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Investigation of the Dielectric Response of PPy/V_2C MXene—ZnO Using Quantum Mechanical Calculations †

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Abstract: Considering the snowballing of electronic devices with the wide spreading usage of miniaturized energy storage gadgets, the need for sustainable, flexible, lightweight, and higher power density devices to supplement the global fossil fuel challenges and depletion, is gathering attention. In this regard, polymer/ceramics nanocomposites have recently accrued more attention as a promising material for future energy storage technology, which requires a breakdown strength and high dielectric constant. High dielectric constant, which is caused by interface polarization and electric polarization, could be created by the inclusion of conductive hybrid fillers of MXene (V_2C) and ZnO particles into the polymers to form a nanocomposite with improved dielectric constant. Herein, quantum mechanical calculations are employed to investigate the charge distribution and the bonding that exist between the ceramic/ceramic boundary area of V_2C Mxene–ZnO in the PolyPyrrole matrix. The non-uniform distribution of charges is expected to improve the dielectric response for energy storage applications. Also, the structure of the ternary nanocomposite can also be improved by the interfacial ionic bonding of the hybrid fillers. Furthermore, to understand the electron migration mechanism, the electron localization function, and the density of state of the V_2C–ZnO are studied.

Keywords: Ternary nanocomposites; MXene; polypyrrole; quantum mechanical calculations; hybrid filler; ZnO

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1. Introduction

The dielectric property of a material determines its response towards electric field. Consequently, it affects several other material properties which include electrical conductivity, capacitance, and polarization. Hence, the dielectric response of a material is a significant factor to be considered when choosing a material for technological applications such as sensors, electronic components, and energy storage devices [1].

Conductive polymeric nanocomposites have recently proven useful for energy storage material for future electronic gadgets [2–5]. Polypyrrole based nanocomposites have been researched for dielectric applications, exploring other properties such as its light

weight to strength ratio, flexibility, and thermal stability when filled with metallic oxides and, or 2D materials [4,6–9]. The inclusion of these materials into a polypyrrole matrix has proven to improve the dielectric constant of the nanocomposite as well as low dielectric losses [10,11].

Vanaduim Carbide (V_2C), also a class of MXene, is a 2D material inorganic compound with a prevalent vanadium metal and alloy. In a study, MXene-V_2C has account for high dielectric constant of 11,800 and low dielectric loss of 1.31 when combine with Polyvinyl chloride [6,12,13]. Also, MXene-V_2C when filled with ceramics of about 5%, has shown a low dielectric loss of 0.2 and improved dielectric constant of 232 [14]. Again, the nanocomposite of ionic liquid/V_2C/polymer with 4% weight of V_2C, has recorded a high dielectric constant of 54 with a low dielectric loss of 0.15 at 1 kHz [15].

On the other hand, ZnO, which has broad band gap and good chemical stability can be used to achieve improved dielectric constant for several applications. Its nanocomposites have been studied for their possible use in dielectric applications [15–19]. The resulted nanocomposites depict improved breakdown strength, electrical conductivity, good dissipation factor, and high dielectric permittivity. In a study, ZnO accounts for the high dielectric performance of (PVA-PEO)-ZnO ternary composites [20] as well as its strong thermal stability.

Finally, it is expected that the inclusion of ZnO and MXene- V_2C hybrid into polypyrrole matrix could result to a ternary nanocomposite with enhanced dielectric characteristics. To understand and optimize the dielectric properties of PPy/V_2C Mxene-ZnO, it is important to investigate the dielectric response of the material for potential applications and academic knowledge in material science. In this study, quantum mechanical calculation is employed to study the dielectric behavior of PPy/V_2C Mxene-ZnO ternary nanocomposites, with the objectives of understanding the charge distribution, bonding, and electron transfer mechanism at the ceramic interface.

2. Computational Method

The dielectric response of PPy/V_2C Mxene-ZnO is investigated using the first principle calculations. Density functional theory (DFT) method, which is based on Kohn-Sham equation, is used. From the equation, the electron density function can be represented by the total energy of the system [21–29]. To define the electron-electron exchange within the composite, the exchange-correlation functionals were used in our calculations and was modelled using Perdew–Burke–Ernzerh (PBE) and generalized gradient approximation (GGA).

Firstly, the MXene structure was modelled with 3 × 3 periodic supercell lattice structure, after which the ZnO structure was modelled with with 2 × 2 non-periodic supercell. Thereafter, structural optimization was carried out using DMol3 in Material studio software to reduce the overall energy of the system and adjust the atomic positions. This was preceded by adsorption calculation to formulate the configurations for optimized V_2C Mxene-ZnO. Furthermore, Cambridge Sequential Total Energy Package (CASTEP) was employed to perform series of calculations to determine electronic properties of the hybrid filler using 571ev for wave cut off energy and 10×10×1 k-points Brillouin zone. Finally, the pseudopotential and relativistic treatment were considered using OTFG ultrasoft with Koelling-Harmon.

3. Results and Discussion

The dielectric mechanism of the hybrid fillers was examined using DFT calculations (Figure 1a,b). The values of the charges were established by Mulliken population analysis. Figure 2 shows that several Zn atoms from ZnO absorbed unto V2C surfaces, also, the figure shows the 3D geometric structure of ZnO/V_2C interface. Zn-V metallic bonds were formed after hybridization, with bond length of 2.62 Å. The charge transfer values are represented by the values in red as stipulated by the Mulliken population study. The Zn-

V dipole has a lower hole amount, which indicates an increase in the quantity of electricity charged at Zn atom. Hence, an improved dielectric response in PPy/V_2C Mxene-ZnO nanocomposites. The nature of the chemical bonding at the hybrid filler interface suggests the non-uniform charge distribution. This improves the dipole polarization at the ceramic-ceramic interface, as such, the dielectric response [29]. Again, the hybrid structure of V_2C-ZnO enhances the dielectric responsiveness of the ZnO filler.

The density of states (DOS) diagram (Figure 3a) shows the orbital electrons in the structure of V_2C/ZnO. As shown in the diagram, both the d and p-orbitals are prevalent at the Fermi level. Therefore, the increase in the amount of d and p-orbitals could ultimately improve the Fermi level contributions. Figure 3b shows the DOS values of V_2C/ZnO and V_2C structures. The simple measure of molecular systems/electron localization in an atom known as electron localization function (ELF) is established by Becke and Edgecombe [30]. The electron localization contribution of the electrons at the surface of the V_2C/ZnO hybrid filler is elucidated through the ELF of its structure. The findings for the side and top surfaces of the hybrid filler are shown in Figure 3c,d. It was observed that the electron localization in ZnO, which was enhanced, caused the increase in electron migration within V_2C/ZnO structure, as shown on the electron localization map. This confirms the DOS for the V_2C/ZnO and V_2C structures.

Finally, the nature of the bonding at V_2C/ZnO interface prevented an increase in conduction leakage at the interface. The results show that the ternary nanocomposite has high electrical breakdown strength. Therefore, the nanocomposite film has appreciable electrical characteristics for desired energy storage applications.

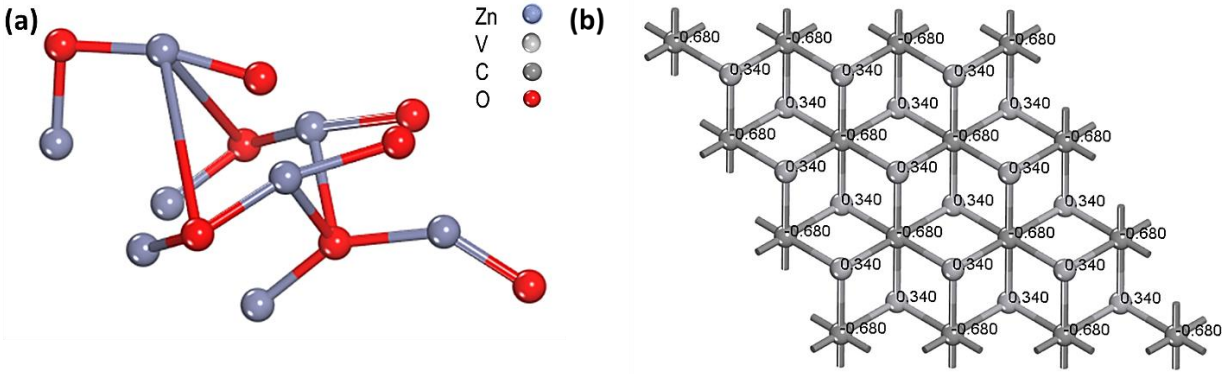

Figure 1. (**a**) Optimized 3D structural representation of ZnO, (**b**) Structural representation of the Top-surface of V_2C–MXene.

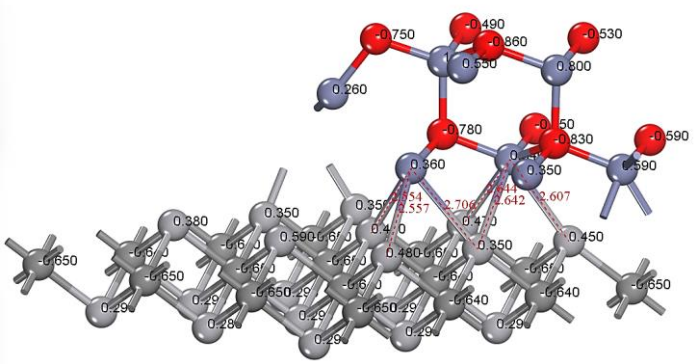

Figure 2. The 3D structural configuration of optimized V_2C/ZnO hybrid with charge distribution.

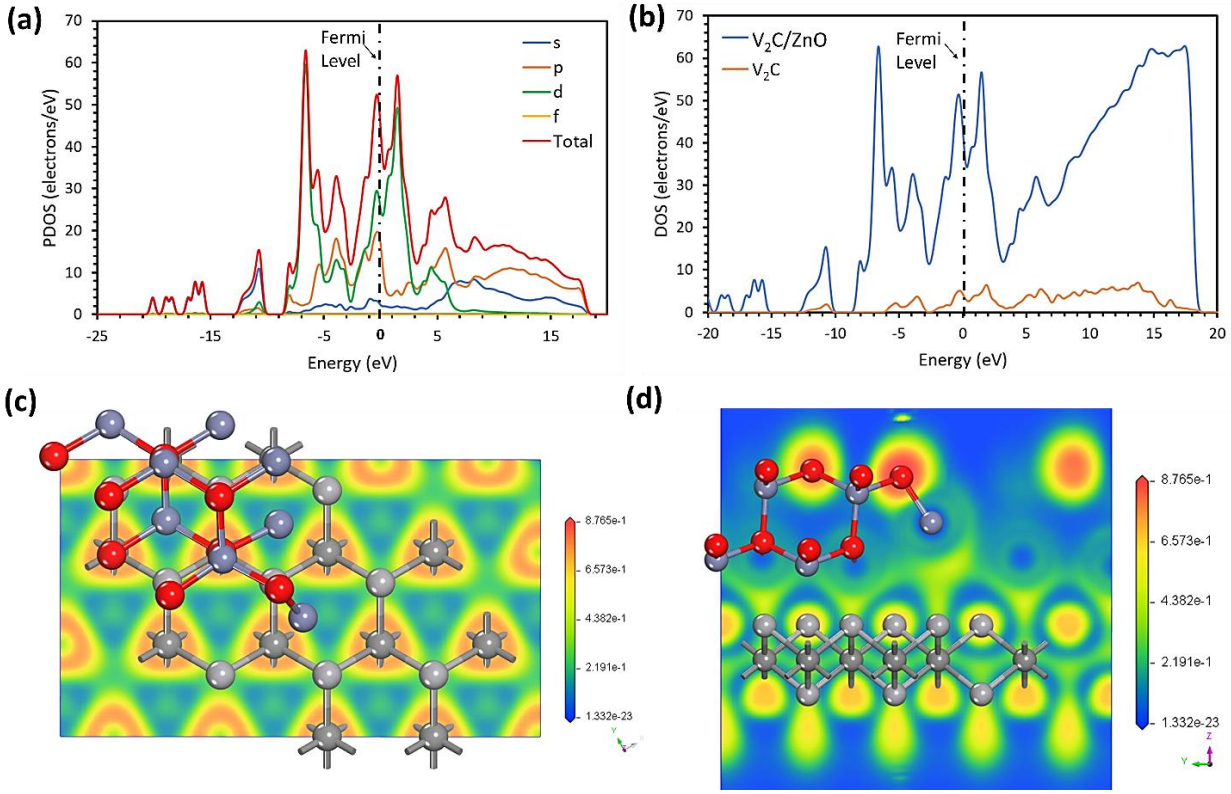

Figure 3. (**a**) The DOS diagrams for the s, p, and d-orbital atoms in the V_2C-ZnO, (**b**) The DOS results of the atoms for the structure (**c**), The ELF result of the Top-surface, and (**d**) The side-surface.

4. Conclusions

This study utilized the DFT calculations to examine the dielectric response of PPy/V_2C-ZnO ternary nanocomposite at ceramic-ceramic interface. From the calculations, the results showed a strong dielectric response of the ternary nanocomposites at the ceramic-ceramic boundary. This suggests PPy/V_2C-ZnO a potential material for applications where dielectric response is a factor, such as electronics, sensors, and energy storage applications. The results offer a clearer understanding to this novel material which can be optimized for future designs and technology. Further research on the dielectric properties of this material could help to prove it is a promising material for unlimited electronic applications.

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