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Probing Changes in the Electronic Structure and Chemical Bonding of Ti_3C_2 MXene Sheets with Electron Energy-Loss Spectroscopy

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Layered metal carbides and nitrides (MXenes) have generated substantial research interest since their discovery in 2011 due to their 2D nature and their unique properties of hydrophilicity, good metallic conductivity, and structural diversity. [1] Surface terminations are a natural consequence of the MXene synthesis, traditionally consisting of O, OH, and F. The location of these surface-terminating functional groups and/or their chemical nature play a key role in tuning of MXenes' magnetic and electronic properties. There have been several theoretical investigations regarding the role of these surface groups on the electronic structure, yet there remains a lack of direct observations at nanometer resolution. These measurements will be critically important to advance the understanding of MXenes functionalization for their potential diverse applications. For this reason, our approach focuses on studying $Ti_3C_2T_x$ with various T functional groups as representatives of MXenes to characterize the role of the surface groups on modifying the electronic structure using aberration-corrected STEM-EEL.

The Ti_3C_2 MXene unit cell consists of three Ti and two C atoms organized in a close-packed structure (see Figure 1A). Surface groups such as those mentioned above have been proposed to attach to the surface Ti layer and modify their d-band occupation [2,3]. Therefore, in order to probe the electronic structure both inside the MXene sheet and on its surface, we focus on the core-loss edges of the titanium and carbon atoms (i.e. $L_{2,3}$ and K-edges). Specifically, the energy-loss near-edge structure (ELNES) of the carbon atom reflects the unoccupied electron density of states (DOS) and gives access to the electronic structure of the investigated material. Figure 1B shows the obtained high-resolution C K-edge spectra of $Ti_3C_2T_x$. The EELS spectra consist of two regions: pre-edge and main-edge. Features in the pre-edge region are assigned to C2p − Ti3d hybridized molecular orbital excitation, in agreement with earlier theoretical predictions. [4] Since the surface Ti d states dominate the electronic structure around the Fermi level in $Ti_3C_2T_x$, [5] detecting any changes of the intensity in the pre-edge features (Figure 2B, highlighted region) likely provides evidence for the modification of the electronic structure of the $Ti_3C_2T_x$ sheet. This result, which is very challenging to obtain by other techniques, demonstrates how electron energy loss spectroscopy can be used to probe the MXene surfaces to shed more light on the electronic structure and chemical interaction which is relevant knowledge when designing MXenes for various applications.

In this contribution, we will further discuss the Ti $L_{2,3}$ edge and how it can be correlated with the changes in the surface termination groups at the atomic level using integrated differential phase contrast (iDPC) in combination with electron energy loss spectroscopy.

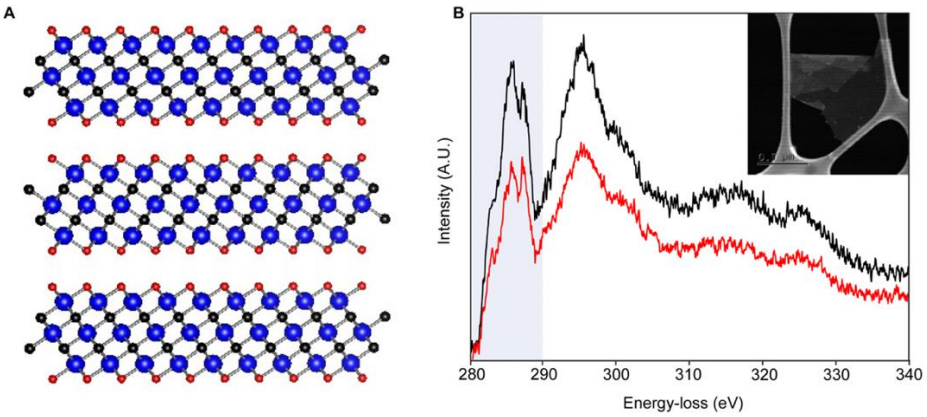

Figure 1. (A) Schematic structure of $Ti_3C_2T_x$ MXene sheet with various termination sites of T_x (red). Blue and black spheres are Ti and C atoms, respectively. **(B)** Comparison between EELS spectra of the C K-edge from two different regions of the same $Ti_3C_2T_x$ MXene sheet. Pre-edge features (~283 - 287 eV, highlighted in blue) are characteristic of the C 2p-Ti 3d hybridized molecular orbitals. Inset shows a STEM micrograph of the investigated $Ti_3C_2T_x$ sheet on which EELS data were collected.

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