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Semimetal transition in 2D MoS_2/ZnS Van der Waals heterostructure

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Abstract:

Semimetals hold significant promise in the realms of science and technology, catalyzing various innovations in electronics, quantum research, and energy conversion. Their distinctive properties find application in a diverse array of advancements in processing, computing, and data storage, offering novel efficiencies and capabilities, particularly within the realm of spintronics. In this study, we have meticulously examined the electronic structure of a 2D MoS2/ZnS heterostructure, revealing its semimetallic nature. Our investigation delves into the phenomenon of semimetal transition emerge within this two-dimensional MoS_2/ZnS Van der Waals heterostructure. Through comprehensive theoretical analysis, we demonstrate the intriguing electronic properties arising from the interaction between these two distinct materials. The findings of this study disclose a unique semimetal transition due to interlayer coupling and lattice mismatch. The transition exhibits as a dramatic shift in the electronic band structure and density of states and leads to tunable conductive properties. This work illustrates the interesting interplay of materials' properties in 2D heterostructures and opens new horizon for utilising semimetal transitions in future spintronics, nanoelectronic and quantum technologies applications.

1. Introduction:

The unearthing of graphene has spurred the investigation into various other two-dimensional (2D) materials, as these materials exhibit remarkable performance in contrast to their bulk counterparts[1]. The 2D materials are particularly considered as an interesting and promising materials in recent years due to their unique electronic, optical and mechanical properties[2,17]. Among all other 2D materials, 2D ZnS and 2D MoS_2 and the 2D heterostructure made up of stacking of monolayers of both 2D ZnS and 2D MoS_2. Basically, 2D MoS_2 refers to a single-layer of Molybdenum Disulfide, composed of a hexagonal (puckered honeycomb shape like structure) lattice of Molybdenum atoms sandwiched between two layers of Sulphur atoms. 2D MoS_2 demonstrates astonishing properties such as a direct bandgap, strong light-matter interaction, high electron mobility, and excellent mechanical flexibility[3]. All these properties make it a promising material for various applications including electronics, optoelectronics, catalysis, energy storage, and sensing etc. On the other hand, 2D ZnS consists of a hexagonal (Graphene like honey comb structure) lattice structure with Zinc atoms bonded to Sulphur atoms. 2D ZnS exhibits unique properties such as a direct or indirect bandgap (depending on the layer thickness), high electron mobility and good optical transparency in the visible range[4] making it suitable for various

applications in optoelectronics, photovoltaics catalysis and sensors etc . In recent years, there has been a rapid emergence of 2D heterostructures, which have gained significant attention in the scientific community. The unique 2D characteristics of ZnS open up possibilities for its integration with other 2D materials, facilitating the creation of 2D heterostructures that enable the development of innovative devices with improved functionalities. One notable example is the 2D MoS_2/ZnS heterostructure, which combines Molybdenum Disulfide (MoS_2) and Zinc Sulfide (ZnS) - two distinct 2D materials. The stacking of these materials in a layered structure can result in intriguing electronic and optical properties. Furthermore, the heterostructure facilitates efficient charge transfer between the two materials, ultimately leading to enhanced device performance[5-7]. Li, Xin, et al. in their work on the 2D MoS_2/SnS semiconductor heterostructure[8] found that the heterostructure showed a suitable small band gap compared to individual constituents, enabling light absorption in the visible and infrared regions which lead to enhanced electron transfer efficiency. Consequently, the heterostructure displayed promising and superior photocatalytic performance under solar light irradiation. [8]. Chen, Xing, et al. in their study on 2D ZnS/SnS_2 heterojunction[9], confirmed high electron mobility, moderate hole mobility, and enhanced visible light absorption of 2D ZnS/SnS_2 heterojunction, making this an active and direct Z-scheme photocatalyst with great promise for water splitting[10] . Semimetals possess a small bandgap, higher carrier mobility and potentially longer spin lifetimes than the semiconductors, enable efficient spin-polarized transport. It allows for independent manipulation of spin-up and spin-down electrons, which is key for controlling electron spin in spintronics devices. It can facilitate the conversion between spin and charge current. The spin-orbit coupling of such structure enhances the generation, detection, and manipulation of spin currents, leading to more efficient spintronic devices[11]. Moreover, as the semimetal based spintronic devices normally offers lower energy consumption compared to devices based on traditional semiconductors, so this can lead to more energy efficient electronics in case of semimetals. On the other hand, semimetal confined to low-dimensional structures, can display quantum confinement effects, resulting in modified electronic properties and improved spin-dependent transport. This offers a promising field for the development of next-generation spintronic devices with enhanced performance, energy efficiency, and novel functionalities. The conduction of electrons is thus selective with specific spin orientations which enable the creation of spin valves[11] . So, a heterostructure possessing the semimetallic nature might be very promising in the field of spintronics. In this work, we present a DFT based calculation to study the structural and electronic properties of 2D MoS_2/ZnS heterostructure. Our results clearly indicate the semiconductor to semimetal transition in the hybrid structure. This 2D MoS_2/ZnS heterostructure has potential applications in fields such as optoelectronics, photovoltaics, and sensors etc. Here the unique properties of each material can be used to generate novel devices with improved efficiency, multiple functionalities[12] and performance.

2. Computational details:

For density functional theory calculations, we employ the projector augmented wave (PAW)[13] pseudopotential method implemented in the Vienna ab initio simulation package (VASP)[14] . The calculations are performed within the generalized gradient approximation, utilizing the Perdew, Burke, and Ernzerhof exchange-correlation functional (PBE)[15].The energy cut-off of 520 eV has been chosen for the plane-wave basis expansion and a

Monkhorst–Pack 36 × 36 ×1 k-point mesh were used to relax the 2D hexagonal MoS_2 crystal structure . An energy cut-off of 520 eV and a Monkhorst–Pack 15 × 15 × 2 k-point mesh were used to relax the 2D hexagonal ZnS crystal structure . An energy cut-off of 600 eV and a Monkhorst–Pack 7 × 7 × 9 k-point mesh were used to relax the 2D MoS_2/ZnS heterostructure. The atomic positions in the periodic unit cell have been allowed to relax until the total forces on each atom became less than ~10^{-4} eV/Å. The dynamical stabilities of the heterostructure were tested using the PHONOPY calculation.

3. Result and Discussion:

To obtain the 2D MoS_2/ZnS heterostructure, the monolayer of 2D Hexagonal MoS_2 and monolayer of 2D hexagonal ZnS have been used. Fig 1 (a-d) shown the crystal structure of 2D ZnS, 2D MoS_2 and hybrid structure. The interlayer distance between the monolayer of 2D Hexagonal MoS_2 and monolayer of 2D hexagonal ZnS has been kept as 11.17 Å[18].The 2D MoS_2 hexagonal monolayer crystal structure has a bond length of 2.43Å (Mo–S) and 2D ZnS hexagonal monolayer crystal structure is 2.25 Å (Zn-S) . So, the two different monolayers have a relative difference in their bond lengths as 7.6% , which leads to a good agreement in forming a heterostructure[19] with a precise AB/stacking in 2D directions, using these two monolayers[10]. Our optimized lattice parameters for all the structure are tabulated in table 1.

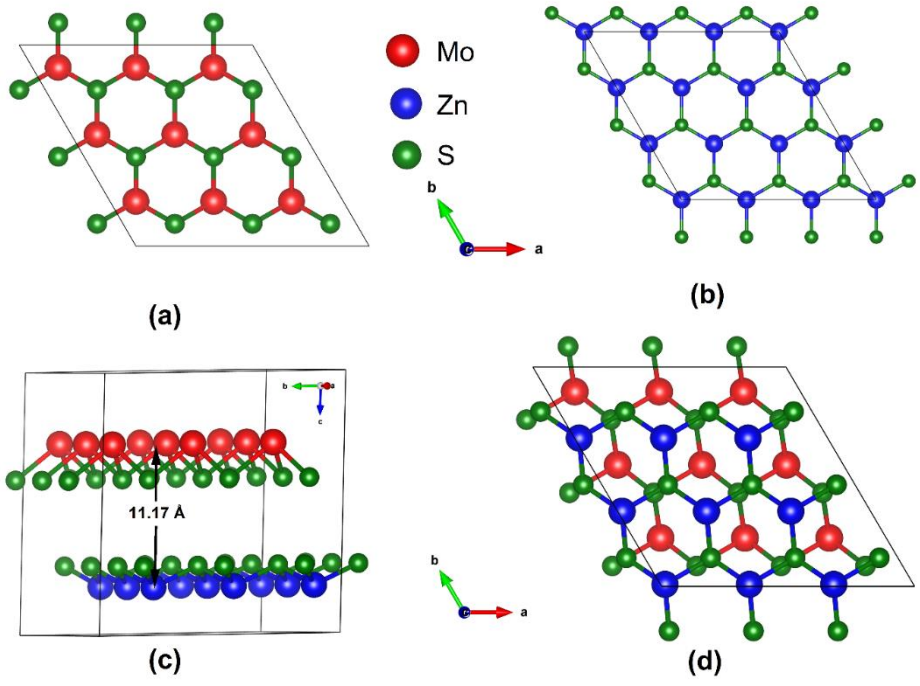

Fig.1 Structure of **(a)** 2D MoS_2 monolayer, **(b)** 2D ZnS monolayer, **(c)** 2D MoS_2/ZnS heterostructure (d) MoS_2/ZnS heterostructure view along c

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Table. 1 The Optimized lattice parameters a and c (Å), c/a ratio of individual 2D MoS_2 monolayer, 2D ZnS monolayer and 2D MoS_2/ZnS heterostructure

Material	a	c	c/a
MoS_2	3.24	12.27	3.79
ZnS	3.96	20.16	5.09
MoS_2/ZnS	3.42	11.17	3.27

3.1 Dynamic Stability:

To analyse the dynamical stability of the structures, we investigated the phonon density of states (DOS). The structures were fully relaxed until the force per atom was less than 0.001 eV $Å^{-1}$. The phonon DOS of all the system, shown in Fig. 2. It is seen that monolayer of 2D MoS_2 and 2D ZnS separately, exhibits no negative frequency modes, indicating the structures are dynamically stable. On the other hand, the calculation of phonon DOS of 2D heterostructure also shows a positive DOS at all frequencies indicating dynamical stability of the structure as shown in **Fig.2(c).**

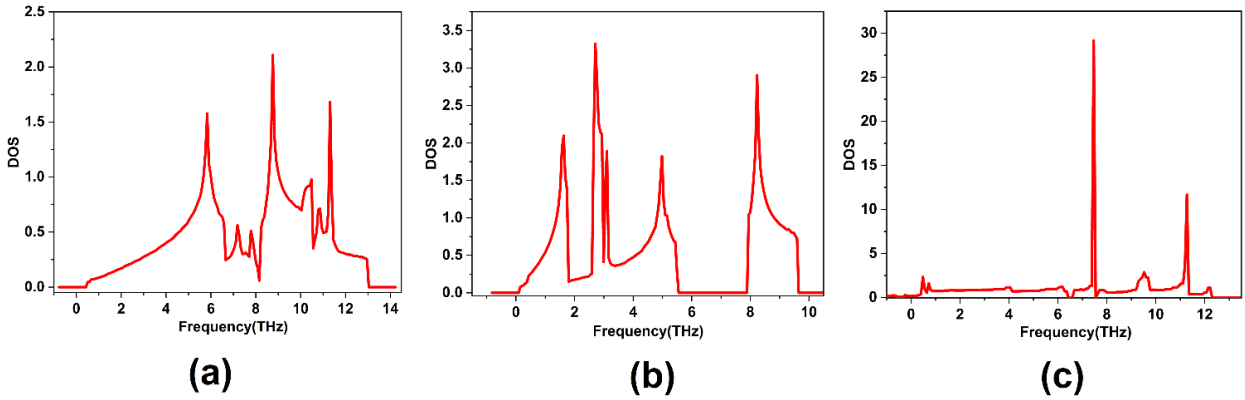

Fig.2 Phonon DOS of **(a)** 2D MoS_2 monolayer , **(b)** 2D ZnS monolayer , **(c)** 2D MoS_2/ZnS heterostructure.

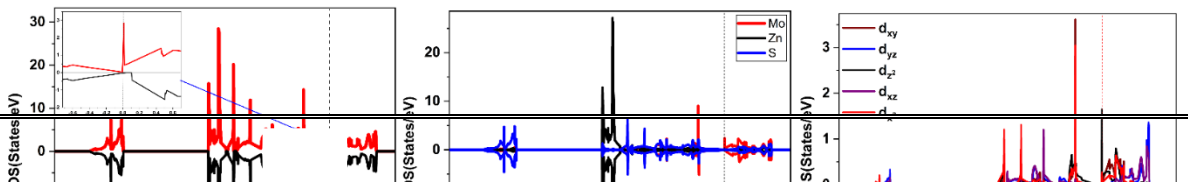

Fig.3 The DOS of **(a)** The DOS of 2D MoS_2 monolayer , **(b)** PDOS of Mo d-orbital in MoS_2 monolayer , **(c))** PDOS of S atom in MoS_2 **(d)** The DOS of 2D ZnS monolayer **(e)** PDOS of Zn d-orbital in ZnS monolayer, **(f)** PDOS of S atom in ZnS, **(g)** The DOS of 2D MoS_2/ZnS heterostructure, **(h)** PDOS of each elements in MoS_2/ZnS heterostructure, and **(i)** PDOS of Mo d-orbital in MoS_2/ZnS heterostructure.

3.2 Density of states:

The density of states (DOS) and partial (DOS) of MoS_2, ZnS and MoS_2/ZnS heterostructure[20] has been plotted in Fig.3(**a-i**). The majority and minority spin bands of both MoS_2 and ZnS shows symmetric behaviour, justifying the non-magnetic nature of the compound. The monolayer of MoS_2 and ZnS exhibits a band gap around the fermi level as expected for semi-conductor nature[21]. The contribution to the total DOS of MoS_2 is mainly from the Mo atom as seen from the PDOS graph in Fig. 3(a), the dominant contribution from the lower occupied states is from the S atom whereas Mo contributions dominant in the higher region of the occupied states near the fermi level and in the unoccupied states. Fig.3 (b) shows the PDOS of Mo atom for the 3d orbitals, it is observed that the peak at -3 eV is contributed from the d_{yz} orbital, while the d_{z^2} and d_{x^2}shows a major contribution near the fermi level in the occupied state. However, the combination of s and p orbitals from the S atom contributes to the overall DOS in the monolayer of MoS_2, where the s orbitals shows a huge contribution at the lower energy state around -12 eV and p orbitals (i.e p_x, p_y and p_z) shows significant contribution near the fermi level and in the unoccupied state. From the Fig.3 (d), we observed a peak in the DOS at -5.6 eV, which mainly arises from d_{yz} and d_{xz} of the 3d orbital of Zn atom, whereas the minor peak at -11.25 eV and the states near the fermi level are from the s and p orbitals of S atom. The DOS of MoS_2/ZnS heterostructure[8] shows an unusual behaviour as compared to monolayer of MoS_2 and ZnS. We observed shifting of bands towards the lower energy states for both the Mo and Zn d orbitals as shown in Fig.3 (h). As a result of band shifting, the spin-up states of the unoccupied region of Mo moves towards the fermi level, where the d orbital of Mo atom overlap the fermi level showing a metallic nature. Whereas, the spin-down state exhibits an energy gap across the fermi level showing semiconducting nature. Thus, the overall DOS calculation result of the MoS_2/ZnS heterostructure shows semimetallic[22] in nature.

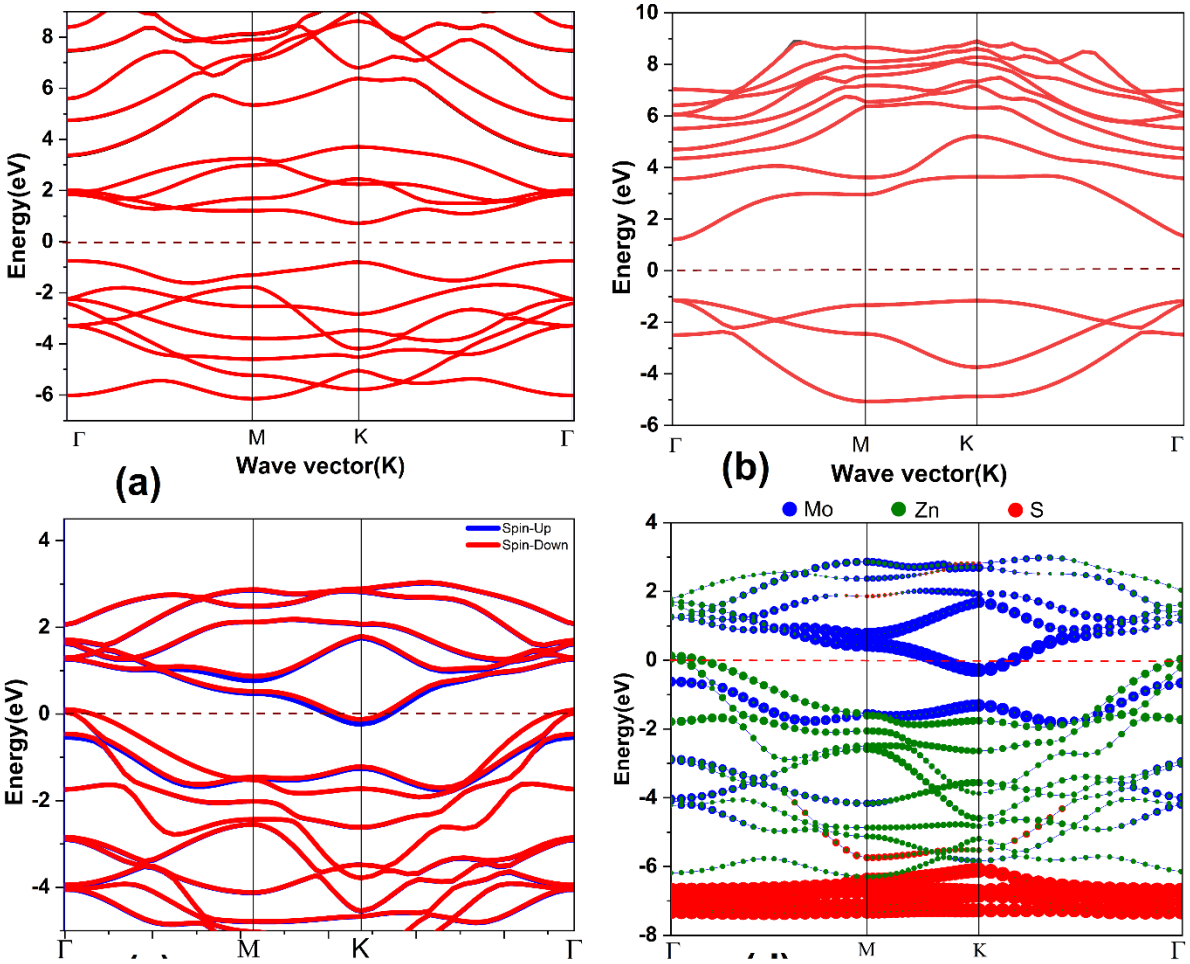

Fig.4 Bandstructure of (a) MoS_2 monolayer (b) ZnS monolayer (c) MoS_2/ZnS heterostructure (d) projected bandstructure of MoS_2/ZnS heterostructure

3.3 Bandstructure:

The band structure of the MoS_2,ZnS monolayer and MoS_2/ZnS heterostructure have been depicted in Fig.4. As both MoS_2 and ZnS possess semiconductor in nature, we observed a band gap across the fermi level. The calculated band gap value of MoS_2 monolayer is 1.46 eV, which is closely aligns with the reported band gap value 1.57 eV[23]. The conduction band minimum (CBM) and valence band maximum (VBM) coincidence at the same k point, indicating that MoS_2 monolayer is a direct band gap semiconductor. Again, the calculated band gap of ZnS monolayer is 2.34 eV, with the CBM and VBM meeting at the gamma (Γ) point confirming it as direct band gap semiconductor. In contrast, the conduction bands are intersecting at fermi level at K point for MoS_2/ZnS heterostructure. This observation confirms that the heterostructure possess semimetal characteristics which is well

agreement with DOS results. The PDOS (Fig 4(d)) indicates that the conduction band near the fermi level primarily originates from the orbitals of the Mo atoms. The CBM of monolayer of 2D MoS_2 is comparatively having lesser energy than that of the monolayer of 2D ZnS and so this mainly contributes more in charge transfer in conduction band of the heterostructure and hence helps to transit the heterostructure to semimetallic nature[24] .

4. Conclusion:

The result of our studies confirmed that both 2D MoS_2 and ZnS monolayers are semiconductors with distinct band gaps. The 2D heterostructure, formed by combining the MoS_2 and ZnS monolayers, exhibits a semimetallic nature, a conclusion supported by the calculated density of states (DOS) and band structure. This semimetallic behavior suggests the potential for heightened electron mobility within the 2D heterostructure compared to the semiconductors. This enhanced mobility holds significance for efficient spin manipulation and transport in spintronic devices. The semimetallic characteristic of the heterostructure likely results in strong spin-orbit coupling, facilitating efficient spin manipulation and control. Consequently, based on these findings, we conclude that the 2D MoS_2/ZnS heterostructure can serve as a multifunctional semimetallic platform, offering valuable contributions to the field of spintronics across various applications. The semimetal behavior exhibited by the 2D MoS_2/ZnS heterostructure holds potential for future applications in fields such as chemical catalysis, quantum computation, and spintronics.

References:

[1] Prasad, SV Satya, et al. "Introduction, history, and origin of two dimensional (2D) materials." *Advanced Applications of 2D Nanostructures: Emerging Research and Opportunities* **1**, 1-9 (2021):.

[2] Mas-Balleste, Ruben, et al. "2D materials: to graphene and beyond." *Nanoscale* **3**(1), 20-30 (2011).

[3] Yamusa, Shehu Aminu, et al. "Elucidating the Structural, Electronic, Elastic, and Optical Properties of Bulk and Monolayer MoS2 Transition-Metal Dichalcogenides: A DFT Approach." *ACS omega* **7**(49), 45719-45731 (2022).

[4] Majidiyan Sarmazdeh, M., et al. "Investigation of the electronic and optical properties of ZnS monolayer nanosheet: first principles calculations." *Journal of materials science* **52**, 3003-3015 (2017)..

[5] Liao, Cheng-Sheng, et al. "First-principles investigations of electronic and optical properties in the MoS2/CsPbBr3 heterostructure." *Journal of Physics and Chemistry of Solids* **135,** 109060 (2019). [6] Xiong, Aihu, and Xiaolong Zhou. "First-principles calculations of the structural, electronic, and optical properties of a ZnS/GaP van der Waals heterostructure." *Journal of Computational Electronics* **18**, 758-769 (2019).

[7] Yin, Xianglu, et al. "Investigations on Structural, Electronic and Optical Properties of MoS2/CDs Heterostructure via First-Principles Study." *Catalysts* **12**(5), 456 (2022).

[8] Li, Xin, et al. "A two-dimensional MoS2/SnS heterostructure for promising photocatalytic performance: first-principles investigations." *Physica E: Low-dimensional Systems and Nanostructures* **126**, 114453 (2021).

[9] Chen, Xing, et al. "Two-Dimensional ZnS/SnS2 Heterojunction as a Direct Z-Scheme Photocatalyst for Overall Water Splitting: A DFT Study." *Materials* **15**(11), 3786 (2022).

[10] Venkateswara, Y., et al. "FeRhCrSi: Spin semimetal with spin-valve behavior at room temperature." *Physical Review B* **107**(10), L100401 (2023).

[11] Androulidakis, Charalampos, et al. "Tailoring the mechanical properties of 2D materials and heterostructures." *2D Materials* **5**(3), 032005 (2018).

[12] Blöchl, Peter E. "Projector augmented-wave method." *Physical review B* **50**(24), 17953 (1994).

[13] Hafner, Jürgen. "Ab-initio simulations of materials using VASP: Density-functional theory and beyond." *Journal of computational chemistry* **29**(13), 2044-2078 (2008).

[14] Kraus, Peter. "Extrapolating DFT toward the complete basis set limit: lessons from the PBE family of functionals." *Journal of Chemical Theory and Computation* **17**(9), 5651-5660 (2021).

[15] Kaur, Sumandeep, et al. "van der Waals heterostructures based on allotropes of phosphorene and MoSe 2." *Physical Chemistry Chemical Physics* **19**(33), 22023-22032(2017).

[16] A.Togo and I.Tanaka, "First principles phonon calculations in materials science," *Scr Mater* **108**, 1–5 (2015).

[17] Lin, Yin-Pai, et al. "Excited states calculations of MoS2@ ZnO and WS2@ ZnO two-dimensional nanocomposites for water-splitting applications." *Energies* **15**(1), 150 (2021).

[18] Pham, Phuong V., et al. "2D heterostructures for ubiquitous electronics and optoelectronics: principles, opportunities, and challenges." *Chemical Reviews* **122**(6), 6514-6613 (2022).

[19] Zhao, Ailun, et al. "Review of 2D group VA material-based heterostructures." *Journal of Physics D: Applied Physics* **53**(29), 293002 (2020).

[20] Chabi, Sakineh, and Kushal Kadel. "Two-dimensional silicon carbide: emerging direct band gap semiconductor." *Nanomaterials* **10**(11), 2226 (2020).

[21] Meng, Weizhen, et al. "Two-dimensional Weyl semimetal with coexisting fully spin-polarized type-I and type-II Weyl points." *Applied Surface Science* **540**, 148318 (2021)

[22] Ahmad, Sohail, and Sugata Mukherjee. "A comparative study of electronic properties of bulk MoS2 and its monolayer using DFT technique: application of mechanical strain on MoS2 monolayer." Graphene **3**, 52-59 (2014).

[23] Zhang, Chenxi, et al. "Systematic study of electronic structure and band alignment of monolayer transition metal dichalcogenides in Van der Waals heterostructures." 2D Mater **4**, (2017).