Combining DFT simulations with *in-situ* X-ray photoelectron spectroscopy for the characterization of 2D titanium carbide (MXene) layers surface functionalization

Vincent MAUCHAMP[1]
[1]Université de Poitiers, CNRS, ISAE-ENSMA, PPRIME, 86073 Poitiers, France
F. Brette[1,2], S. Célérier[3], C. Canaff[3], L. Loupias[3], M. Paris[2], A. Habrioux[2], M. Schied[4], H. Pazniak[5], P. Lacovig[4], S. Lizzit[4], F. Boucher[2], R. Larciprete[8]
[2] Nantes Université, CNRS, Institut des Matériaux De Nantes Jean Rouxel, 44000 Nantes, Fr / [3] IC2MP, Université de Poitiers, CNRS, F-86073 Poitiers, Fr / [4] Elettra Sincrotrone Trieste, S.S. 14 Km 163.5, 34149 Trieste, It. / [5] CNR-Institute for Complex Systems, Via dei Taurini 19, 00185 Roma, It
vincent.mauchamp@univ-poitiers.fr

Two-dimensional (2D) transition metal carbides or nitrides - so-called MXenes - are a large family of 2D materials,[1] Ti_3C_2 being the most studied among them (see Fig1-a). This later compound combines high metallic conductivity with hydrophilicity, allowing cost-effective processing as thin films for a very large range of applications. Because of the synthesis process, Ti_3C_2 layers are functionalized with different chemical species (*e.g.*, T = O, OH, F and/or Cl) whose nature and distribution have a strong impact on the physicochemical properties.[2] Accurately characterizing the layers surface functionalization is thus a major issue, and X-ray Photoelectron Spectroscopy (XPS) is one of the go-to methods to do so with however strong divergences in terms of data interpretation in the literature. In order to rationalize XPS data taken for the Ti_3C_2 MXene, we combine density functional theory (DFT) simulations of XPS chemical shifts with a series of experiments, including *in situ* measurements performed under controlled atomic hydrogen exposure, which allowed modifying the layers surface chemistry and corresponding spectroscopic signatures. Focusing on the core level spectra of the different elements composing the layers, we show that XPS signatures exhibit a nontrivial behavior due to peculiar electronic structure effects that can be explained using DFT calculations.[3] Among others outcomes, our results allow explaining the very different shapes of the F and O spectra in terms of the sensitivity of these functional groups to their local environment. The possibility to discriminate homogeneous from disordered surface coverage is also evidenced and O/OH contributions are clearly resolved (see Fig. 1-b), further confirmed by XPS valence band analysis.[4]

References

[1] A. VahidMohammadi, J. Rosen, Y. Gogotsi, Science, 372 (2021) 1165.
[2] V. Kamysbayev, A.S. Filatov, H. Hu, X. Rui, F. Lagunas, D. Wang, R.F. Klie, D.V. Talapin, Science, 369 (2020) 979
[3] F. Brette, S. Célérier, C. Canaff, L. Loupias, M. Paris, A. Habrioux, F. Boucher, V. Mauchamp, Small Methods, 9 (2024) 2400848
[4] M. Schied, H. Pazniak, F. Brette, P. Lacovig, M. Paris, F. Boucher, S. Lizzit, V. Mauchamp, R. Larciprete, Chemistry of Materials, 36 (2024) 11905

Figures

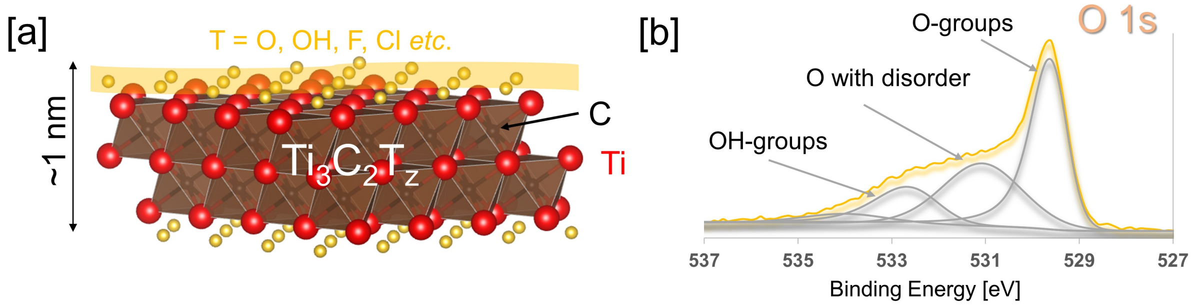

Figure 1: (a) Structural model of a $Ti_3C_2T_z$ layer with T being O, OH, F and/or Cl groups. (b) O 1s peak recorded by XPS, and corresponding spectral decomposition according to DFT simulations and allowing to, *e.g.*, distinguish between O and OH groups. This later contribution reversibly increases as a function of exposure to atomic hydrogen, confirming the theoretical results.[4]