

Electronic structure of two dimensional titanium carbide multilayers from valence EELS and *ab initio* calculations: insights into the surface functionalization groups.

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1. INTRODUCTION

$Ti_3C_2T_2$, where $T \equiv OH$ or F are surface functionalization groups, belongs to the large family of MXenes (M being a transition metal and X either C or N) which are few atomic layers thick two-dimensional (2D) transition metal carbide or carbonitride sheets. Among the many MXene reported to date, $Ti_3C_2T_2$ is by far the most studied: it has been shown to exhibit outstanding properties for energy storage applications among others. [1,2] In these systems, the surface groups (e.g. their chemical nature and localization) play a key role since they affect the energy storage performances [3] or modify their optical and magnetic properties.[4] Given their crucial role, these functionalization groups have been intensively investigated, mainly from a theoretical point of view. In particular, density functional theory (DFT) calculations predict two stable sites for T labeled C1 (the T groups are on top of the volume Ti – see fig. 1 a-b) and C2 (the T groups are on top of the carbon atoms – see fig. 1 a-b). A third configuration, labeled C3, corresponds to a mix of C1 and C2 (see figure 1-b). However, such predictions have hardly been confirmed experimentally. In this context, we present a combined experimental and theoretical investigation of the electronic structure of $Ti_3C_2T_2$ based on valence electron energy-loss spectroscopy. In particular, we provide experimental evidence allowing for the identification of the T group localization at the nanometer scale and investigate their role on the MXene dielectric and related optical properties.

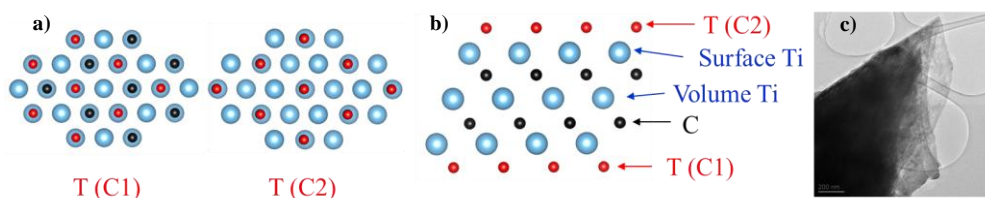


Figure 1: a) Top views corresponding to the C1 and C2 configurations b) Side view of a $Ti_3C_2T_2$ single sheet evidencing the C3 configuration with the T groups in C1 and C2 on each side of the sheet. c) TEM micrograph evidencing a several hundreds of nanometer long $Ti_3C_2T_2$ multilayer stacks.

2. RESULTS

2.1 Experimental and calculations details

The $Ti_3C_2T_2$ samples were prepared as described in the literature by etching Al from Ti_3AlC_2 powders using hydrofluoric acid. The VEELS spectra were recorded on the as-obtained powders (see fig. 1c for a typical TEM micrograph) in a JEOL 2200FS microscope equipped with an in-column omega filter and operated at 200 kV. The energy resolution, given by the zero-loss peak full width at half maximum, is 0.8 eV. The choice for VEELS is motivated by the intense signal that can be collected in short acquisition times: this is particularly important for the study of the radiation sensitive T groups. Moreover, VEELS provides versatile information combining collective excitations and localized interband transitions.

The theoretical VEEL spectra were obtained from the MXene dielectric response computed within the DFT framework in the independent particle approximation (IPA) using the WIEN2k package. The VEELS cross-section was computed accounting for crystallographic orientation, collection angles, sample thickness and relativistic as well as surface modes using the Kröger cross-section. This approach proved to give very good results for these systems.[4] The structural models, used as inputs for the DFT calculations, were obtained from

DFT relaxations of the atomic positions considering the different configurations for the surface groups (C_1 , C_2 and C_3). Experimental unit cell parameters, determined from Reitveld refinements of powder X-ray diffractograms, were used: these data evidence that the MXene stack exhibit a long range ordering with a periodicity corresponding to two single sheets. The chemical composition was checked by wavelength dispersive x-ray spectroscopy performed in a JEOL 7001F-TTLS scanning electron microscope.

2.2 Results and discussion:

The comparison between a typical $Ti_3C_2T_2$ VEEL spectrum with spectra recorded in the same conditions on Ti_3AlC_2 (the material from which the MXene is obtained) and TiC samples, reveal important similarities between the electronic structure of the MXene and TiC (see fig. 2a). In particular the bulk plasmon energy is almost equal in the two systems evidencing similarities in the behaviors of their valence electron gases.

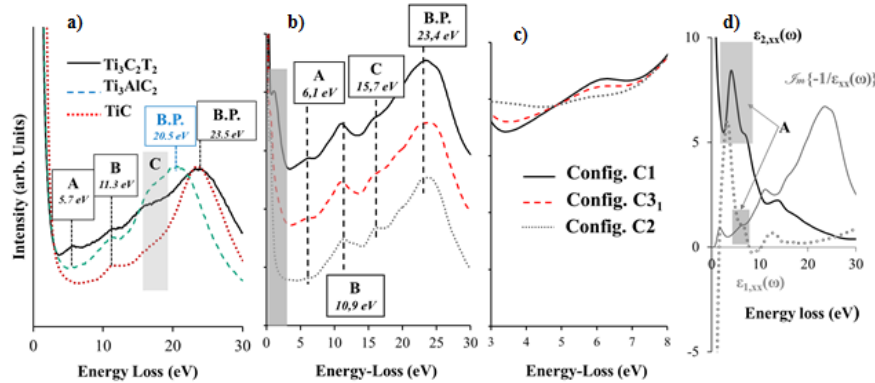


Figure 2: a) Experimental VEEL spectra recorded on $Ti_3C_2T_2$ (full black lines), Ti_3AlC_2 (dashed blue lines) and TiC (red dotted lines). b) Theoretical VEEL spectra obtained for the different T-groups configurations in the $Ti_3C_2(OH)_2$ system. c) Enlargement of the energy range corresponding to structure A in b). d) Imaginary (full black line) and real (gray dots) parts of $\epsilon_{xx}(0,\omega)$

Figure 2 a) reveals a noticeable difference between the three compounds: the peak A is characteristic of the MXene's electronic structure. From the comparison with the theoretical VEEL spectra obtained considering the different configurations for the T groups (see fig. 2b and c), this peak is clearly assigned to the C1 configuration, opening the way to the investigation of the MXene's functionalization sites at the nanometer scale. From the analysis of the dielectric response, peak A is shown to be an intense interband transition (IBT) emerging around 4 eV in the basal plane dielectric response of the system (see the shaded peak in fig. 2d). The origin of this interband transition will be discussed in terms of hybridization changes within the TiC layer as a function of the localization of the T groups and its role in the optical properties of $Ti_3C_2T_2$ will be discussed. Of special interest is the fact that this IBT leads to a 40% drop in the optical conductivity in the middle of the visible spectrum which is very promising for sensing or transparent thin films applications.

CONCLUSION

In conclusion, the VEEL spectra and related dielectric properties of 2D titanium carbide staked layers have been investigated both experimentally and theoretically. Besides evidencing important similarities between the $Ti_3C_2T_2$ and TiC valence electron gases, a clear spectroscopic signature of the MXene most stable functionalization sites is highlighted. On the basis of DFT calculations, this signature is identified as an interband transition having a prominent role on the optical properties of this system.

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