

Understanding the Surface Chemistry Dependent Plasmon Response in $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes using Monochromated STEM-EELS

Sudhajit Misra¹, Jordan A. Hachtel¹, Matthew G. Boebinger¹, Murali Gopal Muraleedharan², Andrea Konečná³, Tyler S. Mathis⁴, Paul R. C. Kent², Michael Naguib⁵, Yury Gogotsi⁶, and Raymond R. Unocic¹

¹. Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, USA.

². Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA.

³. Central European Institute of Technology, Brno University of Technology, Brno, Czech Republic.

⁴. Centre Inter-Universitaire de Recherche et d'Ingénierie des Matériaux, Paul Sabatier Université, Toulouse, France.

⁵. Department of Physics and Engineering Physics, Tulane University, New Orleans, LA, USA.

⁶. A.J. Drexel Nanomaterials Institute and Department of Material Science and Engineering, Drexel University, Philadelphia, PA, USA.

MXenes are an emerging class of two-dimensional (2D) transition metal carbides, nitrides, and carbonitrides that have demonstrated their potential in a wide variety of applications including energy storage, electromagnetic shielding, gas sensing, smart textiles, optoelectronics, and environmental applications [1]. MXenes have the general formula $\text{M}_{n+1}\text{X}_n\text{T}_y$, where M is a transition metal, X is carbon or nitrogen, and T is the surface-terminating group (e.g., -O, -OH, -F). Among all MXenes, $\text{Ti}_3\text{C}_2\text{T}_x$ is the most widely studied one for its potential plasmonic applications due to its high metallic conductivity and tunable optical properties [2-4]. Considering that $\text{Ti}_3\text{C}_2\text{T}_x$ MXene is surface-terminated with various functional groups (such as -O, -OH, and -F) during its synthesis, it is crucial to understand the effect of these surface terminations on these properties. A detailed understanding of the effect surface chemistry of MXenes has on its plasmonic response would enable pathways to engineer MXene based devices with tunable plasmonic properties.

In this study, we use scanning transmission electron microscopy (STEM) and monochromated electron energy loss (EEL) spectroscopy to study the effects of surface chemistry on the plasmonic response of $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes. Monolayer flakes of $\text{Ti}_3\text{C}_2\text{T}_x$ were dispersed on a carbon-coated copper TEM grid and STEM-EELS characterization was done using a monochromated aberration-corrected Nion Hermes microscope operating at 60 kV. The probe convergence semi-angle was 30 mrad and the EEL spectrometer collection semi-angle was 25 mrad. The full width at half maximum of the zero-loss peak was ~8 meV while the spectrometer dispersion of 1.2 meV/channel was used to record the EEL spectra.

Figure 1a shows the high angle annular dark-field (HAADF) image of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene single flake and the relative position on the probe. Figure 1b is the background-subtracted EEL spectra in the 0.1 – 1.2 eV range. Two broad peaks at 0.3 eV and 0.62 eV respectively were observed corresponding to the two surface plasmon (SP) modes. *In situ* heating of the $\text{Ti}_3\text{C}_2\text{T}_x$ (T= OH or F) MXene (dispersed on a silicon nitride heating chip) was done to selectively remove these functional groups. Figure 2 shows the normalized STEM-EEL spectra of the MXene flake from 100-500°C. The SP mode at 0.62 eV reduces on increasing temperature and is below detectible limits at 500°C. In $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes, OH functional group loss occurs in the 300-500°C range while the fluorine terminations are desorbed above 500°C [5]. This indicates that the SP mode at 0.62 eV is due to -OH termination in $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes. The results presented here demonstrate that in $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes, the SP response depends on the surface chemistry. Since MXenes can be synthesized with varying surface chemistries their plasmonic response can

therefore be directly tuned to selectively activate or deactivate specific SP modes in the near-infrared to mid-infrared region. [6]

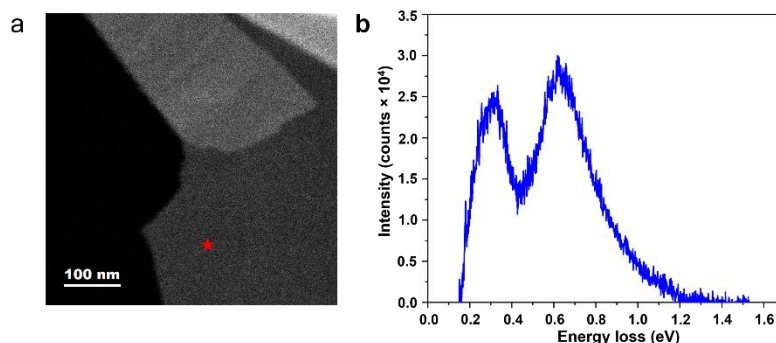


Figure 1. (a) HAADF STEM image of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene single flake showing the probe position relative to the sample. (b) Background-subtracted EEL spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ single flake showing two strong broad plasmonic peaks at 0.3 eV and 0.62 eV respectively. A power law background subtraction model was used.

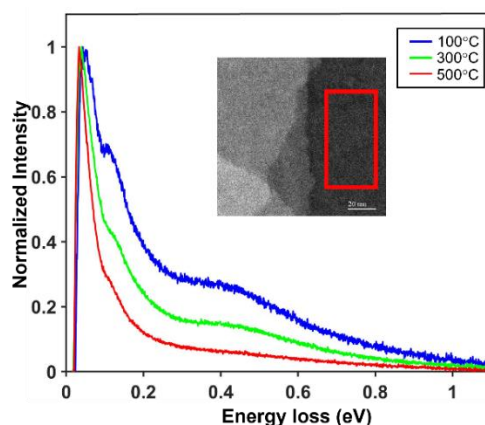


Figure 2. Background subtracted temperature-dependent EEL spectrum of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene showing reduction of the plasmon peak at 0.62 eV with increasing temperature. Inset is the HAADF STEM image of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene dispersed on a silicon nitride heating chip. The red box in the HAADF image is the region used to average the EEL spectra.

References:

- [1] Anasori, B., et al., *Nature Reviews Materials* 2 (2017), p. 1-17.
- [2] Lipatov, A., et al. *Matter* 4.4 (2021), p. 1413-1427.
- [3] Mauchamp, V., et al. *Physical Review B* 89.23 (2014), p. 235428..
- [4] El-Demellawi, J. K., et al., *ACS Nano* 12.8 (2018), p. 8485-8493.
- [5] Hart, J. L., et al., *Nature Communications* 10.1 (2019), p. 1-10.
- [6] This research was supported by the Fluid Interface Reactions, Structures, and Transport (FIRST) Center, an Energy Frontier Research Center (EFRC) funded by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences. Electron Microscopy was performed at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory, which is a US DOE, Office of Science User Facility. This manuscript has been authored by UT-Battelle, LLC, under contract DE-AC05-00OR22725 with the US Department of Energy (DOE). The US government retains and the publisher, by accepting the article for publication, acknowledges that the US government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for US government purposes. DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).