

## O 76: Focus Session: 2D Transition Metal Carbides, Nitrides and Carbonitrides II (joint session DS/MM/O)

Surface functionalization & defects and Water & gas Interaction

Time: Thursday 9:30–12:15

Location: A 053

### Invited Talk

O 76.1 Thu 9:30 A 053

**Computational insights into the surface functionalization and defects in MXenes** — ●HANNU-PEKKA KOMSA — Microelectronics Research Unit, University of Oulu, Finland

Two-dimensional (2D) transition metal carbide and nitride MXenes offer rich chemistry with extraordinary properties. The surface of MXenes is terminated by -O, -OH, and -F groups during the synthesis. However, there is limited understanding on how the surface composition depends on the synthesis conditions and on the type of MXene (transition metal, carbon vs. nitrogen, and the number of atomic layers).

We developed a multi-scale computational scheme to simulate the distribution and the thermodynamically favorable composition of the functional groups on the MXene surfaces. We considered the most popular MXene systems such as  $Ti_2C$ ,  $Ti_3C_2$ ,  $Ti_2N$ ,  $Ti_4N_3$ ,  $Nb_2C$ , and  $Nb_4C_3$ . The surface accommodates mixtures of functional groups for all considered MXenes with similar distributions regardless of the type of metal, carbon or nitrogen species and number of atomic layers. These findings are shown to be important for an accurate prediction of properties and stability of these materials. Next, we investigated the propensity of metal vacancy formation under synthesis conditions. The results suggest that vacancy formation is crucial step in initiating MXene oxidation. Finally, to support experimental characterization, we simulated the Raman spectra as a function of functional group distribution, temperature, and disorder, and the materials' response to electron irradiation in electron microscope.

O 76.2 Thu 10:00 A 053

**In situ monitoring of surface termination of  $Ti_3C_2Tx$  MXene with Raman spectroscopy** — ●JULIAN PLAICKNER<sup>1,2</sup>, TRISTAN PETIT<sup>2</sup>, PEER BÄRMANN<sup>2</sup>, THORSTEN SCHULTZ<sup>2,3</sup>, NORBERT KOCH<sup>2,3</sup>, and NORBERT ESSER<sup>1,4</sup> — <sup>1</sup>Technische Universität Berlin, Institut für Festkörperphysik, Hardenbergstrasse 36, 10623 Berlin — <sup>2</sup>Hardenbergstrasse 36 — <sup>3</sup>Institut für Physik & IRIS Adlershof, Humboldt Universität zu Berlin, 12489 Berlin — <sup>4</sup>Leibniz Institut für Analytische Wissenschaften ISAS eV, Schwarzschildstrasse 8, 12489 Berlin

In the last years, MXenes have attracted attention due to an interesting combination of physical properties. A better knowledge of the surface chemistry of MXenes is critical for the implementation in applications. A promising investigation approach is annealing-induced desorption of surface terminations, because it might make the surface very active for further functionalizations. In this work, the effect of annealing on the  $Ti_3C_2Tx$  MXene surface chemistry in UHV has been investigated with Raman spectroscopy in ultra-high vacuum. Changes in the Raman spectra are correlated with the desorption of the major part of the F surface termination at 650 °C. Most of the observed spectral features show a significant broadening already before annealing. We attribute this to the intrinsic disordered nature of the MXenes due to a mixed surface termination and a broad background associated to electronic Raman scattering. With this study we identified the vibrational signatures associated with F-termination and provided new insights into the interpretation of the vibrational spectra of  $Ti_3C_2Tx$  MXenes.

O 76.3 Thu 10:15 A 053

**Hydrogenation as a mean to remove halogen functionalization from of  $Ti_3C_2Tz$  thin films** — ●SILVANO LIZZIT<sup>1</sup>, FLORIAN BRETTE<sup>2,3</sup>, HANNA PAZNAK<sup>4</sup>, MONIKA SHIED<sup>1</sup>, PAOLO LACOVIG<sup>1</sup>, FLORENT BOUCHER<sup>3</sup>, VINCENT MAUCHAMP<sup>2</sup>, and ROSANNA LARCIPRETE<sup>5</sup> — <sup>1</sup>Elettra-Sincrotrone Trieste, Trieste (I) — <sup>2</sup>Uni. Poitiers, ISAE-ENSMA, CNRS, PPRIME, Poitiers (F) — <sup>3</sup>CNRS-IMN, Nantes (F) — <sup>4</sup>Uni. Grenoble Alpes, CNRS, Grenoble INP, Grenoble (F) — <sup>5</sup>CNR- ISC, Roma (I)

The nature and the density of the chemical groups terminating the MXenes surface determine their electronic and chemical properties. Therefore, the manipulation of the surface termination allows to change the way these compounds interact with the surrounding environment. In this study we explored the possibility of using the functionalization with H atoms as a mean to modify the surface termination of  $Ti_3C_2Tz$  thin films. To this aim we used photoelectron spectroscopy with syn-

chrotron radiation to investigate the surface reactions induced by the exposure to atomic hydrogen. Simulation of the valence band spectra by DFT calculations combined with the analysis of the core level spectra allowed us to elucidate the changes in the chemical bonding determined by the interaction with H atoms. It turned out that, in addition to the formation of C-H and -O-H bonds, sample hydrogenation removed the halogen terminating atoms, decreasing the F and Cl concentrations to less than 20% of the initial values. After removing the hydrogenated phases at 400 K, the dehydrogenated surface exhibited a chemical reactivity higher than that of the pristine sample.

O 76.4 Thu 10:30 A 053

**Chemical characterization of defects in  $Ti_3C_2Tx$  MXenes by soft X-ray spectroscopy** — ●ARSÈNE CHEMIN<sup>1</sup>, ZOÉ DESSOLIERS<sup>1</sup>, ROBERT W. LORD<sup>2</sup>, YURY GOGOTSI<sup>2</sup>, and TRISTAN PETIT<sup>1</sup> — <sup>1</sup>Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany — <sup>2</sup>A.J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, Pennsylvania, USA

MXenes offer a wide spectrum of properties with numerous fields of application. Yet, these properties can be strongly affected by defects, and a detailed understanding of their nature and structure is essential. Despite many observations of such defects, grasping their chemical natures is challenging. In this work, high-resolution X-ray Photoelectron Spectroscopy (HR-XPS) and, at the Ti L- and C, O K-edges, soft X-ray Absorption Spectroscopy (XAS), performed at the BESSY II synchrotron in Berlin, are used to investigate the chemical nature of defects in  $Ti_3C_2Tx$  MXenes.

### 15 min. break

### Invited Talk

O 76.5 Thu 11:00 A 053

**MXenes as materials for carbon capture, storage, and usage technologies: Computational insights & predictions** — ●FRANCESC VINES — Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, c/ Martí i Franquès 1-11, 08028 Barcelona, Spain

Environmentally-wise, pristine MXenes have been proposed as suited materials for carbon capture and storage (CCS) technologies, as predicted by computational density functional theory (DFT) simulations on suited models.<sup>1</sup> Such MXenes display a high affinity towards carbon dioxide (CO<sub>2</sub>), strongly binding it, and activating it by charge transfer, gaining a bent CO<sub>2</sub> with elongated bonds. The CCS capabilities highlighted through kinetic phase diagrams (KPD) were confirmed by experiments,<sup>2</sup> showing a high CO<sub>2</sub> uptake due to the MXene high surface area, specially high when MXene is made of light transition Ti or V metals. Furthermore, given the CO<sub>2</sub> activation pristine MXenes can be used in carbon capture and use (CCU) technologies, acting as heterogeneous catalysts. A recent DFT study shows MXenes use as heterogeneous catalysts for the reverse water gas shift reaction (RWGS), where a KPD analysis reveals a swing mode RWGS operation, where CO<sub>2</sub> is first converted into CO oxidizing the MXene surface, later regenerated by hydrogen treatment releasing water.

<sup>1</sup> Morales-García et al. J. Mater. Chem. A 6 (2018) 3381. <sup>2</sup> Persson et al. Adv. Mater. 31 (2019) 1805472. <sup>3</sup> Morales-Salvador et al. ACS Catal. 11 (2021) 11248.

O 76.6 Thu 11:30 A 053

**Effect of Surface Terminations on the Water Intercalation into  $Ti_3C_2Tz$  MXene Thin Films** — ADITYA SHARMA<sup>1</sup>, THIERRY OUISE<sup>1</sup>, ULF WIEDWALD<sup>2</sup>, ANDREI CHUMAKOV<sup>3</sup>, FABRICE WILHELM<sup>4</sup>, and ●HANNA PAZNAK<sup>1</sup> — <sup>1</sup>Université Grenoble Alpes, CNRS, Grenoble INP, LMGP, Grenoble, France — <sup>2</sup>University of Duisburg-Essen and Center for Nanointegration Duisburg-Essen, Duisburg, Germany — <sup>3</sup>Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — <sup>4</sup>European Synchrotron Radiation Facility, Grenoble, France

MXenes are 2D materials whose surface is terminated by functional groups that drastically affect the properties of MXenes, including their

affinity for water. In this study, we synthesized  $\text{Ti}_3\text{C}_2$  MXenes with 1) mixed (=O, -F, and -OH) and 2) halogen (-Cl) terminations and prepared thin films by drop casting. X-ray absorption near edge structure shows different local chemical environment of Ti depending on the terminations, which is also confirmed by density functional theory. Next, we expose the MXene thin films to various humidity levels and studied the water intercalation by wide angle X-ray scattering. We observed that the interplanar spacing of mixed-terminated MXenes varied from 11.74 Å to 16.97 Å with increasing relative humidity from 0% to 100%, respectively. In the Cl-terminated MXenes, however, the interplanar spacing remains much smaller and only changes from 11.0 Å to 12.8 Å as function of relative humidity. In both cases, the process of water intercalation is reversible.

Funded by ANR-23-CE09-0031-01 project.

O 76.7 Thu 11:45 A 053

**Isotopic Analysis of Intercalated Protons in  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene for Electrochemical Energy Storage using in-situ FTIR Spectroscopy** — ●ANDREAS WEISSER<sup>1</sup>, MAILIS LOUNASVUORI<sup>1</sup>, NAMRATA SHARMA<sup>1</sup>, KYLE MATTHEWS<sup>2</sup>, TENG ZHANG<sup>2</sup>, YURY GOGOTSI<sup>2</sup>, and TRISTAN PETIT<sup>1</sup> — <sup>1</sup>Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin, Germany — <sup>2</sup>A. J. Drexel Nanomaterials Institute and Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104, USA

MXenes, a family of 2-dimensional transition metal carbides, are a promising candidate for use in energy storage applications due to their high capacitance. Here, we monitor the confined water and protons in  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene electrodes during cyclic voltammetry using operando FTIR spectroscopy. Isotopic exchange with deuterium oxide is used to allow for a better understanding of the proton dynamics inside the MXene interlayers. In-situ FTIR measurements are being performed with a dedicated electrochemical cell able to measure the different vibrational modes of the confined species. The measurements are conducted in attenuated total reflectance mode (ATR).

The focus of this presentation will be on analyzing the change of the vibrational modes of water and deuterium during electrochemical cycling versus the applied potential to the working electrode. This behaviour will be discussed with regard to the intercalation of protons and the reordering of the intercalated water or deuterium. The results will be placed in the context of MXene in the role of an electrode for pseudocapacitor applications.

O 76.8 Thu 12:00 A 053

**Electronic Structure of  $\text{V}_2\text{CT}_x$  MXene in aqueous solutions studied using in situ Scanning Transmission X-Ray Microscopy.** — ●NAMRATA SHARMA<sup>1</sup>, KYLE MATTHEWS<sup>2</sup>, ANDREAS WEISSER<sup>1</sup>, MAILIS LOUNASVUORI<sup>1</sup>, MARKUS WEIGAND<sup>1</sup>, YURY GOGOTSI<sup>2</sup>, and TRISTAN PETIT<sup>1</sup> — <sup>1</sup>Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin, Germany — <sup>2</sup>A. J. Drexel Nanomaterials Institute and Department of Materials Science and Engineering Drexel University Philadelphia, 19104 PA, USA

MXenes, a class of 2D transition metal carbides and nitrides have attracted much attention in many applications, thanks to their layered structure, hydrophilicity, and surface terminations. Recently, a new synthesis protocol has significantly improved the quality and shelf life of  $\text{V}_2\text{CT}_x$  MXene. This study focuses on the behaviour of  $\text{V}_2\text{CT}_x$  MXene in aqueous solutions studied using In-situ Scanning Transmission X-Ray Microscopy (STXM) with dedicated electrochemical flow cell at the synchrotron BESSY II. STXM provides element-specific nanomaterial electronic structure characterization in liquid at ~50nm spatial resolution. Here we characterize the electronic structure of pristine and aged  $\text{V}_2\text{CT}_x$  MXene in air, water,  $\text{ZnSO}_4$ , and  $\text{H}_2\text{SO}_4$ , using X-ray Absorption Spectroscopy (XAS) at V L-edge and O K edge. The stability of individual  $\text{V}_2\text{CT}_x$  MXene flakes is monitored through high resolution chemical imaging over several hours in aqueous electrolyte. In this work we stress upon on the relevance of chemical imaging allowed by STXM for insights into oxidation and hydrolysis of MXene in aqueous environment at the nanoscale.