*materials proceedings*

MDPI

*Proceeding Paper*

# Investigation of the Dielectric Response of PPy/$V_2C$ MXene–ZnO Using Quantum Mechanical Calculations †

**Anthony Chidi Ezika [1,*], Emmanuel Rotimi Sadiku [1], Gbolahan Joseph Adekoya [1], Suprakas Sinha Ray [2,3] and Yskandar Hamam [4,5]**

[1] Institute of NanoEngineering Research (INER), Department of Chemical, Metallurgical and Materials Engineering, Faculty of Engineering and the Built Environment, Tshwane University of Technology, Pretoria 0183, South Africa; sadikur@tut.ac.za (E.R.S.); gadekoya2@gmail.com (G.J.A.)
[2] Centre for Nanostructures and Advanced Materials, DSI-CSIR Nanotechnology Innovation Centre, Council for Scientific and Industrial Research, CSIR, Pretoria 0001, South Africa; rsuprakas@csir.co.za
[3] Department of Chemical Sciences, University of Johannesburg, Doornfontein, Johannesburg 2028, South Africa
[4] French South African Institute of Technology (F'SATI)/Department of Electrical Engineering, Tshwane University of Technology, Pretoria 0001, South Africa; hamama@tut.ac.za
[5] École Supérieure d'Ingénieurs en Électrotechnique et Électronique, Cité Descartes, 2 Boulevard Blaise Pascal, Noisy-le-Grand, 93160 Paris, France
* Correspondence: tonero2017@gmail.com
† Presented at the 4th International Online Conference on Nanomaterials, 5–19 May 2023; Available online: https://iocn2023.sciforum.net/.

**Abstract:** Considering the snowballing of electronic devices with the widespread 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 nonuniform distribution of charges is expected to improve the dielectric response for energy storage applications. In addition, 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



**Citation:** Ezika, A.C.; Sadiku, E.R.; Adekoya, G.J.; Ray, S.S.; Hamam, Y. Investigation of the Dielectric Response of PPy/$V_2C$ MXene–ZnO Using Quantum Mechanical Calculations. *Mater. Proc.* **2023**, *14*, 70. https://doi.org/10.3390/IOCN2023-14467

Academic Editor: Ullrich Scherf

Published: 5 May 2023



## 1. Introduction

The dielectric property of a material determines its response towards the 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 consider 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 been

proven to improve the dielectric constant of the nanocomposite as well as low dielectric losses [10].

Vanadium 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–$V_2C$ accounted for high dielectric constant of 11,800 and low dielectric loss of 1.31 when combined with polyvinyl chloride [6,11,12]. In addition, 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 [13]. 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 [14].

On the other hand, ZnO, which has a 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 [15–18]. The resulted nanocomposites depict improved breakdown strength, electrical conductivity, good dissipation factor, and high dielectric permittivity. In a study, ZnO contributed to the high dielectric performance of (PVA-PEO)–ZnO ternary composites [19] as well as their strong thermal stability.

Finally, it is expected that the inclusion of ZnO and MXene–$V_2C$ hybrid into a polypyrrole matrix could result in 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 behaviour 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. The density functional theory (DFT) method, which is based on the Kohn–Sham equation, is used. From the equation, the electron density function can be represented by the total energy of the system [20–28]. To define the electron–electron exchange within the composite, the exchange-correlation functionals were used in our calculations and were modelled using Perdew–Burke–Ernzerhof (PBE) and generalized gradient approximation (GGA).

Firstly, the MXene structure was modelled with a $3 \times 3$ periodic supercell lattice structure, after which the ZnO structure was modelled with a $2 \times 2$ nonperiodic 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, the Cambridge Sequential Total Energy Package (CASTEP) was employed to perform a series of calculations to determine electronic properties of the hybrid filler using 571 ev for wave cut-off energy and $10 \times 10 \times 1$ 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 the 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 the Zn atom, hence resulting in an improved dielectric response in PPy/$V_2C$ Mxene–ZnO nanocomposites. The nature of the chemical bonding at the hybrid

filler interface suggests the nonuniform charge distribution. This improves the dipole polarization at the ceramic–ceramic interface; i.e., the dielectric response [28]. Again, the hybrid structure of $V_2C$–ZnO enhances the dielectric responsiveness of the ZnO filler.

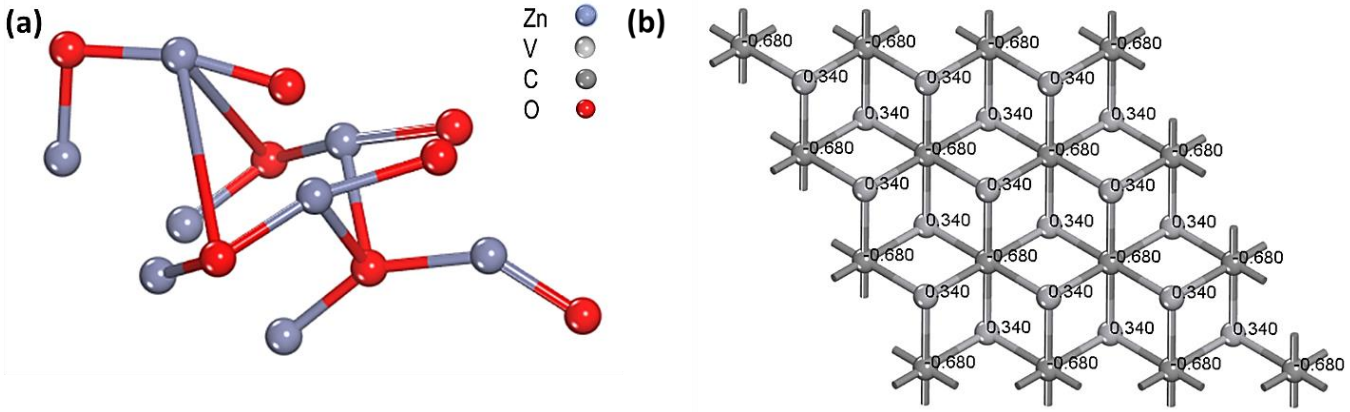


**Figure 1.** (**a**) Optimized 3D structural representation of ZnO. (**b**) Structural representation of the top surface of $V_2C$–MXene.

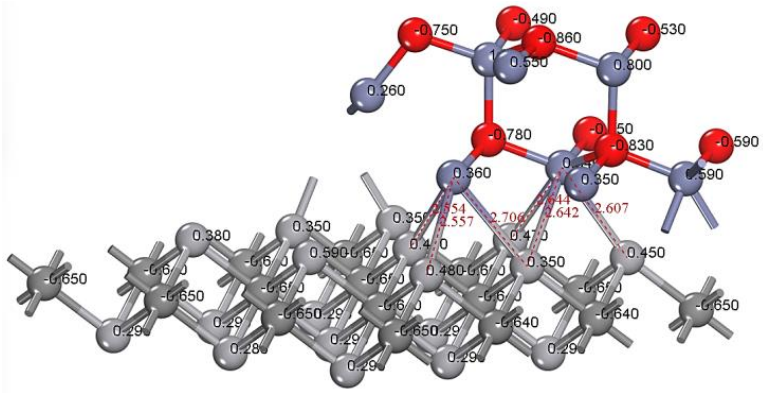


**Figure 2.** The 3D structural configuration of the optimized $V_2C$/ZnO hybrid with charge distribution.

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 [28]. 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 the $V_2C$/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 the $V_2C$/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.

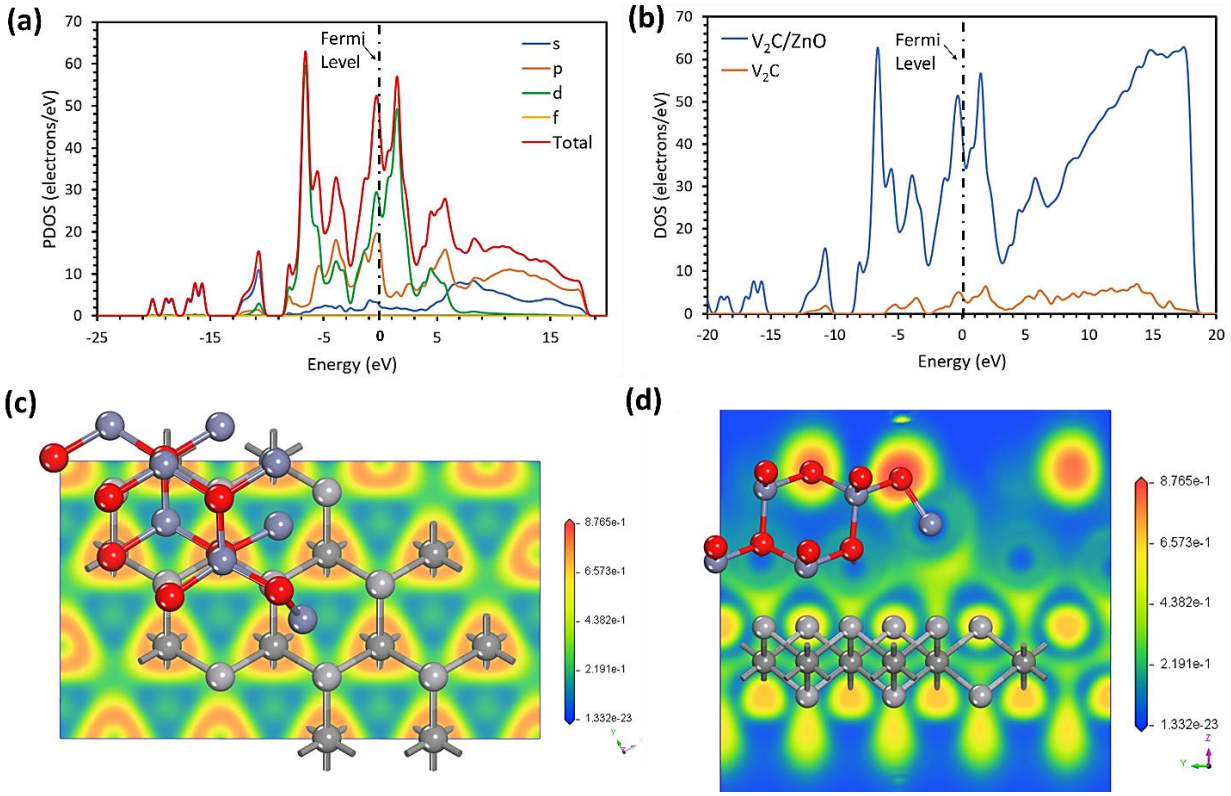


**Figure 3.** (**a**) The DOS diagrams for the s-, p-, and d-orbital atoms in the $V_2C$–ZnO. (**b**) The DOS results of the atoms for the structure. (**c**) The ELF result of the top surface. (**d**) The side surface.

## 4. Conclusions

This study utilized the DFT calculations to examine the dielectric response of a PPy/$V_2C$–ZnO ternary nanocomposite at the ceramic–ceramic interface. From the calculations, the results showed a strong dielectric response of the ternary nanocomposites at the ceramic–ceramic boundary. This suggests that PPy/$V_2C$–ZnO is 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 of 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 that it is a promising material for unlimited electronic applications.

**Author Contributions:** A.C.E. and G.J.A.: Software, Data curation, Conceptualization, Methodology and Formal Analysis; E.R.S., S.S.R. and Y.H.: Supervision, Validation, Review and Editing. All authors have read and agreed to the published version of the manuscript.

**Funding:** Anthony Chidi Ezika with scholarship no 222892236 would like to acknowledge the financial support of the Tshwane University of Technology, Pretoria, South Africa.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Data availability is on request.

**Acknowledgments:** The author would like to thank the Center for High Performance Computing (CHPC), South Africa, for access to computing resources.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References


1. Feng, Q.-K.; Zhong, S.-L.; Pei, J.-Y.; Zhao, Y.; Zhang, D.-L.; Liu, D.-F.; Zhang, Y.-X.; Dang, Z.-M. Recent Progress and Future Prospects on All-Organic Polymer Dielectrics for Energy Storage Capacitors. *Chem. Rev.* **2022**, *122*, 3820–3878. [CrossRef] [PubMed]
2. Liu, Y.; Liu, Y.; Zhao, X. The influence of dopant on the dielectric properties of flexible polypyrrole composites. *J. Text. Inst.* **2017**, *108*, 1280–1284. [CrossRef]
3. Adekoya, G.J.; Sadiku, R.E.; Ray, S.S. Nanocomposites of PEDOT:PSS with Graphene and its Derivatives for Flexible Electronic Applications: A Review. *Macromol. Mater. Eng.* **2021**, *306*, 2000716. [CrossRef]
4. Ezika, A.C.; Sadiku, E.R.; Idumah, C.I.; Ray, S.S.; Adekoya, G.J.; Odera, R.S. Recently emerging trends in MXene hybrid conductive polymer energy storage nanoarchitectures. *Polym.-Plast. Technol. Mater.* **2022**, *61*, 861–887. [CrossRef]
5. Adekoya, G.J.; Adekoya, O.C.; Sadiku, R.E.; Ray, S.S. Structure-property relationship and nascent applications of thermoelectric PEDOT:PSS/carbon composites: A review. *Compos. Commun.* **2021**, *27*, 100890. [CrossRef]
6. Ezika, A.C.; Sadiku, E.R.; Idumah, C.I.; Ray, S.S.; Hamam, Y. On energy storage capacity of conductive MXene hybrid nanoarchitectures. *J. Energy Storage* **2022**, *45*, 103686. [CrossRef]
7. Ezika, A.C.; Sadiku, E.R.; Ray, S.S.; Hamam, Y.; Folorunso, O.; Adekoya, G.J. Emerging advancements in polypyrrole MXene hybrid nanoarchitectonics for capacitive energy storage applications. *J. Inorg. Organomet. Polym. Mater.* **2022**, *32*, 1521–1540. [CrossRef]
8. Ezika, A.C.; Sadiku, E.R.; Ray, S.S.; Hamam, Y.; Adekoya, G.J.; Lolu, O.J. Fabrication and investigation of electrically conductive spark plasma sintered polypyrrole-based MXene–Ti3C2Tx hybrid nanoarchitectonics for electrode material. *J. Mater. Sci. Mater. Electron.* **2023**, *34*, 168. [CrossRef]
9. Ezika, A.C.; Sadiku, E.R.; Adekoya, G.J.; Hamam, Y.; Sinha Ray, S. Response surface optimization and finite element homogenization study of the effective elastic modulus and electrical conductivity of MXene-polypyrrole hybrid nanocomposite as electrode material for electronic energy storage devices. *Polym. Eng. Sci.* **2022**, *63*, 338–352. [CrossRef]
10. He, Z.-Z.; Yu, X.; Yang, J.-H.; Zhang, N.; Huang, T.; Wang, Y.; Zhou, Z.-W. Largely enhanced dielectric properties of poly(vinylidene fluoride) composites achieved by adding polypyrrole-decorated graphene oxide. *Compos. Part A Appl. Sci. Manuf.* **2018**, *104*, 89–100. [CrossRef]
11. Mazhar, S.; Qarni, A.A.; Ul Haq, Y.; Ul Haq, Z.; Murtaza, I. Promising PVC/MXene based flexible thin film nanocomposites with excellent dielectric, thermal and mechanical properties. *Ceram. Int.* **2020**, *46*, 12593–12605. [CrossRef]
12. Deng, Q.; Chen, B.; Bo, M.; Feng, Y.; Huang, Y.; Zhou, J. Interfacial fluorine migration-induced low leakage conduction in PVA based high-k composites with V2C MXene-SWCNT switchboard-like ceramic via ab initio MD simulations. *J. Mater. Chem. C* **2021**, *9*, 1051–1061. [CrossRef]
13. Deng, Q.; Zhao, X.; Zhu, Q.; Bo, M.; Feng, Y. Reinforced dielectric response in polymer/V2C MXene composite high-insulation films enabled through dispersing ionic liquid. *J. Electroceramics* **2021**, *46*, 124–130. [CrossRef]
14. Saadi, H.; Benzarti, Z.; Sanguino, P.; Hadouch, Y.; Mezzane, D.; Khirouni, K.; Abdelmoula, N.; Khemakhem, H. Improving the optical, electrical and dielectric characteristics of ZnO nanoparticles through (Fe + Al) addition for optoelectronic applications. *Appl. Phys. A* **2022**, *128*, 691. [CrossRef]
15. Kaur, D.; Bharti, A.; Sharma, T.; Madhu, C. Dielectric Properties of ZnO-Based Nanocomposites and Their Potential Applications. *Int. J. Opt.* **2021**, *2021*, 9950202. [CrossRef]
16. Ul Haq, Y.; Murtaza, I.; Mazhar, S.; Ahmad, N.; Qarni, A.A.; Ul Haq, Z.; Khan, S.A.; Iqbal, M. Investigation of improved dielectric and thermal properties of ternary nanocomposite PMMA/MXene/ZnO fabricated by in-situ bulk polymerization. *J. Appl. Polym. Sci.* **2020**, *137*, 49197. [CrossRef]
17. Vaishnav, D.; Goyal, R.K. Thermal and Dielectric Properties of High Performance Polymer/ZnO Nanocomposites. *IOP Conf. Ser. Mater. Sci. Eng.* **2014**, *64*, 012016. [CrossRef]
18. Choudhary, S. Dielectric dispersion and relaxations in (PVA-PEO)-ZnO polymer nanocomposites. *Phys. B Condens. Matter* **2017**, *522*, 48–56. [CrossRef]
19. Lei, H.; Li, X.; Wang, J.; Song, Y.; Tian, G.; Huang, M.; Wu, D. DFT and molecular dynamic simulation for the dielectric property analysis of polyimides. *Chem. Phys. Lett.* **2022**, *786*, 139131. [CrossRef]
20. Tang, Z.; Chang, C.; Bao, F.; Tian, L.; Liu, H.; Wang, M.; Zhu, C.; Xu, J. Feasibility of Predicting Static Dielectric Constants of Polymer Materials: A Density Functional Theory Method. *Polymers* **2021**, *13*, 284. [CrossRef]
21. Chen, Y.-C.; Lin, Y.-C.; Chang, E.-C.; Kuo, C.-C.; Ueda, M.; Chen, W.-C. Investigation of the structure–dielectric relationship of polyimides with ultralow dielectric constant and dissipation factors using density functional theory. *Polymer* **2022**, *256*, 125184. [CrossRef]
22. Pieters, P.F.; Lainé, A.; Li, H.; Lu, Y.-H.; Singh, Y.; Wang, L.-W.; Liu, Y.; Xu, T.; Alivisatos, A.P.; Salmeron, M. Multiscale Characterization of the Influence of the Organic–Inorganic Interface on the Dielectric Breakdown of Nanocomposites. *ACS Nano* **2022**, *16*, 6744–6754. [CrossRef]
23. Feng, Y.; Zhou, F.; Bo, M.; Huang, Y.; Deng, Q.; Peng, C. Enabling High Dielectric Response in PVDF/V2C MXene–TiO2 Composites Based on Nontypical V–F–Ti Bonding and Fermi-Level Overlapping Mechanisms. *J. Phys. Chem. C* **2020**, *124*, 27780–27789. [CrossRef]

24. Deng, Q.; Zhou, F.; Bo, M.; Feng, Y.; Huang, Y.; Peng, C. Remarkably improving dielectric response of polymer/hybrid ceramic composites based on 0D/2D-stacked CuO/V2C MXene heterojunction. *Appl. Surf. Sci.* **2021**, *545*, 149008. [CrossRef]
25. Deng, Q.; Huang, Y.; Chen, B.; Bo, M.; Feng, Y. Conductive V2C MXene and paralelectric SrTiO3 containing polymer composites with high dielectric constant. *Colloids Surf. A Physicochem. Eng. Asp.* **2022**, *632*, 127763. [CrossRef]
26. Feng, Y.; Qiu, H.; Mao, B.; Bo, M.; Deng, Q. Preparation of hybrid ceramic/PVC composites showing both high dielectric constant and breakdown strength ascribed to interfacial effect between V2C MXene and Cu2O. *Colloids Surf. A Physicochem. Eng. Asp.* **2021**, *630*, 127650. [CrossRef]
27. Deng, Q.; Xiong, W.; Mao, B.; Bo, M.; Feng, Y. Enhanced dielectric response of ternary polymeric composite films via interfacial bonding between V2C MXene and wide-bandgap ZnS. *Ceram. Int.* **2021**, *47*, 32938–32946. [CrossRef]
28. Becke, A.D.; Edgecombe, K.E. A simple measure of electron localization in atomic and molecular systems. *J. Chem. Phys.* **1990**, *92*, 5397–5403. [CrossRef]