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In situ electron beam irradiation of Ti3C2Tz MXenes. A STEM-EELS study

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Background incl. aims

MXenes are a family of 2D transition metal carbide or nitride layers obtained from the exfoliation of nanolaminated ceramics called MAX phases [1]. Their chemical formula is Mn+1XnTz (n = 1, 2 or 3), with M a transition metal, X being C and/or N, and T are surface terminations (e.g. O(H), F, Cl) inherited from the exfoliation process. They present very good electrical conductivity, as well as high hydrophilicity, making them very promising materials for various applications, including transparent conductive electrodes or energy storage devices [2]. Our previous study [3] showed the strong influence of ion irradiation induced defects on the structural and physical properties of Ti3C2Tz MXenes, resulting in a reduced hydration potential, an increase in the charger carrier density as well as a modification of their optical properties. In the meanwhile, a large conductivity is preserved. Electron beams have also been shown to be a valuable tool for the structural engineering of MXenes on the nanometer scale [4]. Here, we present a new experimental protocol, which aims towards localized defect engineering in MXenes, using electron beam irradiation in situ in a transmission electron microscope (TEM), performed in cryogenic conditions.

Methods

This is achieved by adjusting the exposure time, the beam current and the number of frames in STEM-EELS (electron energy-loss spectroscopy) measurements, to reach an electron dose that allows for the introduction of defects into the sample. The study was performed on pristine Ti3C2Tz, exfoliated from its MAX phase precursors following the protocol detailed in [5], the powder was then dispersed in water to delaminate the MXenes sheets and dropped on a TEM lacey carbon grid. The TEM grid was placed on a cryo sample-holder and measurements were performed at liquid nitrogen temperature.

Results

At low temperature, irradiation conditions can be controlled precisely, by the creation of either punctual depressions, roughly the size of the electron beam, or bigger “crater-like” dips spanning over hundreds of nm^2 (Figure), depending on the irradiation conditions. The evolution of the structure and chemistry of the sample is monitored as a function of the electron dose using core-loss spectra acquired both during and after irradiation.

Conclusion

This study gives a valuable insight into the defect formation mechanisms at play in electron beam irradiation of MXenes, by observing the behavior of the surface functional groups, as well as the core atoms in regards to the incoming high-energy electrons. This innovative approach can potentially be generalized to other MXenes and 2D materials, as well as up scaled to thin films using other electron irradiation techniques such as SEM.

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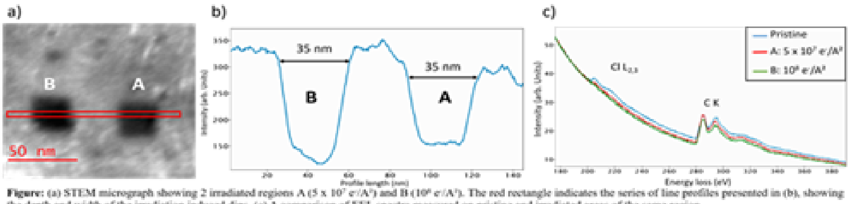

Figure: (a) STEM micrograph showing 2 irradiated regions A (5×10^7 $e^-/Å^2$) and B (10^8 $e^-/Å^2$). The red rectangle indicates the series of line profiles presented in (b), showing the depth and width of the irradiation induced dips. (c) A comparison of EEL spectra measured on pristine and irradiated areas of the same region.

Keywords:

MXenes, STEM-EELS, irradiation, defects, quantification

Reference:

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