SEMARAK ILMU PUBLISHING

Journal of Advanced Research in Applied Mechanics

Journal homepage:
https://semarakilmu.com.my/journals/index.php/appl_mech/index
ISSN: 2289-7895

Ab-Initio and Experimental Study of the Electronic and Optical Properties of Layered 2D Molybdenum Disulphide

Siti Nabilah Mohd Halim[1], Mohamad Fariz Mohamad Taib[2], Siti Nur Fatin Zuikafly[1], Husni Hani Jameela Sapingi[1], Mohamed Sukri Mat Ali[1], Hafizal Yahaya[1], Fauzan Ahmad[1,*]

[1] Malaysia-Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia, Jalan Sultan Yahya Petra, 54100 Kuala Lumpur, Malaysia
[2] Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM), Shah Alam, 45400 Selangor, Malaysia

ARTICLE INFO

Article history:
Received 10 March 2023
Received in revised form 23 May 2023
Accepted 30 May 2023
Available online 12 June 2023

Keywords:
Molybdenum Disulphide; Density Functional Theory; energy bandgap; absorption spectrum

ABSTRACT

Molybdenum disulphide (MoS_2) in its two-dimensional (2D) mono- to few layers is applied in numerous photonic applications owing to its wide bandgap. In this work, the electronic and optical properties of monolayer MoS_2 were successfully investigated by ab initio study through density functional theory (DFT) calculation and experimental work. A 2D monolayer MoS_2 model was simulated using CASTEP in the framework of plane-wave pseudopotential. The simulated bandgap is 1.7 eV which is interestingly close to those determined bandgap of MoS_2 prepared through the liquid-phase exfoliation method. This confirmed the successful formation of 2D layered MoS_2 in the proposed fabrication process. The MoS_2 model also predict well the experimentally derived absorption range which has a significant peak at around ~600 nm wavelength ascribed to the excitonic property.

1. Introduction

The energy bandgap of material plays a fundamentally important role in understanding the interaction of light with matter. Among the numerous types of 2D material besides graphene, molybdenum disulphide (MoS_2) has garnered intense research interest due to its unique layer-dependent energy bandgap. The large bandgap possessed by MoS_2 enables a wide potential application in photonic, optoelectronic, energy storage, supercapacitors and sensors [1,2].

MoS_2 belongs to the transition metal dichalcogenides (TMDC) family and offers a broad range of bandgaps from insulating and semiconducting to metallic. The single-layered material with confining electrons into a single plane led to different properties than the bulk counterpart. Bulk MoS_2 exhibits a lower bandgap of ~1.2 eV while monolayer MoS_2 shows an increasing bandgap of up to around ~1.89 eV [3]. This phenomenon primarily affects its other properties. For instance, photoluminescence intensity increases by 1000-fold for single monolayer MoS_2 when compared to

* *Corresponding author.*
E-mail address: fauzan.kl@utm.my

https://doi.org/10.37934/aram.107.1.1119

its bulk form [4]. MoS_2 also exhibits excellent mechanical strength in its layered form with electronic properties that can be retained when bent to a specific curvature [5]. Besides, the carrier lifetime of electron-hole radiative recombination has been recorded at 150 ps up to ~1 ps [6] which is commensurate with graphene, making monolayer MoS_2 a promising candidate for ultrashort pulse laser generation [7].

The possibility of positioning crystals in controlled proximity to attain such mono- or few layers of MoS_2 is achievable through the chemical vapor deposition (CVD) technique [8]. Although this technique allows a high quality of synthesized 2D material form, it requires expensive equipment and involves a high-temperature procedure [9]. The inevitable structural defects formation during growth transfer can also be cumbersome. Ellipsometry has been the go-to technique to study the optical properties of materials in many forms [10-12]. The main challenge when using this technique is usually in the crucial and time-consuming sample preparation process with ellipsometry requiring smooth and homogenous sample surface. Errors in the measurements can be introduced and thus affecting the accuracy of the results if there are irregularities, roughness, and non-uniformity in the sample. On the other hand, the computational simulation of material modelling is particularly interesting for studying the ideal 2D layered materials formation without compromising experimental drawbacks, after which measurement methods such as ellipsometry can be utilized after successful 2D layered material fabrication. In other fields, it may also be used prior to physiochemical synthesis to study materials compatibility or even used to understand formation of nanoparticles at the molecular levels [13-15] and hence understanding their potential properties. *Ab initio* study using density functional theory (DFT) calculation is a standard tool for materials modelling that can produce reliable characteristics of materials with adequate exchange-correlation functions and basis sets [16].

In this work, the monolayer MoS_2 simulation is performed using DFT calculation to analyse the electronic and optical properties of MoS_2. In addition, a facile and straightforward liquid-phase exfoliation method to fabricate MoS_2 is experimentally demonstrated. The fabricated MoS_2 is successfully characterized with properties similar to the model structure.

2. Methodology

2.1 Ab Initio Simulation

The generated model of MoS_2 in the form of a monolayer is shown in Figure 1. All DFT calculations are performed using Cambridge Serial Total Energy Package (CASTEP) based on plane-wave pseudopotential with the exchange-correlation function described by the Perdew-Burke-Ernzerhorf (PBE) of the generalized gradient approximation (GGA). An optimized supercell of 3 × 3 is employed with 15 Å vacuum to avoid the periodic interaction during calculation. The cut-off energy for plane waves is 400 eV with 2 × 2 × 1 k-point for Brillouin zone integration. The conjugate-gradient algorithm applies an energy of 1.0×10^{-5} eV and force convergence of 0.01 eV $Å^{-1}$ to relax the ions to the ground states. The stated parameters are adopted from the previous MoS_2 studies [3]. Monolayer MoS_2 is built up of Molybdenum (Mo) and Sulphur (S) atomic layers in trigonal prismatic configuration, as shown in Figure 1(b). The average bond length between Mo and S is ~2.409 Å.

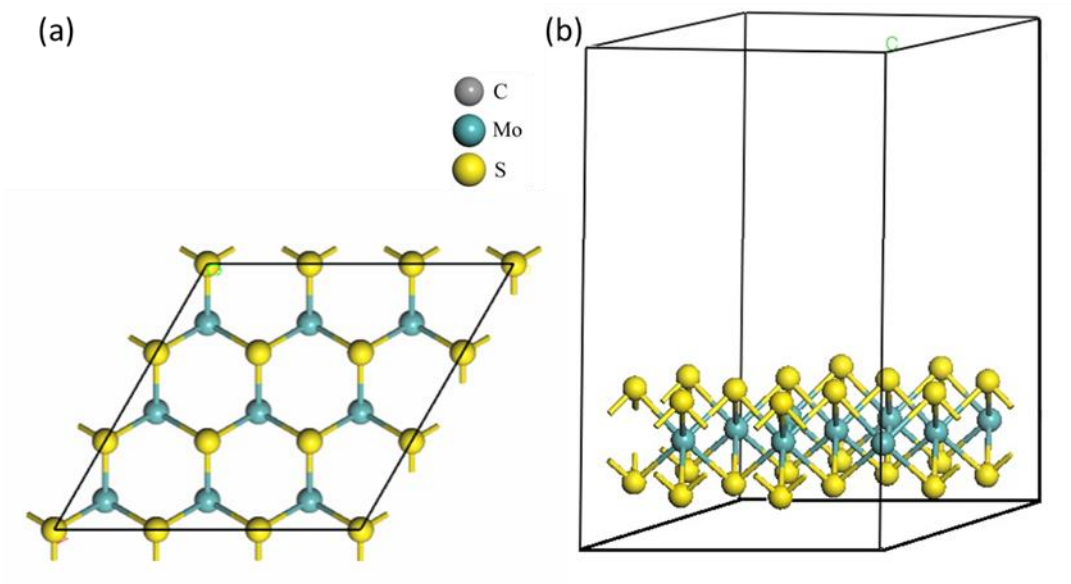


Fig. 1. Atomic structure model of monolayer MoS_2 (a) top and (b) side view

2.2 Experimental Fabrication of MoS_2

MoS_2 solution is prepared with MoS_2 powder (99 % purity, Sigma Aldrich) as the starting material. 5 mg of MoS_2 powder is mixed with 5 ml tetrahydrofuran (THF) as the solvent by using a magnetic stirrer for about three hours at ambient temperature and 1200 rpm until it homogeneously dissolved. Since THF is a toxic organic solvent, the solution was carefully mixed using a proper sealed beaker inside the fume hood as a precaution step. In order to form a free-standing MoS_2 film, MoS_2 solution is then mixed with host polymer chitin and undergoes ultrasonication process in ultrasonic bath for about three hours at room temperature. The preparation process of chitin solution is reported elsewhere [17]. The process allows exfoliation of bulk crystal into nanosheet and reducing crystallinity with a formation of 2D layer. The host polymer binds well with MoS_2 solution and form a free-standing MoS_2-chitin film which will be further used as based material for pulsed laser application.

For characterization, Raman spectroscopy measurement by using WITec Alpha 300R with excitation wavelength of 532 nm is performed to confirm the existence of MoS_2 structure through the feature peaks along the Raman spectrum. Meanwhile, the UV-Vis-NIR spectrophotometer (Perkin Elmer, Lambda 750) is used to characterize the optical transmission and absorption of the samples. Transmission spectrum measures how much light can pass through the material [18] and its logarithmic derivation can produce absorbance value with expression given by Eq. (1).

$$A = 2 - \log(T) \tag{1}$$

where A is the absorbance and T is the transmittance in percentage. Subsequently, a well-known Tauc plot relation can be calculated to determine the bandgap (E_g) of MoS_2. Given that α represents the absorption coefficient, hv is the photon energy, and n is the nature of transition either 2 or ½ depending on the indirect and direct transition, respectively, the Tauc relation can be expressed by [4]

$$(\alpha hv)^n = A(hv - E_g) \tag{2}$$

3. Results

3.1 Theoretical Electronic Properties

Figure 2 shows the simulated electronic band structure and density of states of monolayer MoS_2 with the dotted line representing the Fermi level. From the band structure, the x-axis represents the high symmetric points of the Brillouin zone wavevector, while y-axis shows the corresponding energy values. The bandgap value can be obtained from the difference between the maximum valence band and minimum conduction band energy located around the Fermi level. The simulated bandgap of MoS_2 is recorded to be 1.70 eV which is similar to the previously reported value of ~1.7 eV [3] and ~1.8 eV [19]. As shown in Figure 2(a), the wide gap of monolayer MoS_2 confirmed the semiconducting properties with direct transition type at the *k*-point of Brillouin zone wavevector. In contrast to its bulk form, monolayer exhibit an inversion symmetry loss that results in interesting properties especially in the valley Hall effect [20].

The distribution of electronic configurations inside the MoS_2 structure is computed in details by the density of states (DOS) as shown in Figure 2(b). The partial density of states (PDOS) shows that the bottom of conduction band and the top of the valence band consists of p- and d-type contributions, which is in agreement with studied by [21]. In addition, DOS can be used to understand the effective dimensionality of the simulated material as the number of occupied electronic states (*N*) filled with electrons are constrained within the material's dimension (D), expressed by $N \sim k^D$ [22]. A band edge from the MoS_2 DOS can be observed especially at the top of the valence band indicating the characteristic of 2D systems.

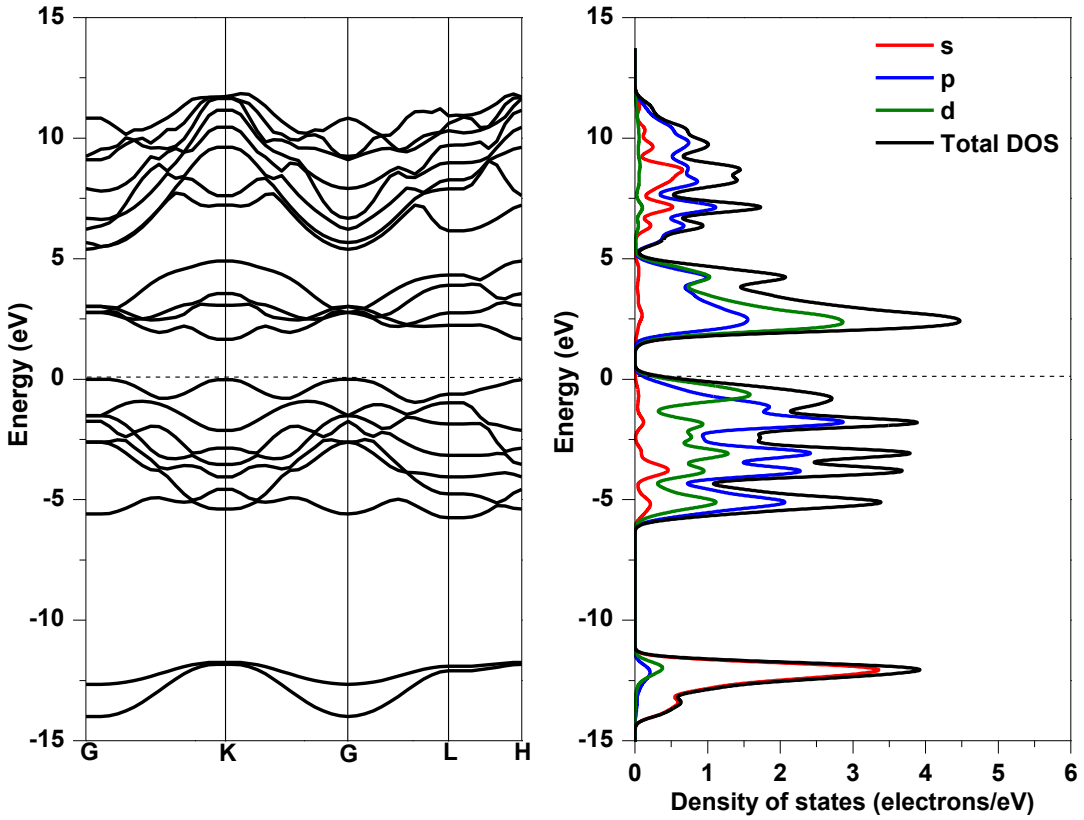


Fig. 2. Theoretical band structure and density of states of monolayer MoS_2 with Fermi level equals to 0 eV

3.2 Theoretical Optical Properties

Figure 3 shows the simulated real and imaginary part of dielectric function of monolayer MoS_2 derived from the Kramers-Kronig relation [3], as expressed by $\varepsilon(\omega) = \varepsilon_{real} + \varepsilon_{imaginary}$. The complex dielectric function (ε) shows dependency to the incident frequency of light (ω). It also describes the dielectric response to the electric field in the medium. The monolayer MoS_2 has static dielectric constant of 12 at the important telecommunication wavelength (~0.8 eV) which matches well with the spectroscopic ellipsometry measurement retrieved from experimental work (ε_{real} > 12) by Ermolaev *et al.,* [18]. The dielectric constant value is also in agreement with other theoretical work [3]. The strong dielectric response is comparable to other photonics semiconductors such as Si (~13), GaSb (~15) and Ge (~18) at the ~0.8 eV or wavelength around 1525 – 1565 nm [18]. The absent of A and B excitonic peaks in imaginary part spectrum of MoS_2 is due to the exclusion of excitonic effects by GW Bethe-Salpeter quasi particle approximation in the simulation.

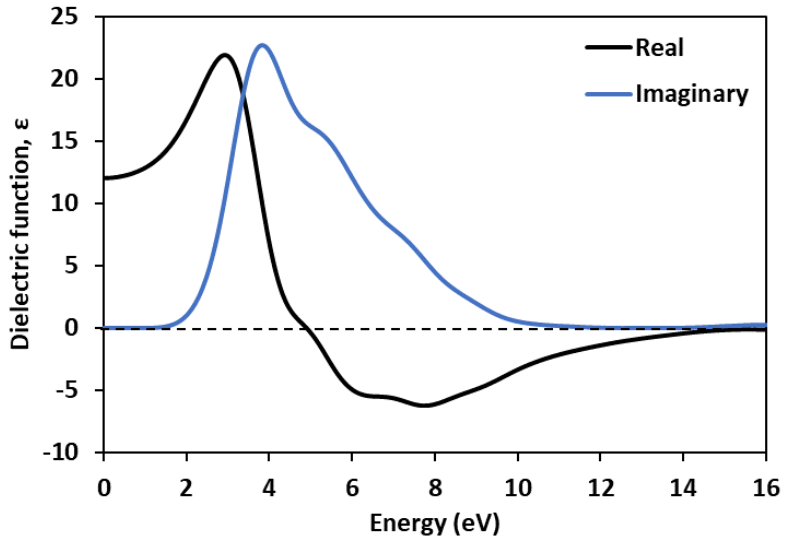


Fig. 3. Real and imaginary part of theoretical dielectric function of simulated MoS_2

The optical properties of MoS_2 are further explored by simulating its absorption spectrum in the function of wavelength and energy, as shown in Figure 4. The absorption spectrum shows that MoS_2 exhibits the highest peak at the visible region of ~678 nm corresponding to the excitonic property and sharp decay afterward as observed in Figure 4(a). The obtained peaks are similar to the previously reported mono and few layer MoS_2 which is high near the visible spectrum of ~500 nm with a subsequent sharp decay [19]. A prominent peak is also observed at ~222 nm corresponds to the strong absorption at ultra-violet region. Due to the quantum confinement, the presence of more than one peak indicates that more than one inter-band transition is involved, and it is found to be strongly dependent on photon energy [18]. Figure 4(b) shows the variation of the absorption spectrum of MoS_2 as a function of photon energy. As shown in the figure, the simulated MoS_2 possess strong absorption at ultra-violet region.

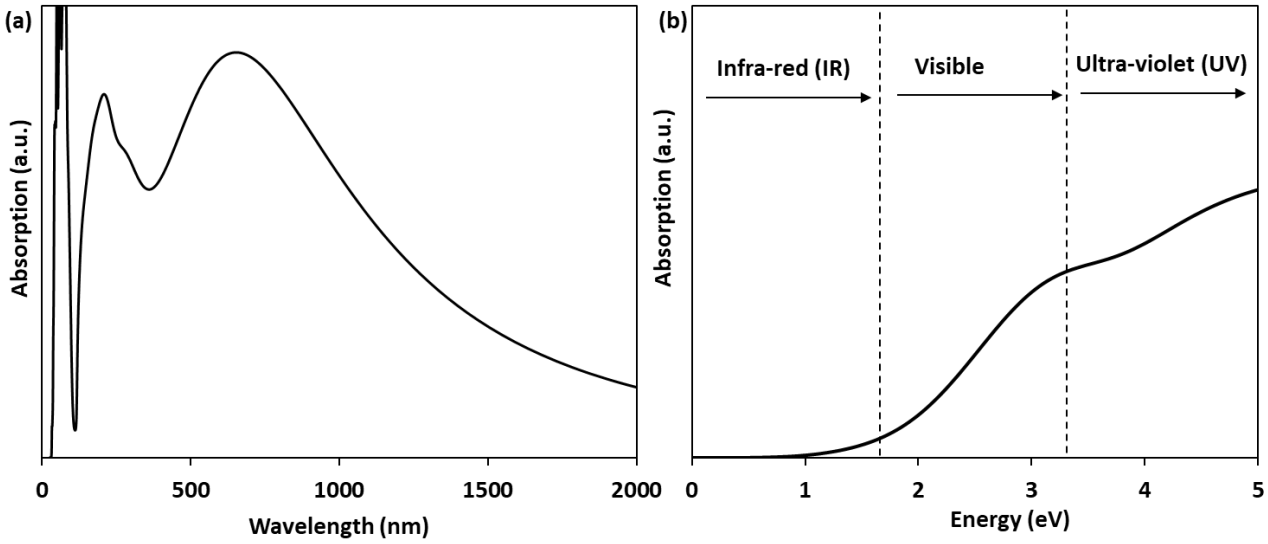


Fig. 4. Theoretical absorption spectrum of simulated MoS_2 in the function of (a) wavelength and (b) energy

3.2 Experimental Section

Experimental data reveals that the electronic and optical characterization of MoS_2-chitin has relatively consistent values with that obtained simulation work. Firstly, the existence of fabricated MoS_2 structure is confirmed by Raman measurement with prominent peaks at around ~371 cm^{-1} and ~395 cm^{-1} which corresponds to E_{2g} and A_{1g}. Figure 5 shows that the two Raman peaks for MoS_2-chitin are similarly found in most literature [4,9,17,19,23] without other peaks can be observed indicating the purity of the MoS_2-chitin fabricated from the proposed method.

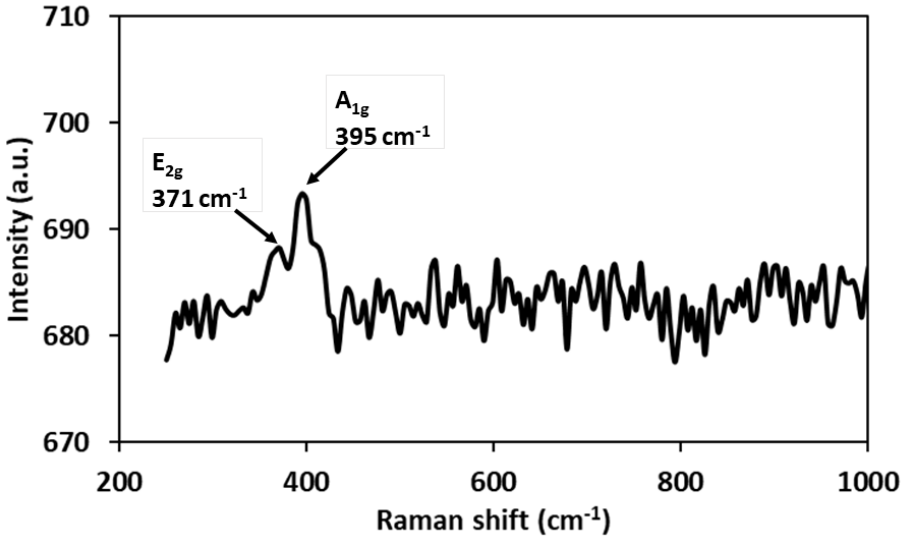
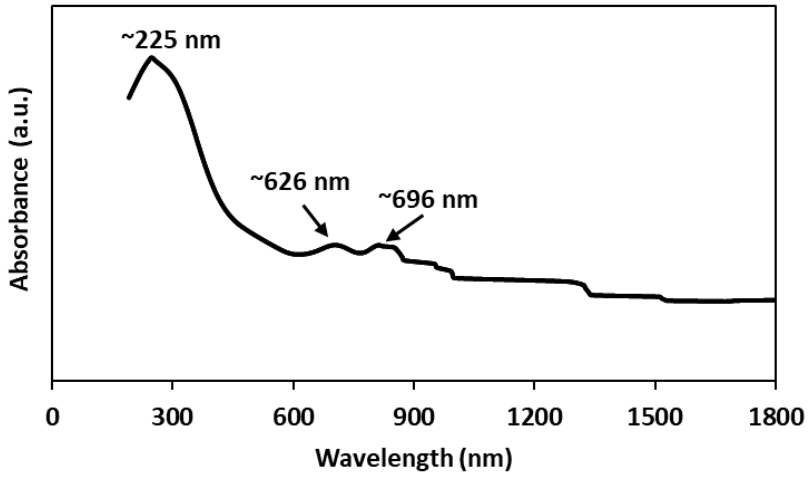


Fig. 5. Raman spectrum of MoS_2-chitin

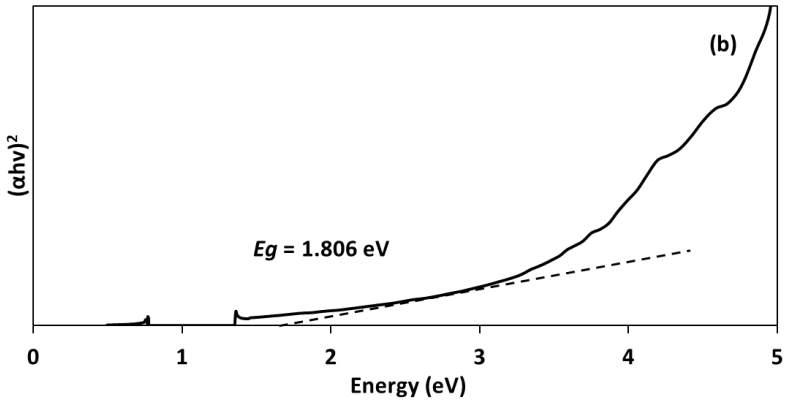
Figure 6 shows that the linear optical properties of MoS_2-chitin obtained from the UV-Vis-NIR spectrophotometer. The transmittance of MoS_2-chitin gives the absorbance value with A and B excitonic peaks at 626 nm and 696 nm, respectively, which is well-known characteristic in TMDC group [17-20], as shown in Figure 5(c). A significant peak at ultra-violet region of ~225 nm is theoretically consistent with our simulated absorption spectrum of MoS_2-chitin. The developed

MoS_2-chitin demonstrates the ability to absorb light in both visible and ultra-violet range of the electromagnetic spectrum.

Next, the Tauc plot is displayed in Figure 5(d). The bandgap (E_g) is determined from the variation of $(\alpha hv)^2$ against hv. From the graph, the intersection of a tangent line to the x-axis giving a bandgap value of 1.806 eV. The obtained bandgap value is close to the simulated bandgap from our DFT calculation with a ~1 % difference. Besides, it is well-matched with the previous experimental bandgap of 1.8 eV [18]. It can be deduced that the prepared MoS_2-chitin has a 2D characteristic owing to the successful exfoliation technique of bulk crystal into 2D layers during fabrication.



(a)



(b)

Fig. 6. Linear optical characterization of MoS_2-chitin; (a) absorption spectrum and (b) Tauc plot

4. Conclusions

In summary, both theoretical and experimental study has successfully investigated the electronic and optical properties of MoS_2. As evidenced by the theoretical study, the bandgap of MoS_2 is recorded at 1.70 eV with absorption spectrum ranging from visible to ultraviolet region. Overall, the predicted results from simulated MoS_2 align with the experiment. The obtained results can be helpful in many photonic applications that employ MoS_2 as the base material.

Acknowledgement
This research was not funded by any grant.

References

[1] Samy, Omnia, Shuwen Zeng, Muhammad Danang Birowosuto, and Amine El Moutaouakil. "A review on MoS2 properties, synthesis, sensing applications and challenges." *Crystals* 11, no. 4 (2021): 355. https://doi.org/10.3390/cryst11040355

[2] Wadhwa, Riya, Abhay V. Agrawal, and Mukesh Kumar. "A strategic review of recent progress, prospects and challenges of MoS2-based photodetectors." *Journal of Physics D: Applied Physics* 55, no. 6 (2021): 063002. https://doi.org/10.1088/1361-6463/ac2d60

[3] Hieu, Nguyen N., Victor V. Ilyasov, Tuan V. Vu, Nikolai A. Poklonski, Huynh V. Phuc, Le TT Phuong, Bui D. Hoi, and Chuong V. Nguyen. "First principles study of optical properties of molybdenum disulfide: From bulk to monolayer." *Superlattices and Microstructures* 115 (2018): 10-18. https://doi.org/10.1016/j.spmi.2018.01.012

[4] Mak, Kin Fai, Changgu Lee, James Hone, Jie Shan, and Tony F. Heinz. "Atomically thin MoS 2: a new direct-gap semiconductor." *Physical review letters* 105, no. 13 (2010): 136805. https://doi.org/10.1103/PhysRevLett.105.136805

[5] Pu, Jiang, Yohei Yomogida, Keng-Ku Liu, Lain-Jong Li, Yoshihiro Iwasa, and Taishi Takenobu. "Highly flexible MoS2 thin-film transistors with ion gel dielectrics." *Nano letters* 12, no. 8 (2012): 4013-4017. https://doi.org/10.1021/nl301335q

[6] Palummo, Maurizia, Marco Bernardi, and Jeffrey C. Grossman. "Exciton radiative lifetimes in two-dimensional transition metal dichalcogenides." *Nano letters* 15, no. 5 (2015): 2794-2800. https://doi.org/10.1021/nl503799t

[7] Lu, Jun, Xiao Zou, Chun Li, Wenkai Li, Zhengzheng Liu, Yanqi Liu, and Yuxin Leng. "Picosecond pulse generation in a mono-layer MoS 2 mode-locked Ytterbium-doped thin disk laser." *Chinese Optics Letters* 15, no. 4 (2017): 041401. https://doi.org/10.3788/COL201715.041401

[8] Novoselov, K. S㐆, Artem Mishchenko, O. A. Carvalho, and A. H. Castro Neto. "2D materials and van der Waals heterostructures." *Science* 353, no. 6298 (2016): aac9439. https://doi.org/10.1126/science.aac9439

[9] Zafar, Amina, Haiyan Nan, Zainab Zafar, Zhangting Wu, Jie Jiang, Yumeng You, and Zhenhua Ni. "Probing the intrinsic optical quality of CVD grown MoS 2." *Nano Research* 10 (2017): 1608-1617. https://doi.org/10.1007/s12274-016-1319-z

[10] El-Agez, Taher M., and Sofyan A. Taya. "Design of a spectroscopic ellipsometer by synchronous rotation of the polarizer and analyzer in opposite directions." *Microwave and Optical Technology Letters* 56, no. 12 (2014): 2822-2826. https://doi.org/10.1002/mop.28704

[11] Alkanoo, Anas A., Sofyan A. Taya, and Taher M. El-Agez. "Effect of the orientation of the fixed analyzer on the ellipsometric parameters in rotating polarizer and compensator ellipsometer with speed ratio 1: 1." *Optical and Quantum Electronics* 47, no. 7 (2015): 2039-2053. https://doi.org/10.1007/s11082-014-0077-y

[12] Taya, Sofyan A., and Taher M. El-Agez. "Effect of noise on the optical parameters extracted from different ellipsometric configurations." *Physica Scripta* 85, no. 4 (2012): 045706. https://doi.org/10.1088/0031-8949/85/04/045706

[13] Moosa, Salmah, Anis Nadia Mohd Faisol Mahadeven, and Kamyar Shameli. "Physiochemical synthesis of Silver/Kaolinite nanocomposites and study their antibacterial properties." *Journal of Research in Nanoscience and Nanotechnology* 1, no. 1 (2021): 1-11. https://doi.org/10.37934/jrnn.1.1.111

[14] Berahim, Muhammad Syahizul Aidi, Mohd Fadhil Majnis, and Mustaffa Ali Azhar Taib. "Formation of Titanium Dioxide Nanoparticles by Anodization of Valve Metals." *Progress in Energy and Environment* 7 (2018): 11-19.

[15] Jowsey, Mohamad Hafzan Mohamad, Natrah Kamaruzaman, and Mohsin Mohd Sies. "Heat and Flow Profile of Nanofluid Flow Inside Multilayer Microchannel Heat Sink." *Journal of Advanced Research in Micro and Nano Engineering* 4, no. 1 (2021): 1-9.

[16] Al-Mahayni, Hasan, Xiao Wang, Jean-Philippe Harvey, Gregory S. Patience, and Ali Seifitokaldani. "Experimental methods in chemical engineering: Density functional theory." *The Canadian Journal of Chemical Engineering* 99, no. 9 (2021): 1885-1911. https://doi.org/10.1002/cjce.24127

[17] Fazli Wan Nawawi, Wan Mohd, Koon-Yang Lee, Eero Kontturi, Richard J. Murphy, and Alexander Bismarck. "Chitin nanopaper from mushroom extract: natural composite of nanofibers and glucan from a single biobased source." *ACS Sustainable Chemistry & Engineering* 7, no. 7 (2019): 6492-6496. https://doi.org/10.1021/acssuschemeng.9b00721

[18] Ermolaev, Georgy A., Yury V. Stebunov, Andrey A. Vyshnevyy, Dmitry E. Tatarkin, Dmitry I. Yakubovsky, Sergey M. Novikov, Denis G. Baranov *et al.,* "Broadband optical properties of monolayer and bulk MoS2." *npj 2D Materials and Applications* 4, no. 1 (2020): 21. https://doi.org/10.1038/s41699-020-0155-x

[19] Ullah, Muhammad S., Abdul Hamid Bin Yousuf, Azzedin D. Es-Sakhi, and Masud H. Chowdhury. "Analysis of optical and electronic properties of MoS2 for optoelectronics and FET applications." In *AIP Conference Proceedings*, vol. 1957, no. 1, p. 020001. AIP Publishing LLC, 2018. https://doi.org/10.1063/1.5034320

[20] Onga, Masaru, Yijin Zhang, Toshiya Ideue, and Yoshihiro Iwasa. "Exciton Hall effect in monolayer MoS2." *Nature materials* 16, no. 12 (2017): 1193-1197. https://doi.org/10.1038/nmat4996

[21] Kadantsev, Eugene S., and Pawel Hawrylak. "Electronic structure of a single MoS2 monolayer." *Solid state communications* 152, no. 10 (2012): 909-913. https://doi.org/10.1016/j.ssc.2012.02.005

[22] Toriyama, Michael Y., Alex M. Ganose, Maxwell Dylla, Shashwat Anand, Junsoo Park, Madison K. Brod, Jason M. Munro, Kristin A. Persson, Anubhav Jain, and G. Jeffrey Snyder. "How to analyse a density of states." *Materials Today Electronics* 1 (2022): 100002. https://doi.org/10.1016/j.mtelec.2022.100002

[23] Garadkar, K. M., A. A. Patil, P. P. Hankare, P. A. Chate, D. J. Sathe, and S. D. Delekar. "MoS2: Preparation and their characterization." *Journal of Alloys and Compounds* 487, no. 1-2 (2009): 786-789. https://doi.org/10.1016/j.jallcom.2009.08.069