doi:10.1017/S1431927622008376
Microsc. Microanal. 28 (Suppl 1), 2022

Studying Electronic Structure in Two-Dimensional Functionalized Organic-Metallic MXenes with Cryo-STEM

Francisco J. Lagunas Vargas,[1] Chenkun Zhou[2], Dmitri V. Talapin[2, 3] and Robert F. Klie[1]

[1.] Department of Physics, University of Illinois at Chicago, Chicago, IL, United States.
[2.] Department of Chemistry and James Franck Institute, University of Chicago, Chicago, IL, United States.
[3.] Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL, United States.

Since their discovery in 2011, MXenes- $M_{n+1}X_nT_x$ with n=1,2,3 – have diversified into a large family of two-dimensional materials [1]. In their chemical formula, M denotes an early transition metal, X is carbon or nitrogen, and T_x indicates the element comprising their functional surface group. The MXene family owes their rapid growth to wide varieties of modification in M and T_x groups. Huge strain in Ti_3C_2Te and T_x group dependent superconductivity in Nb_2C MXenes show that their large design space opens the door to many interesting properties [2].

In this contribution, we will further probe this design space by characterizing the structure and electronic properties of MXenes with organic surface group terminations. To preserve the structure of the MXenes in the high vacuum, high electron beam dosage environment, we will cool the sample *in-situ* to liquid nitrogen temperatures. We will show this can significantly reduce signs of degradation in metallic-organic hybrid MXenes as seen by Ti_3C_2 layer spacing.

To increase the stability of the MXenes in the microscope, we will use a Gatan cold stage capable of reaching liquid nitrogen temperatures with high stability. Our STEM characterization will be conducted using an aberration-corrected JEOL ARM200CF operating at 200kV primary electron energy with the emission current set to 12 μA. The electron probe will be operated at 24 mrad convergence semi-angle. High-angle annular dark-field (HAADF) and low-angle annular dark-field (LAADF) imaging is conducted using inner detector angles of 75 mrad and 30 mrad, respectively. The microscope is fitted with a windowless solid-angle Oxford XMAX100TLE XEDS detector as well as post-columns Gatan Continuum GIF spectrometer. Beam induced degradation to the organic surface groups will be captured using LiveEELS feature within GMS. The sample preparation for cryo STEM imaging will be conducted using a ThermoFisher Helios 5CX dual-beam FIB/SEM.

These organic-metallic MXenes form large flexible nanosheets that, despite their large Ti_3C_2 band spacing, form highly organized heterostructures. In Figure 1a), we show a HAADF image, acquired at 77K, of a region where a four-layer thick nanosheet has folder over on itself exposing a cross sectional view. Figure 1b) also acquired at liquid nitrogen temperatures, shows an HAADF image resolving the atomic columns composing the Ti_3C_2 framework. Due to their light weight, we do not expect to directly observe the organic material between the layers, however the Ti_3C_2 band spacing agrees closely with X-ray measurements and suggest low levels of organic degradation. To gain insights into the structure of the organic material, we turned to EELS measurements of the carbon *K*-edge, which is rich in fine structure arising from the π and σ peaks. In Figure 2, we show that the C *K*-edge ELNES is sensitive to the direction of the incoming electron beam. This anisotropy is particularity pronounced in the lower energy π-orbitals, which correspond to antisymmetric bonding between the highly directional 2p-orbitals. These orientation dependent effects are only observable at low temperatures and do not appear in C K-edge spectra of bare Ti_3C_2 MXenes. We suspect *in-situ* cooling sufficiently preserves the organic material and allows it to be the contributing source of this behavior. Similar orientation dependent effects have been reported in NEXAF measurements of ordered chemisorbed organics [3].

To conclude, in this contribution will show that the implementation of Cryo STEM techniques opens the door to conducting atomistic studies of highly beam sensitive two-dimensional materials. Moreover, these studies can also include analytical measurements such as EELS that reveal features obscured from room temperature experiments. The implementation of Cryo STEM sample preparation will also be explored, particularly in its application to hybrid organic MXenes [4].

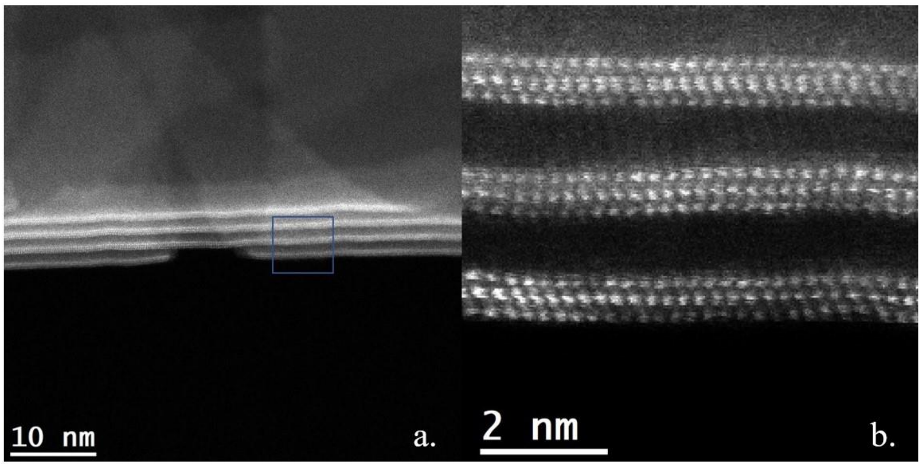

Figure 1. (a) HAADF image acquired at 77K revealing a folded region in multilayer thick metallic-organic hybrid MXene. (b) High magnification HAADF image resolving Ti3C2 framework also acquired at 77K.

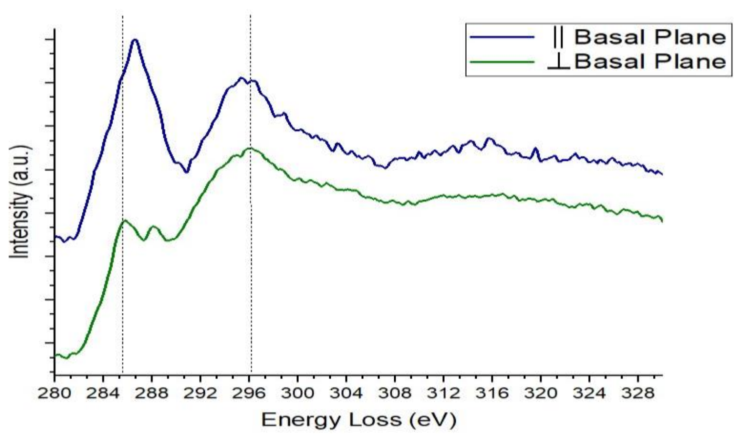

Figure 2. Carbon K-edge acquired along different direction relative to the MXene basal plane. Distinct fine structure, particularly at low energies show preferential transitions because of incoming electron beam orientation.

https://doi.org/10.1017/S1431927622008376 Published online by Cambridge University Press

References

[1] Y Gogotsi and B Anasori, ACS nano **13**(8) (2019), p. 8491.
[2] V Kamysbayev et al., Science **369**(6506) (2020), p. 979.
[3] J Stöhr et al., Physical Review Letters **47**(5) (1981), p. 381.
[4] This work was supported by a grant from the National Science Foundation (NSF DMR-1831406)