The Interfacial Effect of MXene Composites for Dielectric Properties

Engineering Electronic and Dielectric Properties of Early Transition Metal Carbide or Nitride

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In Short

- Determination of the favorite functionalized structures of MXene with varying functional groups
- Computation of band structure of functionalized MXene using DFT method
- Dielectric function calculation using the Random-phase-approximation
- Investigation of the effects of interfacial dipole polarization on the dielectric loss of functionalized MXene
- Explain the mechanism of the dielectric loss from an microscopic viewpoint

Since recently, as a young class of two-dimensional substances, MXene have been attracting tremendous attention, by virtue of their high electrical conductivity, excellent energy storage properties and superior mechanical properties [1, 2]. All these features render MXene a good candidate as novel electromagnetic absorption materials. MXene have a general formula of $M_{n+1}X_nT_x$, where M is an early transition metal (e.g. Ti, Mo, Nb, or V), X stands for carbon and/or nitrogen and T denotes the surface functional groups (OH, O, F) [3].The structure of $Ti_3C_2T_X$ is shown in Fig 1(a). With these functional groups, their physical and chemical properties differ enormously from those of pure MXenes according to previous theoretical predictions. G. R. Berdiyorov. et al [4]. demonstrated the changes of interlayer spacing after introducing surface functionalization on $Ti_3C_2T_X$. Dashuai Wang. et al [5]. compared different possible configurations of different functional group positions on Ti_3C_2, and determined their lowest energy phase. We guess that the presence of functional groups gives rise to ample intrinsic defects, leading to the increase of magnetic polarization and the decrease of metallic conductivity, which can be used to optimize the dielectric loss and impedance matching.

However, these speculated results are hard to be confirmed by experimental tests. We need the theoretical work to simulate and confirm our guess. Therefore, we are planning, by employing density functional theory combined with hybrid functional (PBE0), to study the electronic and optical properties of functional groups on MXene.

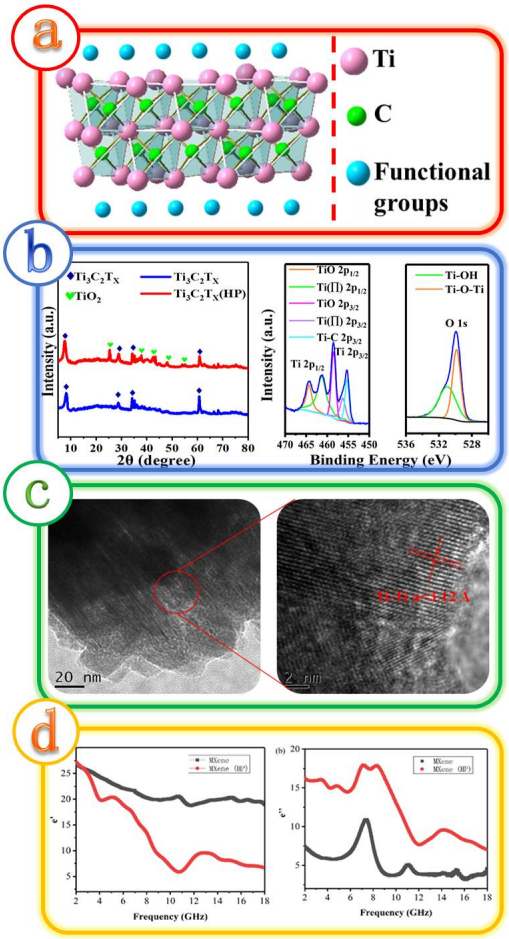

***Figure 1:** (a) Structure of $Ti_3C_2T_X$, (b) XRD patterns (left) and XPS survey spectrum (right) of $Ti_3C_2T_X$ through experiments, (c) TEM images (left) and HRTEM images (right) of $Ti_3C_2T_X$ through experiments, (d) The real part (left) and the imaginary part (right) of dielectric constant through experiments.*

On the other hand, our own experiment has pointed out that transition metal oxide (TiO_2) containing composites can be obtained through the high-temperature oxidation process (HP) of MXene. These materials display promising microwave absorption performance due to the possible collective mechanism of interfacial dipole movement [6]. The existence of TiO_2 on Ti_3C_2 can be confirmed by experimental XRD (X-ray Diffraction) and XPS (X-ray photoelectron spectroscopy) results (see Fig. 1(b)).

Moreover, the lattice constant of $Ti_3C_2T_X$ also

can be confirmed by TEM (Transmission Electron Microscope) and HRTEM (High Resolution Transmission Electron Microscope) images in Fig. 1(c). This provides the basic data for simulation. Fig. 1(c) shows the existence of Ti-OH bond formed between titanium and the surface hydroxyl groups in $Ti_3C_2T_X$. Moreover, the strong peaks of Ti-O-Ti can be attributed to anatase TiO_2.

The electromagnetic experimental tests show that there is a significant difference of dielectric constant after the high-temperature oxidation (as seen in Figure 1(d)), which contribute to the introduced TiO_2 bringing an interfacial dipole polarization into the system [7]. In view of this, we believe that the interfacial dipole polarization is the most important factor that determine the dielectric loss of oxidated MXene. However, it is impossible to measure the degree of interfacial dipole polarization through experiment. Motivated to explore the polarization mechanism, we will carry out first principle calulations in the framework of DFT, as implemented in the VASP.

In this work, we are going to investigate how the adsorption of TiO_2 tunes the electronic, optical and dielectric properties of MXene from the theoretical view, and further compare with our experimental results. The process includes: optimising the structure, band structure, bader analysis, STM, XRD and so on. As the interfacial dipole polarization is the most important factor which will significantly influence the dielectric loss in a macroscopic quantity, the computational calculation is the most efficient method to measure the degree of polarization. our purpose is to explain the mechanism of the dielectric loss from an microscopic viewpoint.

Two main objectives driving this project are the following: (1) study the interfacial effect on electronic, optical and dielectric properties; (2) explore the effect of different functional groups on the MXene. We believe that our investigations can stimulate further development and extend the application in the engineering of MXene.

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More Information

[1] J. Lee et al., *Funct. Compos. Struct.* **1**, 015003 (2019). doi:10.1088/2631-6331/ab0c7f

[2] K. Fan et al., *J. Phys. Chem. C* **123**, 18207-18214 (2019). doi:10.1021/acs.jpcc.9b03963

[3] Z.W. Zhang et al., *ACS Sustainable Chem. Eng.* **4**, 6763-6771 (2016). doi:10.1021/acssuschemeng.6b01698

[4] G. R. Berdiyorov et al., *EPL* **111**, 67002 (2015). doi:10.1209/0295-5075/111/67002

[5] D.S. Wang et al., *ACS Nano* **13**, 11078-11086 (2019). doi:10.1021/jacs.8b08994

[6] T.M. Su et al., *ACS Appl. Energy Mater.* **2**, 4640-4651 (2019). doi:10.1021/acsaem.8b02268

[7] G.Y. Gou et al., *ACS Nano* **13**, 12613-12620 (2019). doi:10.1021/acsnano.9b03889

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