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A First Principle Study of Structural and Electronic Properties of Bulk MoS_2 and Its Monolayer

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ABSTRACT

In this study, we have investigated the structural and electronic properties of bulk and monolayer MoS_2 using a first principle method based on density functional theory. The indirect band gap in the bulk MoS_2 was found to be 0.975 eV, whereas in the monolayer MoS_2 the band gap of 1.85 eV was found to be direct one. The calculated physical parameters of monolayer MoS_2 are found to be very close to the bulk MoS_2 and compare well with available experimental and theoretical results. The calculated density of states (DOS) may help explain this change in the nature of band gap in bulk and in monolayer MoS_2.

KEYWORDS : MoS_2, Electronic properties, monolayer, Band Structure, Density of States.

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1. INTRODUCTION

Transition metal dichal cogenides (TMDs) posses layered structures[1]. Layered transition-metal dichalcogenides (LTMDCs) have been extensively reviewed in the recent past [2-4]. MoS_2 is a typical example of LTMDC family of materials which attracts investigation because of its distinctive industrial applications, ranging from use as a lubricant [5-6] and a catalyst [7] as well as in photo-voltaics [8] and energy storage [9]. In its bulk form MoS_2 is a semiconductor with an indirect band gap of about 1.23 eV while its monolayer has a direct energy gap of 1.8 eV [10]. A special attention has been paid on single layer MoS_2 in the recent years. Upon thinning from the bulk the electronic structure of MoS_2 undergoes an interesting transition[11-13]. Recently, a monolayer MoS_2-based field effect transistor (FET) with HfO_2 as gate insulator has been successfully implemented [14]. These ideal properties make monolayer MoS_2 a very promising candidate for next generation FET and as optoelectronic devices [15]. This has raised enormous interest in exploring the extraordinary properties of mono layers of MoS_2.

Theoretically, there are various possibilities of energy gap manipulation in MoS_2. By reducing the layer thickness from bulk to monolayer, the indirect band gap energies in the bulk are shifted relative to the direct band gap in the monolayer limit [16]. It undergoes a transition from an indirect to direct gap exhibiting strong photoluminescence when confined in a 2D monolayer [17]. It has been suggested a way to engineer 3D semi- conducting MoS_2 nano particles with direct band gaps as well as metallic dichalcogenides nanowires with promising catalytic and thermoelectric properties [18]. Eellis *et al*. carried out a study using HSE screened hybrid functional and offered improvement over semi local density functional. All electron calculations including spin orbit coupling were performed and confirmed indirect to direct band gap transition [19]. Electronic structure of transition metal dichalcogenides has been studied using *ab initio* theory using Troullier-Martin norm conserving, relativistic pseudopotentials in fully separable Kleinman and Bylander form [20]. They used exchange and correlation energies within LDA.

The properties of transition metal dichalcogenides (TMDs) not only can be tuned by varying number of layers, but also can be modified by application of external field or strain engineering. Studies [21-22] have confirmed that applying strain is one of the best possible strategies to tune the band gap, since it neither attenuates the properties nor is inefficacious for single layers. It has been predicted that straining MoS_2 modifies the band gap energy and the carrier effective mass. Moreover, at strains larger than 1% the lowest lying band gap changes from direct to indirect [23-26]. It has been suggested that strain engineering of the band structure of MoS_2 could be used to increase carrier mobility of MoS_2, to create tunable photonic devices and solar cells [27] and even to control the

magnetic properties of MoS_2. While strain perturbs the band structure of all materials, two-dimensional materials such as MoS_2 can sustain strains greater than 11% allowing exceptional control of material properties by strain engineering [28]. In a recent study the conduction band valley structure of a few layer MX_2 by close examination of temperature dependent indirect excitation emission peaks has been explored [29]. A study on elastic constants and electronic structures of two-dimensional monolayer MoS_2 under elastic strain using first principle calculations has been made [30]. It is shown that the band gap of monolayer MoS_2 undergoes a descent trend with the increase in strain. They observed a direct to indirect transition at strain of 0.01 and semiconductor to metal transition at strain of 0.10.

With the goal of understanding the electronic properties of bulk and monolayer MoS_2 and strain engineering, we carried out *ab initio* calculations of bulk and monolayer MoS_2 using gradient corrected exchange-correlation functional in DFT framework and observed a transition from indirect to direct band gap. However if this band gap can be tuned such that a semiconductor with a lower band gap or a semiconductor to metal transition can be achieved with the application of strain, then a wide range of tunable nano device can be fabricated. In the present work, therefore we study the effects of mechanical strains on the electronic properties of monolayer of MoS_2. Our results suggest a way of band gap engineering in MoS_2.

2. COMPUTATIONAL DETAILS

The calculations are performed by using density functional theory (DFT) [31-32] based Atomistix virtual nano lab (ATK-VNL) tool [33]. This method has been previously used to study the electronic properties of undoped and doped graphene [34-35].The exchange correlation potential was approximated by generalized gradient approximation using Perdew-Wang 91 functional (GGA-PW91) [36]. The atomic positions and cell parameters were fully relaxed until an energy convergence of 10^{-9} eV reached. We used wave function and charge-density cut-offs of 70 Ryd and 300 Ryd, respectively. First, we obtained lattice constants *a* and *c* by the process of total energy minimization. Optimized structure (coordinates) was used to perform self consistent calculations with a Monkhorst-Pack [37] $8\times 8\times 8$ *k*-mesh followed by the non-self consistent calculations for band structures, density of states and partial density of states of bulk MoS_2.

We used $80 \times 80 \times 80$ *k*-points mesh along the path Γ-K-M-Γ in the irriducible Brillouin zone to obtain the band structure with a very fine mesh points. However, for monolayer we used $8 \times 8 \times 1$ and $80 \times 80 \times 1$ Monk- horst-Pack of *k*-points respectively for sampling Brillouin zone for calculations of structural properties and electronic structure. In case of monolayer MoS_2, we created 15 Å vacuum along *Z* axis to isolate it and to prevent any interaction between the layers. The

cohesive energy per atom of bulk MoS_2 was calculated as $E_{coh} = E(MoS_2) - E(Mo) - 2E(S)$, where $E(MoS_2)$ is the total energy of the unit cell of Molybdenum disulphide, $E(Mo)$ is the energy of Mo atom and $E(S)$ is the energy of S atom. The cohesive energies per atom of monolayer MoS_2 was also calculated accordingly. A uniform tensile strain ranging from 0 to 10% were applied on monolayer MoS_2 to study the change in behavior of its band gap.

3. RESULTS AND DISCUSSIONS

3.1 *Structural Properties*

Molybdenum disulphide has a hexagonal structure consisting of S-Mo-S layers as shown in Figure 1.

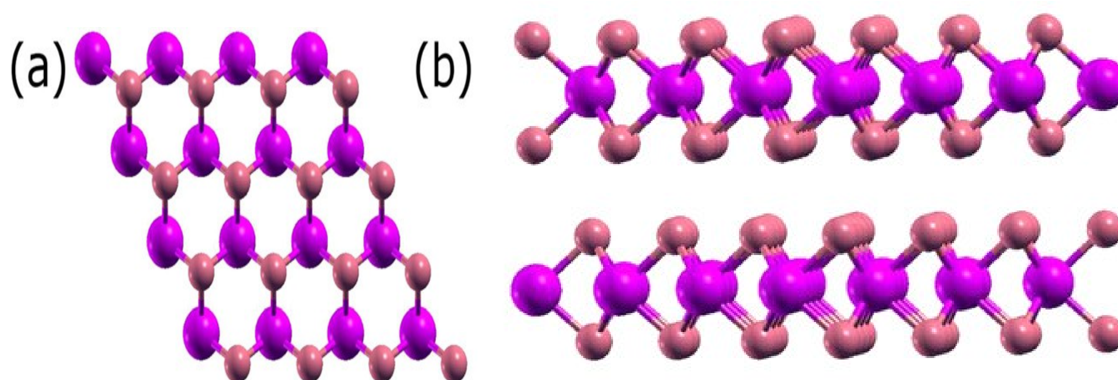

Figure 1. Optimised geometric structures (a) Top view of bulk MoS_2; (b) Side view of bulk monolayer MoS_2. The Mo-atoms are denoted by purple and S-atoms by pink balls.

Bulk MoS_2 has two such layers and Mo atoms of one layer are directly above the sulfur atoms of the other layer and vice versa while monolayer MoS_2 has a single S-Mo-S layer. We have calculated the structural parameters of bulk and monolayer MoS_2 using GGA as shown in Table 1.

Table 1. Calculated structural parameters of bulk MoS_2 and monolayer MoS_2 using GGA. The available results have also been given for the purpose of comparison.

Properties		**Bulk- MoS_2**	**Monolayer- MoS_2**
Lattice Constant (Å)		3.185	3.185
Energy Gaps (eV)	Present calculation	0.975	1.850
	Experimental value	1.25 (Ref 10)	1.80 (Ref 10)
	Theoretical Value	0.89 (Ref 20)	1.55 (Ref 20)
Cohesive Energy (eV/atom)		4.955	4.969
Interatomic Distance d_{Mo-s} (Å)		2.418	2.418

The results of bulk MoS_2 have been compared with experimental data while the results of monolayer are compared with some other theoretical results. We find excellent agreements as can be seen in Table 1. Our calculated lattice parameters overestimate the experimental values which is an

inherent feature of standard GGA functional. It is concluded that all the structural parameters calculated for monolayer MoS_2 are nearly identical to the structural parameters calculated for bulk MoS_2

3.2 *Electronic Properties*

The electronic band structure and density of states can be divided into three sets of bands and states respectively, separated by gaps. In the first set, bands in electronic band structure and states in density of states around -14 eV are mainly due to 3*s* orbital of S atom separated by large gap from second set below Fermi energy in which 3*p* orbital of S and 4*d* orbital of Mo are mainly contributing and show strong hybridization. Third set above the Fermi energy in which main contribution is due to 4*d* orbital of Mo is separated by band gap from second group below Fermi energy. The electronic band structure of bulk MoS_2 and corresponding density of states are shown in Figure 2.

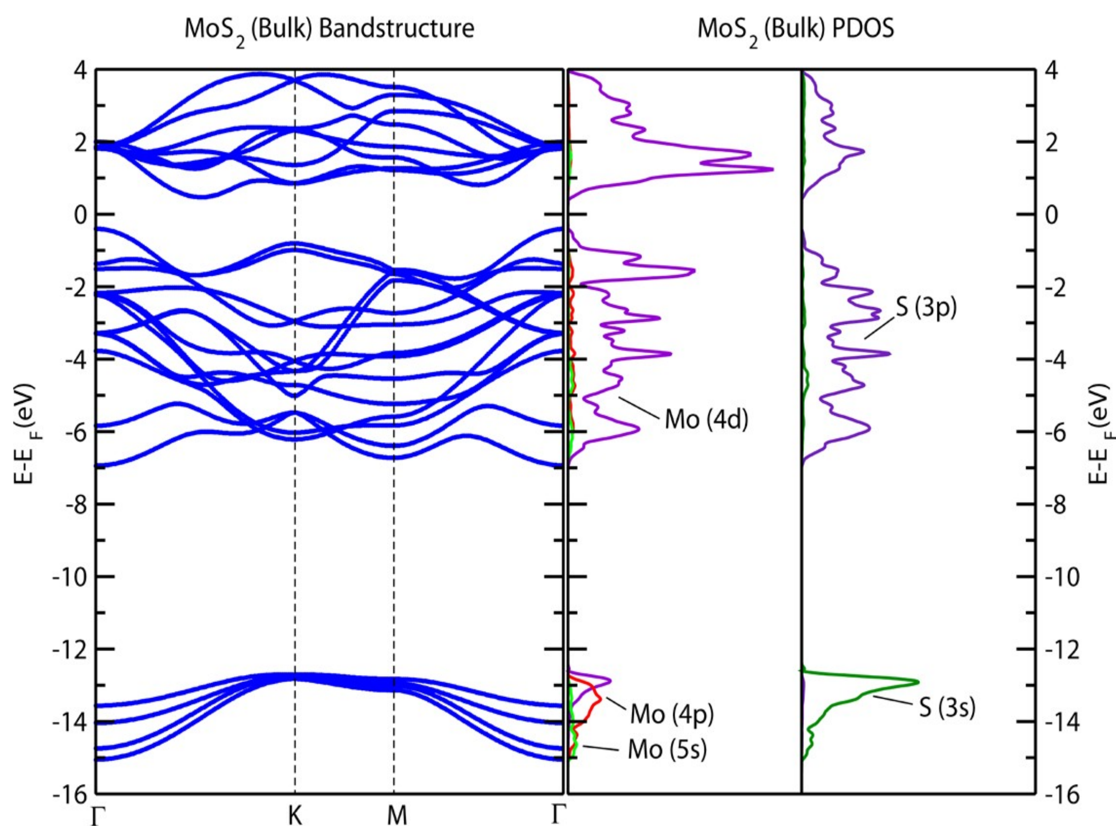

Figure 2. Calculated band structure (left panel) and orbital-projected density of states (PDOS) on Mo (middle panel) and S atoms (right panel) in bulk MoS_2.

A comparative band structure of MoS_2 bulk and its monolayer and bilayer are shown in Figure 3. The bands on each side of the band gap are derived mainly from the 4*d* states of Mo and 3*p* states of S in bulk, bilayer and monolayer MoS_2. The bands around the band gap are relatively flat, as expected from the *d*-character of electron states at these energies.

For bulk MoS_2 the valence band maximum is at high-symmetric Γ-point and conduction band

minima is in between Γ- and K-points, revealing indirect band semiconductor as can be seen in Figure 3. If we compare the band structure of bulk and monolayer MoS_2, we observe that the band edge near Γ point has been shifted up by around 0.7 eV. In case of monolayer, at Λ and Σ point the band edge shifted up in such a way that the conduction band minima occurs at K-point. For monolayer the valence band maxima and conduction band minima are both at high-symmetric K-point revealing direct band gap semiconductor as can be seen in Figure 3.

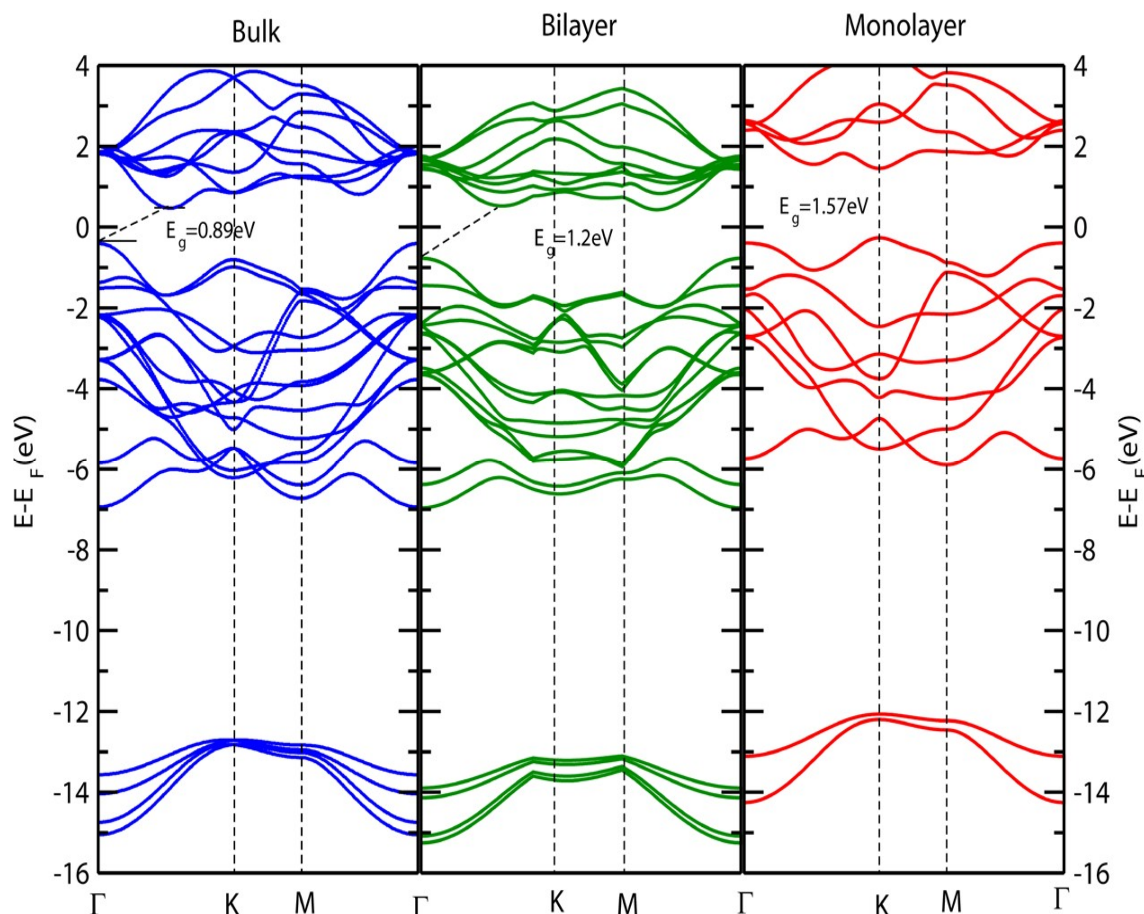

Figure 3. Calculated band structure of bulk (left), bilayer (middle) and monolayer (right) of MoS_2 at high-symmetric points in the irreducible Brillouin zone. The position of valence band maxima, conduction band minima and the band gap (E_g) are indicated. For monolayer MoS_2 the direct band gap occurs at K-point, unlike in other cases.

Thus there is a transition from indirect band gap to direct band gap as we go from bulk MoS_2 to its monolayer. A PDOS comparison of bulk and monolayer MoS_2 (as shown in the Figure 4) reflects that the states are essentially due to d_{z2} and degenerate states d_{xy} and d_{x2-y2}. The states d_{x2-y2} and d_{xy} are degenerate in case of bulk while little bit separating in monolayer. The calculated and measured band gap for monolayer MoS_2 and bulk. Our calculated band gaps are in good agreements with other theoretical values.

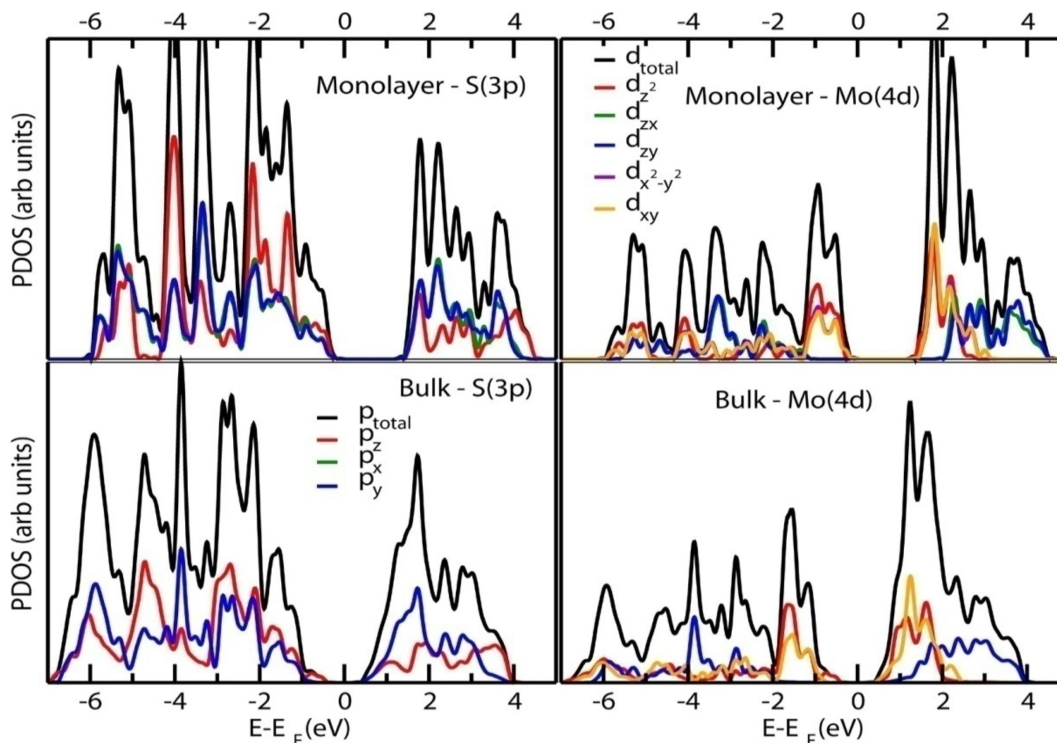

Figure 4. Calculated projected density of states (PDOS) of bulk and monolayer of MoS_2 are shown for Mo(4*d*) and S(3*p*) states. The legends for the *p*- and *d*-orbitals are similar for the monolayer and bulk.

4. CONCLUSION

In summary, we have studied the structural and electronic properties of MoS_2 using plane wave pseudopotential method under GGA scheme based DFT calculations. Electronic band structure and density of states calculation show many similarities between monolayer-MoS_2 and bulk-MoS_2 except the nature of the band gap which is found direct for monolayer-MoS_2 as compared to indirect for bulk-MoS_2. This observation is consistent with the theoretical prediction of indirect to direct band gap transition in going from bulk to monolayer. Such behavior, arising from *d*-orbital related interaction in MoS_2, may also arise in other layered transition metal dichalcogenides. A further variation in band gap has been observed in MoS_2 monolayer on applying strain. It points out a new direction of band engineering hence such capability can lead to engineering novel behaviors and holds promise for new applications.

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REFERENCES

1. M. S. Xu, T. Liang M. Shi and H. Chen, Graphene-Like Two-Dimensional Materials *Chem.*

Revs., 2013; 113: 3766 - 3798.

2. A. Kumar and P. K. Ahluwalia, Electronic stability and electron transport properties of atomic wires anchored on the MoS_2 monolayer, Phys. Chem, chem.. Phys., 2014; 16: 20157 - 20163.
3. Wilson, J.A. and Yoffe, A.D. The Transition Metal Dichalcogenides Discussion and Interpretation of the Observed Optical, Electrical and Structural Properties. *Advances in Physics*, 1969; 18: 193.
4. R. S. Chen, C. C. Tang, W. C. Shen and Y. S. Huang, Thickness-dependent electrical conductivities and ohmic contacts in transition metal dichalcogenides multilayers. *Nanotechnology*., 2014; 25: 415706.
5. C. Kamal, A. Chakrabarti and M. Ezawa, Aluminene as highly-doped graphene, New J. Phys. 2015; 17(8): 083014.
6. Kim, Y., Huang, J.L. and Lieber, C.M. Characterization of Nanometer Scale Wear and Oxidation of Transition Metal Dichalcogenide Lubricants by Atomic Force Microscopy. *Applied Physics Letters*, 1991; 59: 3404.
7. Hu, K.H., Huand, X.G. and Sun, X.J. Morphological Effect of MoS_2 Nanoparticles on Catalytic Oxidation and Vacuum Lubrication. *Applied Surface Science*, 2010; 256: 2517.
8. Fortin, E. and Sears, W. Photovoltaics Effect and Optical Absorption in Mo_{S2}. *Journal of Physics and Chemi- stry of Solids*, 1982; 43: 881.
9. Reshak, A.H. and Auluck, S. Calculated Optical Properties of 2H-Mo_{S2}, Intercalated with Lithium. *Physical Review B*, 2003; 68: Article ID: 125101.
10. Mak, K.F., Lee, C., Hone, J., Shan, J. and Heinz, T.F. Atomically Thin MoS_2: A New Direct Gap Semiconduc- tor. *Physical Review Letter*, 2010; 105: Article ID: 136805.
11. Novoselov, K., Jiang, D., Schedlin, F., Booth, T., Khotkevich, V., Morozov, S. and Geim, A. Two Dimensional Atomic Crystals. *Proceedings of the National Academy of Sciences of the United States of America*, 2005; 102: 10451.
12. Joensen, P., Frindt, R. and Morrison, S. Single Layer MoS_2. *Materials Research Bulletin*, 1986; 21: 457.
13. Coleman, J.N., Lotya, M., O'Neill, A., Bergin, S.D., King, P.J., Khan, U., Young, K., Gaucher, A., De, S., Smith, R.J., Shvets, I.V., Arora, S.K., Stanton, G., Kim, H.Y., Lee, K., Kim, G.T., Duesberg, G.S., Hallam, T., Bolland, J.J., Wang, J.J., Donegan, J.F., Grunlan, J.C., Moriarty, G., Shmeliov, A., Nicholls, R.J., Perkins, J.M., Grieveson, E.M., Theu- wissen, K., McComb, D.W., Nellist, P.D. and Nicolosi, V. Two-Dimensional Nanosheets

Produced by Liquid Exfoliation of Layered Materials. *Science*, 2011; 331: 568.

14. Radisavljevic, B., Radenovic, A., Brivio, J., Giacometti, V. and Kis, A. Single Layer MoS_2 Transistors. *Nature Nanotechnology*, 2011; 6: 147.
15. Yoon, Y., Ganapathi, K. and Salahuddin, S. How Good Can Monolayer MoS_2 Transistors Be? *Nano Letters*, 2011; 11: 3768-3773.
16. Kumar, A. and Ahluwalia, P.K. Electronic Structure of Transition Metal Dichalcogenides Monolayers 1H-MoS_2 (M = Mo, W; X = S, Se, Te) from *ab Initio* Theory: New Direct Band Gap Semiconductors. *European Physical Jour- nal B*, 2012; 85: 186.
17. Eellis, J.K., Lucero, M.J. and Scuseria, G.E. The Indirect to Direct Band Gap Transition in Multilayered Mo_{S2} as Predicted by Screened Hybrid Functional Density Functional Theory. *Applied Physics Letters*, 2011; 99: Article ID: 261908.
18. Li, T. and Galli, G. Electronic Properties of MoS_2 Nanoparticles. *Journal of Physical Chemistry C*, 2007; 111: 16192- 16196.
19. Kadantsev, E.S. and Hawrylak, P. Electronic Structure of Single MoS_2 Monolayer. *Solid State Communications*, 2012; 152: 909-913.
20. Kumar, A. and Ahluwalia, P.K. A First Principle Comparative Study of Electronic and Optical Properties of 1H-MoS_2 and 2H-MoS_2. *Materials Chemistry and Physics*, 2012; 135: 755-761.
21. Topsakal, M., Cahangirov, S. and Ciraci, S. The Response of Mechanical and Electronic Properties of Graphane to the Elastic Strain. *Applied Physics Letters*, 2010; 96: Article ID: 091912.
22. Guinea, F., Katsnelson, M.I. and Geim, A.K. Energy Gaps and a Zero Field Quantum Hall Effect in Graphene by Strain Engineering. *Nature Physics*, 2010; 6:30-33.
23. Lu, P., Wu, X., Guo, W. and Zeng, X.C. Strain Dependent Electronic and Magnetic Properties of Mo_{S2} Mono- layer, Bilayer, Nanoribbons and Nanotubes. *Physical Chemistry Chemical Physics*, 2012; 14: 13035-13040.
24. Pan, H. and Zhang, Y.W. Tuning the Electronic and Magnetic Properties of MoS_2 Nanoribbons by Strain Engi- neering. *Journal of Physical Chemistry C*, 2012; 116: 11752-11757.
25. Scalise, E., Houssa, M., Pourtois, G., Afanas'ev, V. and Stesmans, A. Strain Induced Semiconductor to Metal Transition in the Two Dimensional Honeycomb Structure of MoS_2. *Nano Research*, 2012; 5: 43-48.
26. Shi, H., Pan, H., Zhang, Y.W. and Yakobson, B.I. Quasiparticle Band Structures and Optical

Properties of Strained Monolayer MoS_2 and WS_2. *Physical Review B*, 2013; 87: Article ID: 155304.

27. Feng, J., Qian, X., Huang, C. and Li, J. Strain Engineered Artificial Atom as a Broad Spectrum Solar Energy Funnel. *Nature Photonics*, 2012; 6: 866-872.
28. Bertolazzi, S., Brivio, J. and Kis, A. Stretching and Breaking of Ultrathin Mo_{S2}. *ACS Nano*, 2011; 5: 9703-9709.
29. Zhao, W.J., Ribeiro, R.M., Toh, M., Carvalho, A., Kloc, C., Neto, A.H.C. and Eda, G. Origin of Indirect Optical Transitions in Few Layer MoS_2, WS_2 and WSe_2. *Nano Letters*, 2013; 13: 5627-5634.
30. Yue, Q., Kang, J., Shao, Z., Zhang, X., Chang, S., Wang, G., Qin, S. and Li, J. Mechanical and Electronic Properties of Monolayer Mo_{S2} under Elastic Strain. *Physics Letters A*, 2012; 376: 1166-1170.
31. Sholl D, Steckel JA Density functional theory: a practical introduction 2009.
32. Dreizler R M, Gross EKU Density functional theory. Springer, Berlin 1990.
33. Atomistix Tool Kit version 18.12.6, Quantum Wise A/S (www. quantumwise.com).
34. Kaloni, T.P. and Mukherjee, S. Comparative Study of Graphite and Hexagonal Boron Nitride Using Pseudopo- tential Plane Wave Method. *Modern Physics Letters B*, 2011; 25: 1855-1866.
35. Mukherjee, S. and Kaloni, T.P. Electronic Properties of Boron and Nitrogen-Doped Graphene: A First-Prin- ciples Study. *Journal of Nanoparticle Research*, 2012; 14: 1059.
36. Perdew, J., Chevary, J., Vosko, S., Jackson, K., Pederson, M., Singh, D. and Fiolhais, C. Atoms, Molecules, Solids and Surfaces: Applications of the Generalized Gradient Approximation for Exchange and Correlation. *Physical Review B*, 1992; 46: 6671-6687.
37. Monkhorst, H.J. and Pack, J.D. Special Points for Brillouin Zone Integrations. *Physical Review B*: *Solid State*, 1976; 13: 5188-5192.