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Atomic-Resolution Imaging and Spectroscopy of Functionalized MXene Nanosheets

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MXenes are a large and fast-growing family of two-dimensional materials. Their name highlights their sheet-like nature (as is often associated with graphene) and their synthesis from a parent MAX phase material. MXenes - $M_{n+1}X_nT_x$, where M is a transition metal, X is carbon or nitrogen and T is the surface functional group - are typically synthesized from a MAX phase bulk material though etching the main group element (A) with aqueous HF solutions or more recently with Lewis acidic molten salts 1. With over 80 experimentally synthesized MAX phases, the MXene family has potential to become the most diverse family among 2D materials. Since first synthesized in 2011 [2], MXenes have been an active field of research due to their exciting properties; for example, reports have shown MXenes to have higher conductivity than graphene, tunable band structure, and high charge capacitance. This has made MXenes a promising candidate material for applications in energy storage, fuel cells, electronic interference shielding, supercapacitors and many more[3].

Here, we will report atomic-resolution characterization of the effects that various functional groups have on the atomic and electronic structures of MXenes. Specifically, we will utilize the aberration-corrected cold field emission JEOL ARM200CF operated at 200kV primary electron energy. To avoid beam damage on the sample we will operate at a reduced emission current of 12μA. The electron probe will be operated at 24 mrad convergence semi-angle and the inner angle detector will be set to 75 mrad [30mrad] for high angle annular dark field [low angle annular dark field] imaging. The ARM200CF is also equipped with an Oxford XMAX100TLE X-ray detector and a post-columns Gatan Continuum GIF spectrometer.

In this contribution, we will demonstrate a new strategy to install and remove surface functional groups on 2D transition-metal carbides (MXenes) by performing substitution and elimination reactions in molten inorganic salts. MXenes with O, NH, S, Cl, Se, Br and Te surface terminations, as well as bare MXenes (no surface termination) are characterized and we find that the surface groups control interatomic distances in the MXene lattice. Figure 2 shows atomic-column-resolved images of Ti2C3 MXenes sheets in the [2 -1-1 0] projection with Te as the functional group. These images, and similar ones for the other functionalized MXenes, were analyzed to extracted spacings between the projection of M_{n+1} (in this case, Ti) and Tx (Te) columns. XEDS spectrum images (shown in Figure 2c) are used to determine the composition of the terminal groups and verify the stoichiometry of the MXene flakes. Our STEM imaging and chemical analysis was then compared to x-ray diffraction and SEM EDS analysis, revealing 25% change in the in-plane lattice parameter in the presence of a fully occupied Te^{2-} layer.

We will explore how these structural modifications of the MXene nano-flakes affect their thermal and transport properties and correlate the observed changes in the electron energy core-loss spectroscopy with the observed transport behaviors [4].

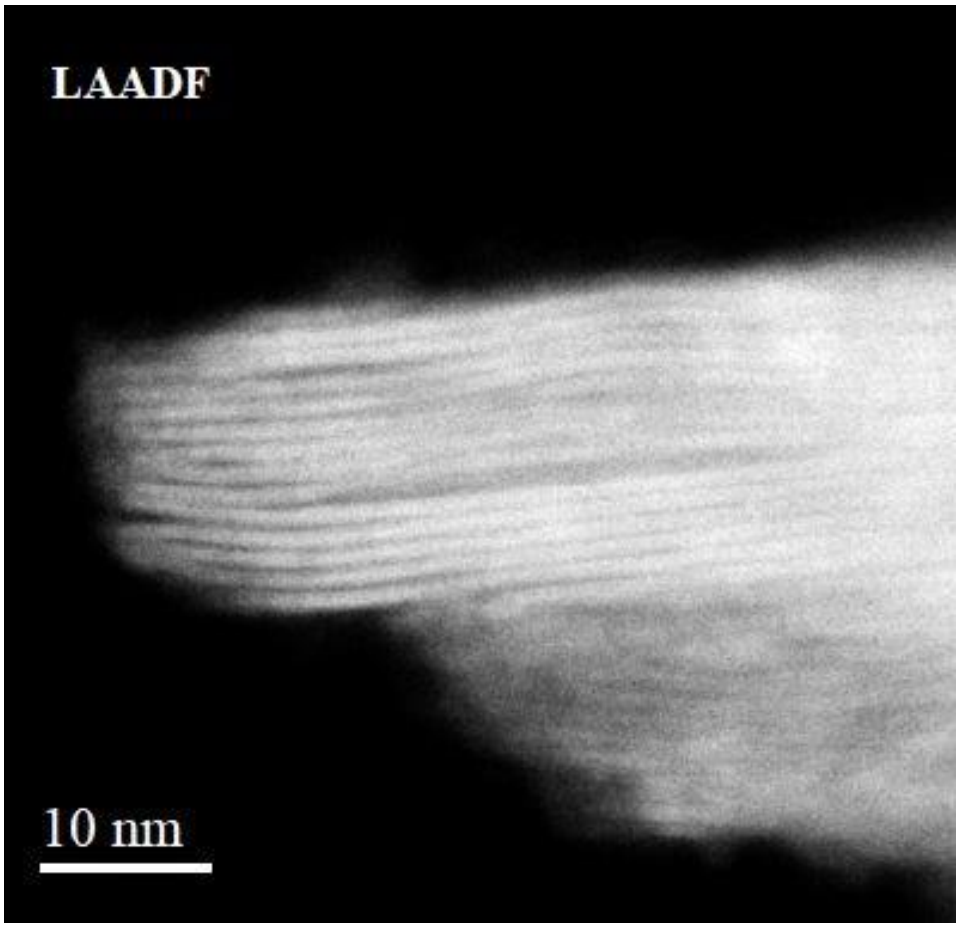

Figure 1. Low Angle Annular Dark Field (LAADF) image of Ti3C2Br2 MXenes sheets.

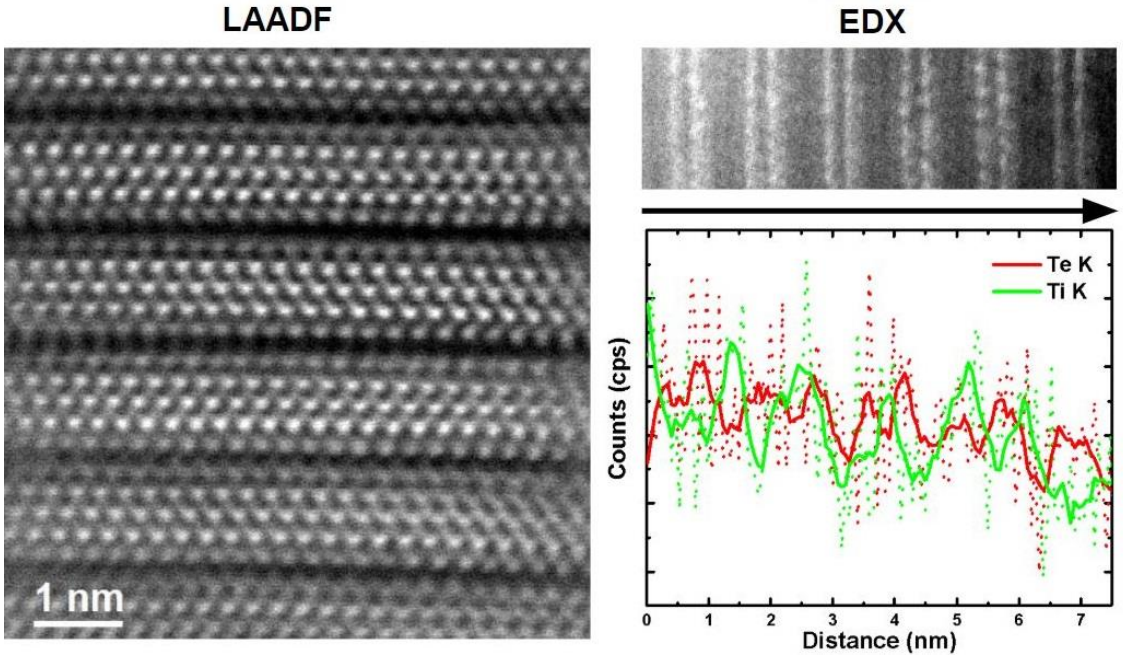

Figure 2. (a) LAADF image of Ti3C2Te, (b) High Angle Annular Dark Field Image of Ti3C2Te and (c) accomplaning XEDS line scan displaying the concentration of Te and Ti.

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