flakes is difficult because the natural edges always fold back or are contaminated from the etching process. However, the edge structures for single-layer $Ti_3C_2T_x$ MXene can be imaged at elevated temperatures using a Protochips *in situ* heating cartridge designed for use in the Nion UltraSTEM. Figure 2a shows a STEM image after electron beam scanning for ~20 min. at 500 °C with 100 kV accelerating voltage. Faceted holes are formed in the $Ti_3C_2T_x$ due to a combination of beam and thermal effects. All the facets are aligned along the $Ti_3C_2T_x$ {100} planes. Figure 2b compares the observed edge structure with the crystal structure model. The stability of different types of edges and their influence on electronic and catalytic properties will be discussed. Combined with density functional theory and molecular dynamics simulation, this study will therefore shed light on utilizing point defects and edge defects in MXene materials to improve the catalysis and supercapacitance behaviors [4].

References:

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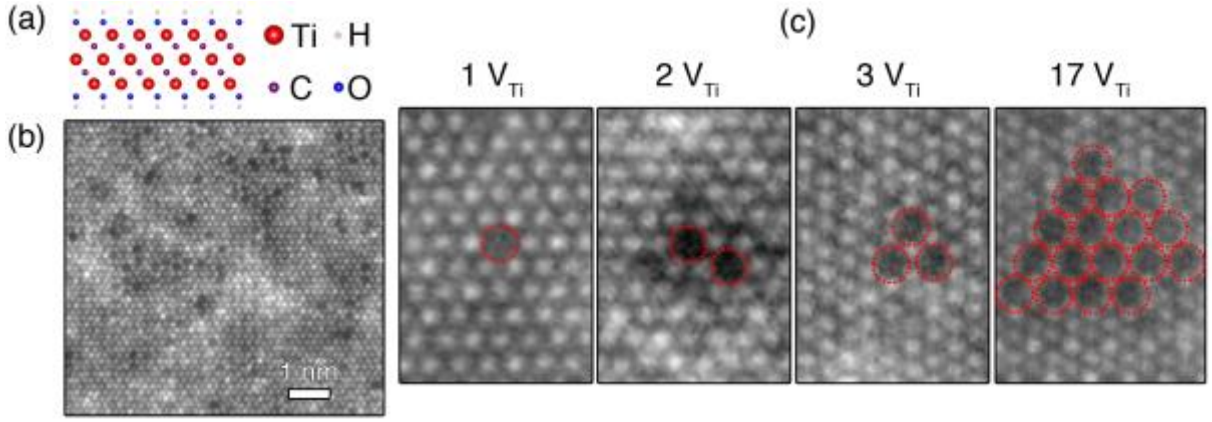

Figure 1. (a) Crystal structure of $Ti_3C_2T_x$ MXene. (b) Atomic-resolution annular dark field (ADF)-STEM images acquired from single-layer $Ti_3C_2T_x$ MXene flakes. (c) STEM images showing Ti vacancy (V_{Ti}) and vacancy clusters indicated by the red circles.

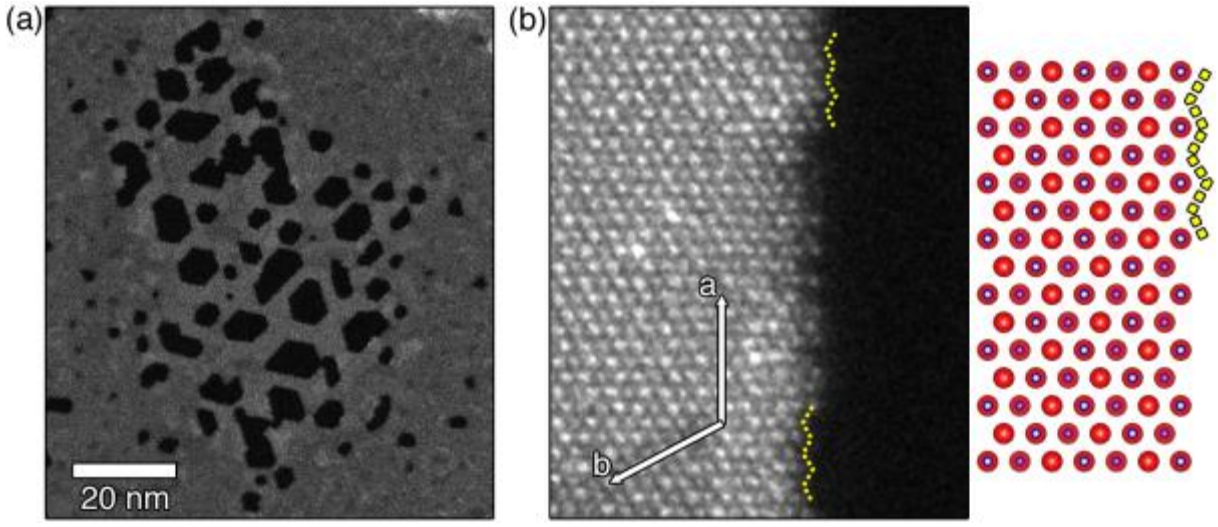

Figure 2. (a) ADF-STEM image of a single-layer $Ti_3C_2T_x$ MXene flake after heating at 500 °C for about 20 min. (b) Enlarged area of the flake's edge showing zig-zag edge structure and crystal structure model. The zig-zag edges are indicated by the yellow dotted lines.

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