

## Characterization of the surface functionalization of composites 2D titaniumcarbides/transition metal oxides using a combination of TEM, first-principles calculations and electrochemistry

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Due to the constant increase of the global energy consumption and the intermittence of renewable energy it is crucial to develop efficient electricity storage systems. Among the possibilities, hydrogen gas is a very promising energy vector since it can be directly used in a fuel cell without dangerous by products. Since the conversion of energy into hydrogen can be achieved by an electrolyzer through the water splitting reaction, the combination electrolyzer-fuel cell could be the key to the renewable energy systems. The limitation to this process comes from the sluggish reactions involving the oxygen (oxygen reduction reaction ORR and oxygen evolution reaction OER). Therefore, it is required to develop cost-effective and efficient catalysts to enhance these reactions. Recently a new kind of 2D material has emerged, the MXenes. These materials (fig1) consist in  $M_{n+1}X_n$  octahedrons sheets ( $n = 1$  to  $3$ ) which are obtained by the exfoliation of the A element layers from  $M_{n+1}AX_n$  phases (M = Transition Metal, A: group III-A or IV-A, X : C and/or N). The exfoliation results in the surface passivation of the  $M_{n+1}X_n$  sheets with different T terminal groups (OH, F, O ...) which considerably alter their properties. As an example, the nature of the surface groups which can be modified by adjusting the synthesis protocols,<sup>2,3</sup> play a key role on the electronic structure<sup>2</sup> or the behavior in water.<sup>3</sup> Pioneering works in this domain highlight MXenes as promising catalysts or active supports (co-catalyst) regarding ORR or OER. On the other hand, numerous studies have focused on transition metal oxide nanoparticles (TMO) supported on conductive support such as reduced graphene oxide, showing promising properties<sup>4</sup>. In this way, the preparation of TMO@MXene composites to be used as electrocatalyst for OER and ORR is challenging. We managed to prepare a  $Ti_3C_2@Co_3O_4$  composite by directly synthesize the  $Co_3O_4$  nanoparticles on  $Ti_3C_2$  through different synthesis methods: hydrothermal or polyol. However, a very low oxidation peak (at 1-1.2 V vs RHE) corresponding to the irreversible surface oxidation of the MXene is observed on the electrochemical signature of the composite prepared by hydrothermal method whereas this peak is very intense on the MXene alone (fig2). This indicates a probable modification of the support during the composite synthesis. Indeed, transmission electron microscopy study combining diffraction and Electron Energy Loss Spectroscopy revealed that the synthesis process oxidized the  $Ti_3C_2$  (fig3) while common characterization techniques (XRD) were inconclusive. In an opposite way, polyol method allows to avoid the oxidation of the MXene during the composite synthesis. The influence of the synthesis method on the composite nature and their electrochemical performances will be discussed during this communication. Based on the obtained results, further investigations including in-situ electrochemical studies in the microscope will be performed to highlight the surface oxidation mechanism under potential.

<sup>1</sup> B. Anasori *et al.*, Nature Reviews **2**, 16098 (2017)

<sup>2</sup> D. Magne *et al.*, Physical Chemistry Chemical Physics **18**, 30946 (2016)

<sup>3</sup> X. Wang *et al.*, Journal of Materials Chemistry A **5**, 22012 (2017)

<sup>4</sup> K. Kumar *et al.*, J. Phys. Chem. C, **120**, 7949 (2016)

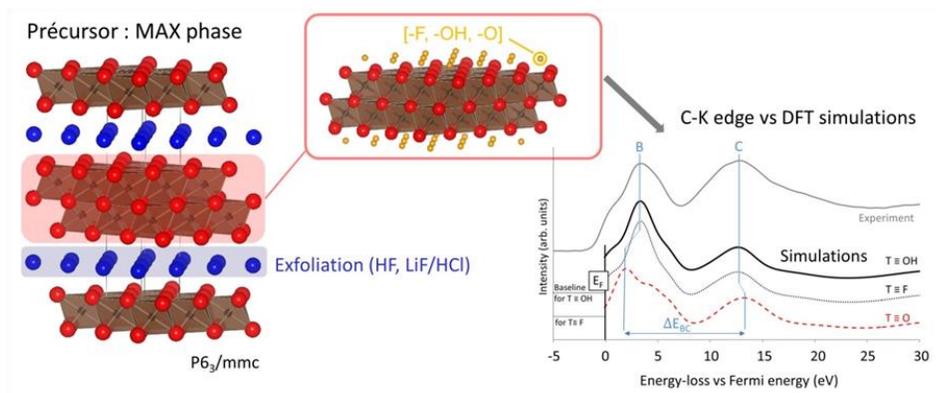


Figure 1: Position of the surface groups, distance between foils and chemical reactivity are intertwined (left). First principles calculations and electron energy loss spectroscopy at the C-K edge give insight on the role of the surface groups on the MXene electronic structure.

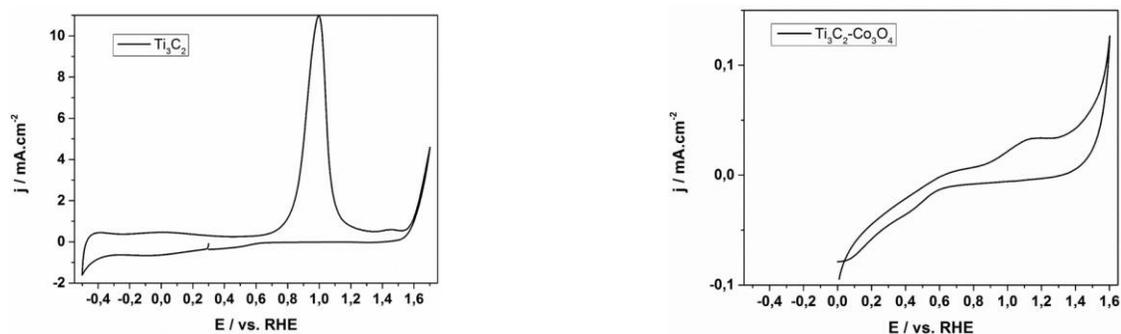


Figure 2:  $\text{Ti}_3\text{C}_2$  and  $\text{Ti}_3\text{C}_2@\text{Co}_3\text{O}_4$  composite voltammograms recorded in a  $\text{N}_2$  saturated KOH electrolyte (0.1 M) at  $25^\circ\text{C}$ , with a scan rate of  $20 \text{ mV s}^{-1}$

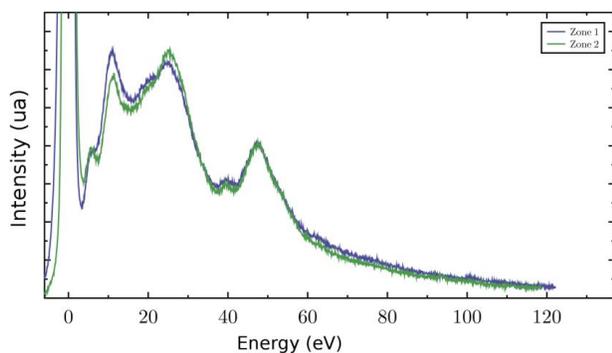


Figure 3a: Low-loss region of the EELS spectrum for two zones on the sample. Characteristic signal of oxidized titanium is obtained.

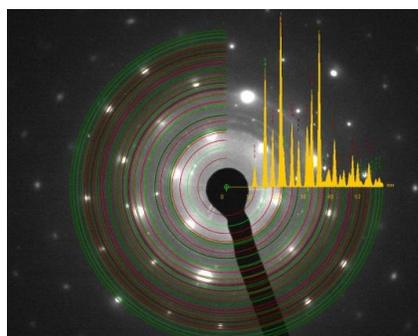


Figure 3b: SAED pattern of the supporting MXene and the ring pattern of the  $\text{TiO}_2$  (with calculated in green) and  $\text{Co}_3\text{O}_4$  (calculated red)