PCCP

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

High Efficient and Ultrastable Visible-light Photocatalytic Water Splitting over ReS_2

Huimei Liu[1]*, Bo Xu[2]*, J. –M. Liu[1], Jiang Yin[2], Feng Miao[1], Chun-Gang Duan[3] and Xiangang Wan[1]

[1]*National Laboratory of Solid State Microstructures, School of Physics, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China*

[2]*National Laboratory of Solid State Microstructures, Department of Materials Science and Engineering, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing, 210093, China*

[3]*Key Laboratory of Polar Materials and Devices, Ministry of Education, East China Normal University, Shanghai 200062, China*

ABSTRACT: Two dimensional materials stand out with many intrinsic advantages that can be utilized to enhance the photocatalytic efficiency of water splitting. Here, based on *ab initio* calculations, we reveal that for monolayer and multilayer Rhenium disulphide (ReS_2), the band gap and band edge positions are in excellent match with the water splitting energy level. Moreover, the effective masses of carriers are relatively light and the optical absorption coefficients are high under visible illumination. Due to the feature of weak interlayer coupling, these properties are independent of the layer thickness. Our results suggest ReS_2 as a stable and efficient photocatalyst with potential applications on using solar energy for water splitting.

KEYWORDS: ReS_2, layer-independent, water splitting, photocatalytic

*Corresponding Author: xubonju@gmail.com; liuhuimeiphy@gmail.com

Introduction

The search for suitable materials as photocatalysts for the splitting of water by using solar energy has become an important research direction because of the important role it plays in solving energy and environmental problems[1-3]. Determining the absorbed range of the solar spectrum, a suitable bandgap is one of the most important parameters for a semiconductor to be used as photocatalysts for the splitting of water. The energy levels of the conduction and valence bands are also vital points for semiconductor photocatalysts: the conduction band minimum (CBM) should be located under the reduction potential of H^+/H_2 (0 V vs. NHE), while the valence band maximum (VBM) should be above the oxidation potential of O_2/H_2O (1.23 V vs. NHE)[4]. Thus electrons and holes can be generated to reduce and oxidize the water molecules respectively. The closer VBM and CBM stand to the redox potential of water, the more efficient the photocatalyst will be.

Based on these two principles, remarkable progress has been made and lots of semiconductors have been proposed as photocatalysts for water splitting, such as metal oxides, sulfides, nitrides, oxynitrides during the past decades[5-12]. Unfortunately, most of these semiconductors with the band gaps satisfying the requirement for water splitting are only active under ultraviolet irradiation, leading to a very inefficient usage of sunlight. Take TiO_2 as an example, it has been extensively investigated due to the potential on splitting water while its wide bandgap (~3.0 eV) limits the activity to the UV region of the solar spectrum[13]. Many methods have been proposed to solve this problem. Reducing the band gap of photocatalyst to the visible light or near-infrared light region through band gap engineering is one of the most popular approaches. The cation or anion (co-)doping effects[14,15] on enhancing the visible light activity of TiO_2 have also been intensively studied both theoretically and experimentally. Employing sacrificial reagents[16] has been applied to enhance the half reactions of water splitting, H_2 evolution reaction or O_2 evolution reaction. Heterojunctions[17,18] by coupling of two narrow band gap semiconductors with well-matched band structures have shown a lot of advantages for overcoming band alignment defects above of traditional photocatalysts. However, the development of photocatalysts with high efficiencies for splitting production from water using solar energy still faces major challenges.

Recently, two dimensional (2D) layered materials[19-23], such as graphitic C_3N_4, $(Mo,W)(S,Se)_2$, and (Ga,In)(S,Se), have gained increasing interest as visible-light photocatalyst in the water splitting hydrogen production process, due to suitable band gaps within visible light regime. The 2D layered semiconductors exhibit two main intrinsic advantages for applications as photocatalysts[24], including the maximum surface area available for water splitting and the minimum distance that the generated electrons and holes have to migrate, thus reducing the possibility of electron–hole recombination and potentially enhancing their photocatalytic performance.

However, for most 2D layered semiconductors, their electronic structures are strongly dependent on their thicknesses. For example, the bandgap and the conduction and valence band positions of MoS_2 are highly dependent on the number of layers[25,26]. Thus thin layer MoS_2 no longer has activity for photocatalytic H_2 evolution if it reaches triple-layer[27,28]. These require accurately control of layer number during the sample preparation if one takes MoS_2 as photocatalytic material. Similar thickness dependent electronic behavior is also observed in other 2D layered semiconductors[26,29]. Since precise control of the layer number is quite challenging, the thickness dependent electronic properties of 2D layered semiconductors significantly limit their potential applications as photocatalysts for water splitting. Thus, searching 2D layered compounds with layer number-independent suitable band gap and energy level positions is highly desired.

ReS_2[30], as a 2D transition metal dichacogenide with the distorted 1T structure, has recently attracted much attention[31,32]. Most strikingly, the electronic and vibrational properties of ReS_2 are almost independent with the number of layers[30,32] due to the weak interlayer interaction, which is different from other 2D transition metal dichalcogenides. Even more, ReS_2 has a suitable band gap and can absorb all of the visible light, making it highly efficient in solar-energy conversion.

In this work, the properties of monolayer and multilayer ReS_2 are systematically studied based on the density functional theory calculations. The band gaps of multilayer ReS_2 are predicted to be about 1.80 eV with suitable band edge alignments for water splitting, which are ideal for photocatalysts. The high carrier mobility, superior optical absorption properties, and the thickness-independent electronic properties ensure multilayer ReS_2 a perfect candidate as a high-efficiency and universal visible-light photocatalysts for water splitting.

Results and Discussion

Different from other transition metal dichalcogenides such as MoS_2 and WS_2, ReS_2 crystallizes in a distorted T structure with clustering of Re_4 units forming a one-dimensional chain inside each monolayer[30]. The top view of the monolayer ReS_2 crystal structure is shown in Figure 1a. The primitive cell of mono-layer ReS_2 is composed of four Re and eight S atoms, with two hexagonal planes of S atoms and an intercalated hexagonal plane of Re atoms bound with S atoms in a trigonal prismatic arrangement. As illustrated by two lines in the top view, there are two principle axes, the *b*- and *a*-axes, which correspond to the shortest and second-shortest axes in the basal plane. They are 61.03° or 118.97° apart, and the *b*-axis corresponds to the direction of the Re-Re atomic chain.

Since the van der Waals (vdW) interaction always plays an important role in 2D materials, such as that in MoS_2. To check the influence of the van der Waals (vdW) interaction, we plot the charge distribution across the layer for the highest valence band and lowest conduction band in Figure 2 before we perform other calculations. The electrons are highly localized within each layers, the overlay in the interlayer region is quite small for ReS_2 which can be served as a direct evidence of the weak interlayer coupling. All these are in good consistent with the previous work[32], in which Feng *et al.* also pointed out that the vdW interaction is relatively weak in ReS_2. Eventually, we present our results without considering the vdW interaction in the following of our work.

Following we calculate the band gap of monolayer ReS_2, which is the key quantity for photocatalysts. Table 1 collects the band gaps obtained from PBE, HSE03, HSE06 and quasi-particle self-consistent *GW* calculations, together with experimental one.

Through the PBE calculations, monolayer ReS_2 is found to have a direct band gap of 1.41eV, which is smaller than the experimental value (1.55 eV) from absorption spectroscopy[30]. Simultaneously the band gap of monolayer ReS_2 calculated through the HSE03 functional is found to be 1.89eV, which is closer to the *GW* value (1.87 eV) compared with the corresponding gap from HSE06 functional (2.2 eV). In general, the *GW* gaps are very close to those direct experimental fitting of the absorption data once excitonic effects are excluded[33,34]. Consequently, we present the results obtained with the HSE03 functional since the GW calculations are much more expensive.

The band dispersion of monolayer ReS_2 calculated through the HSE03 method is shown in Figure 1c. It is clear that both the valence and conduction bands are well dispersed and no localized states are present to act as recombination centers for the photo generated electron-hole pairs. Hence the lifetime of the photo generated charge carriers in monolayer ReS_2 is expected to be longer, which can lead to better photocatalytic efficiency. We have also studied the electronic structure of multilayer ReS_2 (2 to 5 layers), to evaluate the effect of interlayer coupling (band structures in supporting materials). As shown in Figure 1b, the band gap is slightly reduced to 1.80 eV for 5-layer ReS_2, only 0.09eV decreased to monolayer ReS_2. As for the bulk ReS_2, the calculated band gap is found to be 1.76 eV which is in agreement with the experimental value[35,36]. The band gap values of ReS_2 are insensitive to the layer thicknesses, indicating the very weak interlayer coupling compared with other layered materials, such as MoS_2, WS_2, and phosphorene[22,25,28]. The thickness dependent band gap of MoS_2 is calculated for comparison as displayed in Figure 1b. It is found that the band gap of bulk MoS_2 is about 1.20eV, about 0.6 eV decreased from 1.8 eV of monolayer, which is in line with the previous report[24, 25]. Figure 1d displays the projected density of states (DOS) of monolayer ReS_2 and the electronic structures of multilayer ReS_2 are shown in Figure S1 and Figure S2. From the projected DOS, it can be seen that the *d* orbitals of Re are spatially extended, the states around the Fermi energy is dominated by Re-*d* orbital and additional contribution from the S-*p* state indicating hybridization between them. Having a significant *d* character around the Fermi energy may also result in large effective masses which will eventually lead to the low intrinsic carrier mobility. However, a particularly useful aspect is their intrinsic optical absorption, which arises from the existence of partially filled *d* orbitals.

As we know, the photocatalysis of water splitting includes the two basic processes: (1) electron-hole pairs generated by photon irradiation with energy larger than that of band gap; (2) the excited electrons and holes move to the surface of semiconductor for the redox reaction. As more electron–hole pairs migrate to the surface, a higher conversion efficiency of solar energy will be expected. So, the carrier mobility plays a crucial role in photocatalytic water splitting. This issue could be mitigated by the following two factors for the multilayer ReS_2. First, the band structure of monolayer in Figure 1c shows large dispersions near band edges, suggesting good carrier transport properties. The calculated electron (hole) effective masses are -1.463 (0.602), and -3.607 (1.389)m_0 (electron rest mass), respectively, along the Γ−K, and Γ−M directions which is slightly larger than that of monolayer MoS_2. The electron (hole) effective masses of monolayer MoS_2 are -0.57 (2.80) m_0 along the Γ−K, and Γ−M directions[37]. For the multilayer ReS_2, they show the similar results to those of monolayer. Second, Liu *et al.*[31] recently reported experimentally that the carrier mobility of multilayer ReS_2 could be higher than 10 cm^2/Vs, which is comparable with the carrier mobility in oxides.

We observe that multilayer ReS_2 possess bandgap about 1.8eV within the visible light range. To confirm whether they are suitable for water splitting, we need to determine the alignment of the CBM and VBM energies with the redox potentials of water splitting. Figure 3 compares the CBM and VBM energy levels of multilayer ReS_2 with the redox potentials of water splitting. For the single layer ReS_2, the CBM and VBM are found to be located at -6.15 and −4.26 eV respectively. The CBM is located just (0.18eV) above the water reduction level, whereas the VBM is found to be 0.48eV below the water oxidation potentials. The position of the band edges obtained directly from HSE03 functional may be shifted, it can nevertheless give the band gap center (BGC) [38,39], which is the average of the energies at VBM and CBM, quite well. The individual obtained BGC energies as -5.20, -5.16, -5.15, -5.14, and

-5.14 eV for 1- to 5- layer ReS_2. Surprisingly, the resulting CBM (VBM) is still negative (positive) than the redox potential of H^+/H_2 (H_2O/O_2) when use the experimental bandgap of 1.55 eV for monolayer ReS_2. This anomalous result indicates that monolayer ReS_2 with experimental bandgap is able to catalyze the water-splitting reaction.

In the case of multilayer systems, the VBM and CBM energy levels remain almost unchanged comparing with those in single layer. For the 5-layer $ReS_{2,}$ the CBM is about 0.2eV above the water reduction level, whereas the VBM is about 0.37eV below the water oxidation potentials, almost unchanged compared to monolayer ReS_2. Considering the band gap bulk ReS_2 with a band gap of 1.76 eV, and the CBM is about 0.18 eV above the water reduction level, whereas the VBM is about 0.35eV below the water oxidation potentials. Consequently, for all the multilayer $ReS_{2,}$ the CBM is located above the water reduction potential, and the VBM is well below the water oxidation potential at pH=0, suggesting that all the multilayer ReS_2 are suitable photocatalysts under the visible-light irradiation.

Usually, the less negative (positive) for CBM (VBM) locates compared with the redox potential of H^+/H_2 (H_2O/O_2), the more promising it will be for the water reduction (oxidation). For example, TiO_2 prefers to the performance for H_2 evolution, for the CBM is negative than the redox potential of H^+/H_2 by only about 0.1 eV, while the VBM is positive than the redox potential of H_2O/O_2 by about 1.8 eV[13]. For the single layer MoS_2, the CBM is located just (0.13eV) above the water reduction level[28], whereas the VBM is found to be 0.44eV below the water oxidation potentials. And several experiments suggest that they exhibit excellent photocatalytic performance for H_2 evolutions[27, 28]. Similar result has been found in g-C_3N_4[19]. For the multilayer ReS_2, CBM is right above water reduction potential (0.20 eV), and the VBM is just below the water oxidation potential (0.35 eV). This displays that all of the multilayer ReS_2 would exhibit excellent photocatalytic performance in both H_2 and O_2 evolutions of water splitting under the visible-light irradiation. In other words, regardless of its layer number, ReS_2 is an excellent photocatalyst under the sunlight to match the redox potentials of water oxidation and reduction.

In addition to an appropriate bandgap and a suitable band alignment, another important property for photocatalysts is the optical absorption. As mentioned above, both the CBM and VBM are contributed by 5*d* orbitals of Re. The absorption coefficient is large due to the strong hybridization between Re-*d* and S-*p* orbitals. To have a look at the optical absorption characteristics of these multilayer ReS_2 systems, we have calculated the complex frequency dependent dielectric $\varepsilon(\omega) = \varepsilon_1(\omega) +_i \varepsilon_2(\omega)$ function, where ε_1 and ε_2 represent the real and imaginary parts of the dielectric function, respectively. The absorption coefficient α(ω) has been obtained from the relation:

$$\alpha(\omega) = \sqrt{2}\omega\left(\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega)\right)^{1/2}$$

Figure 4 shows the optical absorbance α(ω) of multilayer ReS_2 (from 1 to 5 layer) systems as a function of photon energy ω. Interestingly, the absorption edges are not changed with the layer number, but the absorption increases as the layer number increases. It is seen that multilayer ReS_2 show substantial adsorption in the visible light at about 660 nm (1.9eV). This absorption peak arises from the optical transitions between the valence and conduction bands around the Γ point. It shows that the absorption of multilayer ReS_2 is in visible light region of the spectrum. The high optical absorption efficiency suggests that ReS_2 are promising candidates for the visible light photocatalytic water splitting despite the layer thickness.

Conclusions

In summary, based on the density functional theory calculations, we have systematically studied the properties of multilayer ReS_2 for the applications as a photocatalyst. Due to the thickness-insensitive electronic properties, both the single layer ReS_2 and multilayer ReS_2 are shown to have the direct band gap around 1.8 eV, with suitable band edge positions for photocatalyst to split water. Moreover, both the monolayer and multilayer ReS_2 show the superior visible light absorption and the light carrier effective masses. All these findings suggest that ReS_2 stands stable and efficient photocatalyst under visible illumination. We therefore advocate future experimental studies to confirm the attractive predications.

Methods

Our first-principles calculation is performed using the VASP (Vienna ab-initio simulation package) code[40,41]. A cutoff energy of 500 eV for the plane wave basis set is used throughout all calculations and the atomic relaxations are carried out until the Hellman-Feynman force on each atom is less than 0.001 eV/Å. For few-layer ReS_2, we relaxed the internal coordinates with the in plane lattice constants fixed at the experimental value[42]. The convergence criterion of self-consistent calculations was 10^{-5} eV between two consecutive steps. A 9×9×1 k-point mesh for the Brillouin-zone sampling is used in the calculations. A vacuum spacing of 34 Å along the *c* direction is adopted to ensure that the interactions between the layers are negligible. The electronic calculations are performed using the generalized gradient approximation (GGA) of Perdew-Becke-Erzenhof (PBE) functional[43], Heyd-Scuseria-Ernzerhof (HSE03) hybrid functional[44,45], HSE06 hybrid functional and quasi-particle self-consistent *GW* correction method[46,47]. As presented in the above paragraphs, the simulated band gap using HSE03 functional in good agreement with the experimental value, consequently we use HSE03 functional in the following calculations. It is worth to emphasize that our main results do not depend on the choices of functionals.

Supplementary Information

The band structures and density of states of 2-, 3-, 4-, 5-layer ReS_2.

Acknowledgement

The work was supported by National Key Project for Basic Research of China (Grants No. 2014CB921104, 2015CB921600), NSFC (Grants No. 11374137, 11374142，61574076, 11525417), the Natural Science Foundation of Jiangsu Province (BK20130544, BK20140017, BK20150055), Doctoral Fund of Ministry of Education of China (Grant No. 20130091110003) and China Postdoctoral Science Foundation (2015M571729). The project is also funded by Priority Academic Program Development of Jiangsu Higher Education Institutions.

Contributions

X. B. designs the calculations. H. L. performs the calculations. X. B. and X. W. interpret the numerical results and write the paper. All authors contribute to editing the manuscript.

Competing financial interests

The authors declare no competing financial interests.

References:

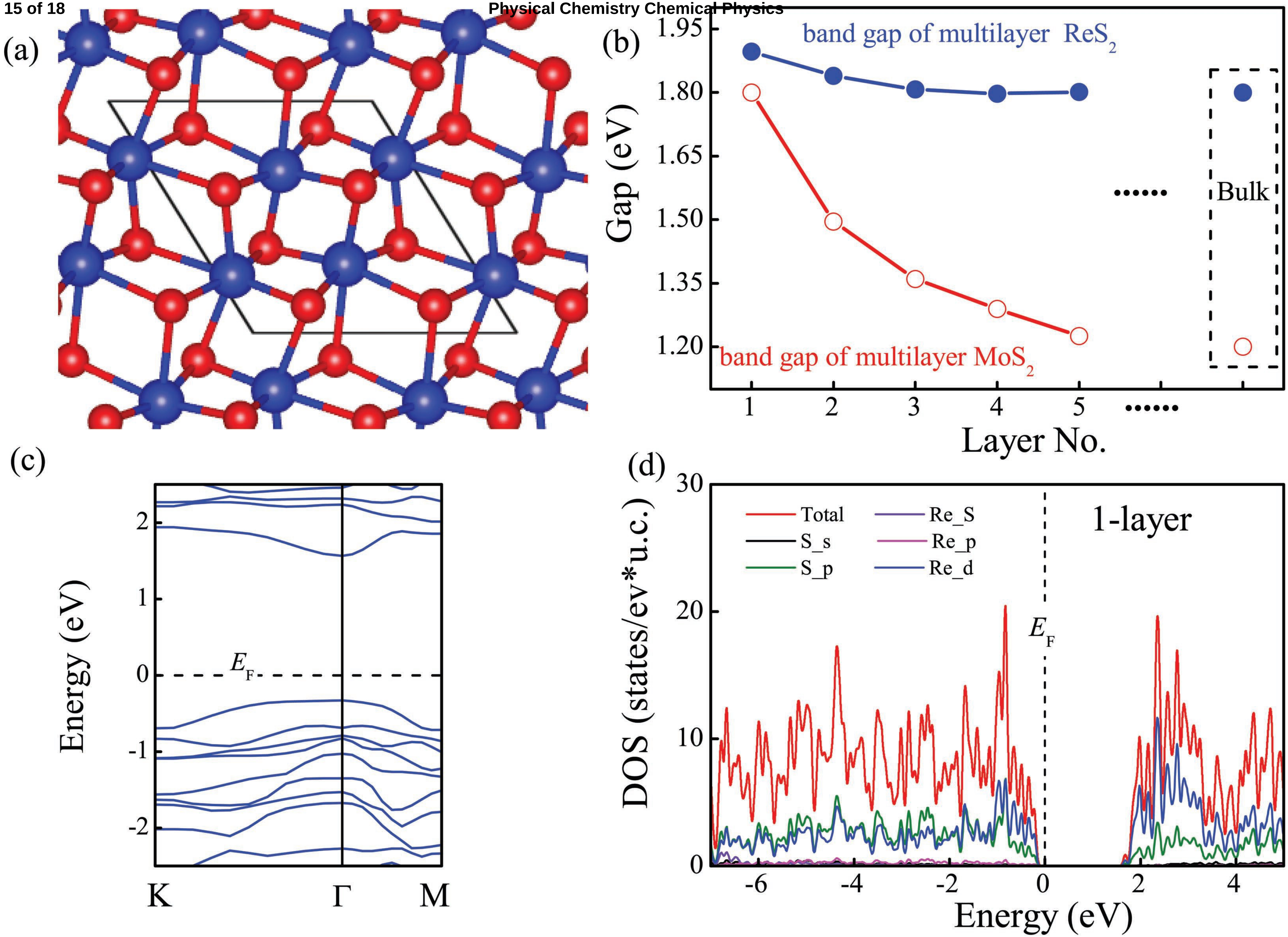
1. X. B. Chen, S. H. Shen, L. J. Guo and S. S. Mao, *Chem. Rev.* 2010, **110**, 6503.
2. A. Kudo and Y. Miseki, *Chem. Soc. Rev.* 2009, **38**, 253.
3. F. E. Osterloh and B. A. Parkinson, *Mater. Res. Soc. Bull.* 2011, **36**, 17.
4. Y. Qua and X. Duan, *Chem. Soc. Rev.* 2013, **42**, 2568.
5. K. Domen, S. Naito, M. Soma, T. Onishi and K. Tamaru *J. Chem. Soc., Chem. Commun.* 1980, **12**, 543.
6. D. Wang, A. Pierre, M. G. Kibria, K. Cui, X. Han, K. H. Bevan, H. Guo, S. Paradis, A. R. Hakima and Z. Mi, *Nano Lett.* 2011, **11**, 2353.
7. M. Matsukawa, R. Ishikawa, T. Hisatomi, Y. Moriya, N. Shibata, J. Kubota, Y. Ikuhara and K. Domen, *Nano Lett.*, 2014, **14**, 1038
8. T. Yanagida, Y. Sakata and H. Imamura, *Chem. Lett.* 2004, **33**, 726.
9. J. Sato, N. Saito, Y. Yamada, K. Maeda, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, K. Domen and Y. Inoue, *J. Am. Chem. Soc.* 2005**, 127**, 4150.
10. K. Maeda, K. Teramura, N. Saito, Y. Inoue and K. Domen, *Bull. Chem. Soc. Jpn.* 2007**, 80**, 1004.
11. G. Hitoki, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi and K. Domen, *Chem. Commun.* (Cambridge) 2002**, 16**, 1698.
12. B. Xu, W. F. Zhang, X.-Y. Liu, J. H. Ye, W. H. Zhang, L. Shi, X. G. Wan, J. Yin and Z. G. Liu, *Phys. Rev. B* 2007, **76**, 125109.
13. S. Sakthivel, M. Janczarek and H. Kisch, *J. Phys. Chem. B* 2004, **108**, 19384.
14. Z. Zou, J. Ye, K. Sayama1and H. Arakawa, *Nature* 2001, **414**, 625.
15. R. Konta, T. Ishii, H. Kato and A. Kudo, *J. Phys. Chem. B* 2004, **108**, 8992.
16. M. D.cHernàndez-Alonso, F. Fresno, S. Suàrez and M. J. Coronado, *Energy Environ. Sci.* 2009, **2**, 1231.
17. K. Sayama, K. Mukasa, R. Abe, Y. Abe and H. Arakawa, *J. Photochem. Photobiol., A* 2002, **148**, 71.
18. H. Kato, M. Hori, R. Konta, Y. Shimodaira and A. Kudo, *Chem. Lett.* 2004, **33**, 1348.

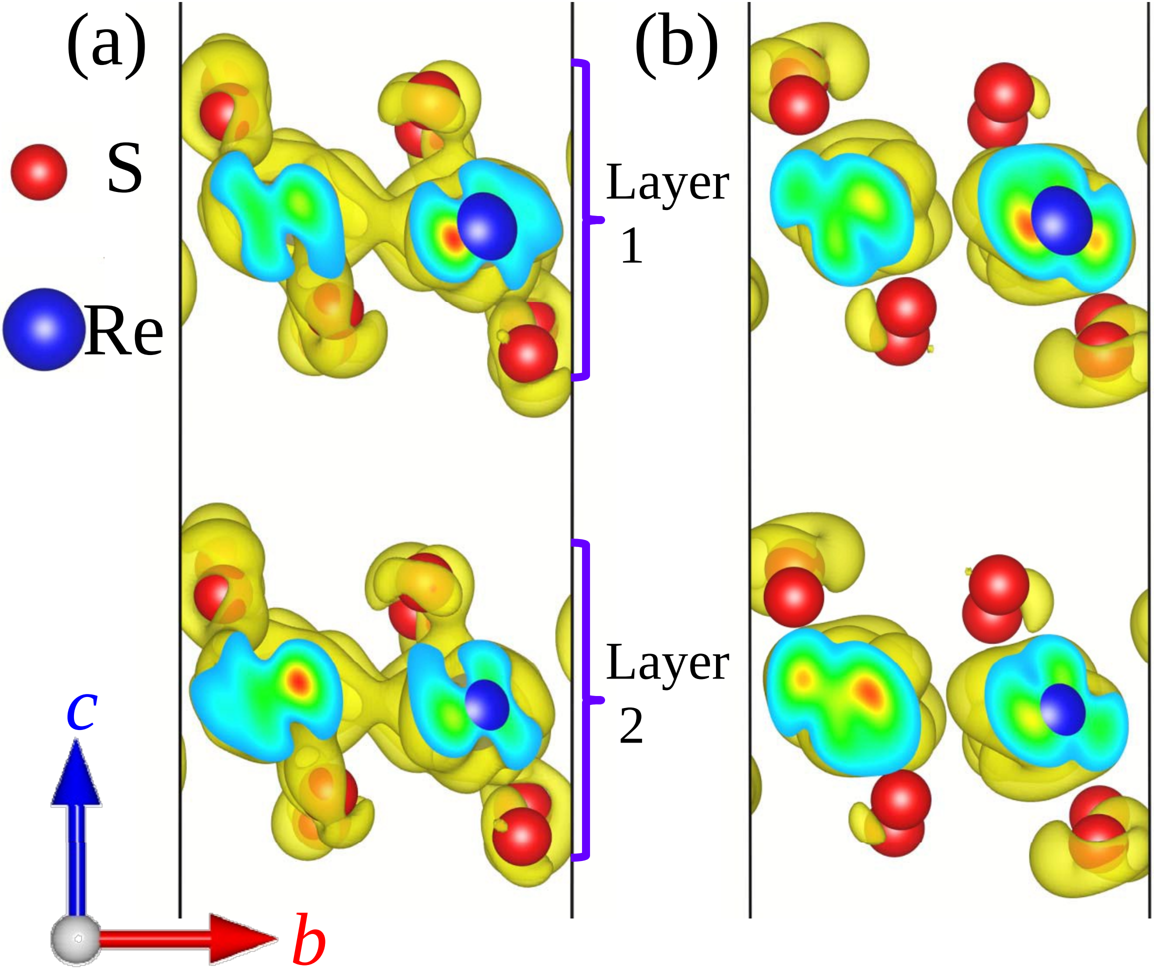
19. X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M.Antonietti, *Nat. Mater.* 2009, **8**, 76.
20. H. L. Zhuang and R. G. Hennig, *J. Phys. Chem. C*, 2013, **117**, 20440.
21. H. Jiang, *J. Phys. Chem. C*, 2012, **116**, 7664.
22. H. L. Zhuang and R. G. Hennig, *Chem. Mater.*, 2013, **25**, 3232.
23. B. S. Sa,; Y. L. Li,; J. S. Qi,; R. Ahuja, ; Z. M. Sun, *J. Phys. Chem. C*, 2014, **118** , 26560.
24. A. K. Singh, Ki. Mathew, H. L. Zhuang and R. G. Hennig, *J. Phys. Chem. Lett.*, 2015, **6**, 1087.
25. W. C. Jin, P. -C. Yeh, N. Zaki, D. T. Zhang, J. T. Sadowski, A. Al-Mahboob, A. M. van der Zande, D. A. Chenet, J. I. Dadap, I. P. Herman, P. Sutter, J. Hone and R. M. Osgood, *Phys. Rev. Lett.* 2013**, 111**, 106801.
26. W. J. Zhao, R. M. Ribeiro, M. Toh, A. Carvalho, C. Kloc, A. H. Castro Neto and G. Eda, *Nano Lett.*, 2013, **13**, 5627.
27. B. Seo, G. Y. Jung, Y. J. Sa, H. Y. Jeong, J. Y. Cheon, J. H. Lee, H. Y. Kim, J. C. Kim, H. S. Shin, S. K. Kwak and S. H. Joo, *ACS Nano*, 2015, **9**, 3728.
28. K. Chang, M. Li, T. Wang, S. X. Ouyang, P. Li, L. G. Liu and J. H. Ye, *Adv. Energy Mater.* 2015, **5**, 1402279.
29. J. Qiao, X. Kong, Z.-X. Hu, F. Yang and W. Ji, *Nat. Commun.* 2014, **5**, 4475.
30. S. Tongay, H. Sahin, C. Ko, A. Luce, W. Fan, K. Liu, J. Zhou, Y.-S. Huang, C.-H. Ho, J. Y. Yan, D. F. Ogletree, S. Aloni, J. Ji, S. S. Li, J. B. Li, F. M. Peeters and J. Q. Wu, *Nat. Commun.* 2014, **5**, 3252.
31. E. F. Liu, Y. J. Fu, Y. J. Wang, Y. Q. Feng, H. M. Liu, X. G. Wan, W. Zhou, B. G. Wang, L. B. Shao, C. -H. Ho, Y. S. Huang, Z. Y. Cao, L. G. Wang, A. D. Li, J. W. Zeng, F. Q. Song, X. R. Wang, Y. Shi, H. T. Yuan, H. Y. Hwang, Y. Cui, F. Miao and D. Y. Xing, *Nat. Commun.* 2015, **6**, 6991.
32. Y. Q. Feng, W. Zhou, Y. J. Wang, J. Zhou, E. F. Liu, Y. J. Fu, Z. H. Ni, X. L. Wu, H. T. Yuan, F. Miao, B. G. Wang, X. G. Wan and D. Y. Xing, *Phys. Rev. B* 2015, **92**, 054110.

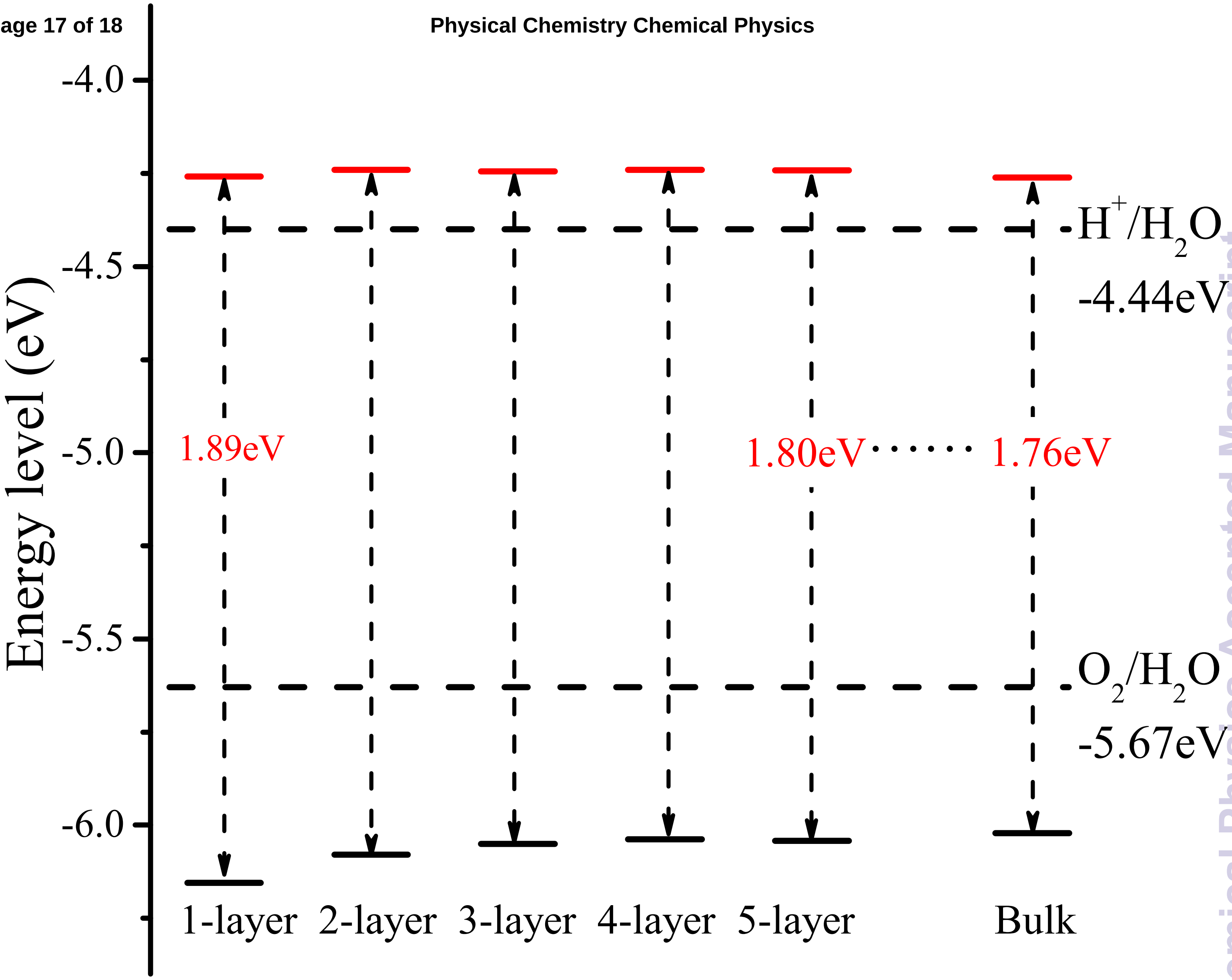
33. C. Ballif, M. Regula, P. E. Schmid, R. Sanjines and F. Levy, *Appl. Phys. A* 1996, **62**, 543.
34. A. R. Beal and W. Y. Liang, *J. Phys. C: Solid State Phys.* 1976, **9**, 2459.
35. C. H. Ho, P. C. Liao, Y. S. Huang and K. K. Tiong, *Phys. Rev. B* 1997**, 55**, 15608.
36. C. H. Ho, Y. S. Huang, K. K. Tiong and P. C. Liao, *Phys. Rev. B* 1998, **58**, 16130.
37. H. Peelaers and C. G. Van de Walle, *Phys. Rev. B* 2012, **86**, 241401(R).
38. M. C. Toroker, D. K. Kanan, N. Alidoust, L. Y. Isseroff, P. Liao and E. A. Carter, *Phys. Chem. Chem. Phys.* 2011, **13**, 16644.
39. H. Jiang, *J. Phys. Chem. C* 2012, **116**, 7664.
40. G. Kresse and J. Furthmüller, *Phys. Rev. B* 1996, **54**, 11169.
41. G. Kresse and J. Furthmüller, *Comp. Mater. Sci.* 1996, **6**, 15.
42. H. H. Murray, S. P. Kelty, and R. R. Cbianelli, *Inorg. Chem.* 1994, **33**, 4418.
43. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77,** 3865.
44. J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.* 2003, **118**, 8207.
45. J. Heyd, and G. E. Scuseria *J. Chem. Phys.* 2004, **120**, 7274.
46. M. Shishkin and G. Kresse *Phys. Rev. B* 2006, **74**, 035101.
47. M. Shishkin and G. Kresse *Phys. Rev. B* 2007, **75**, 235102.

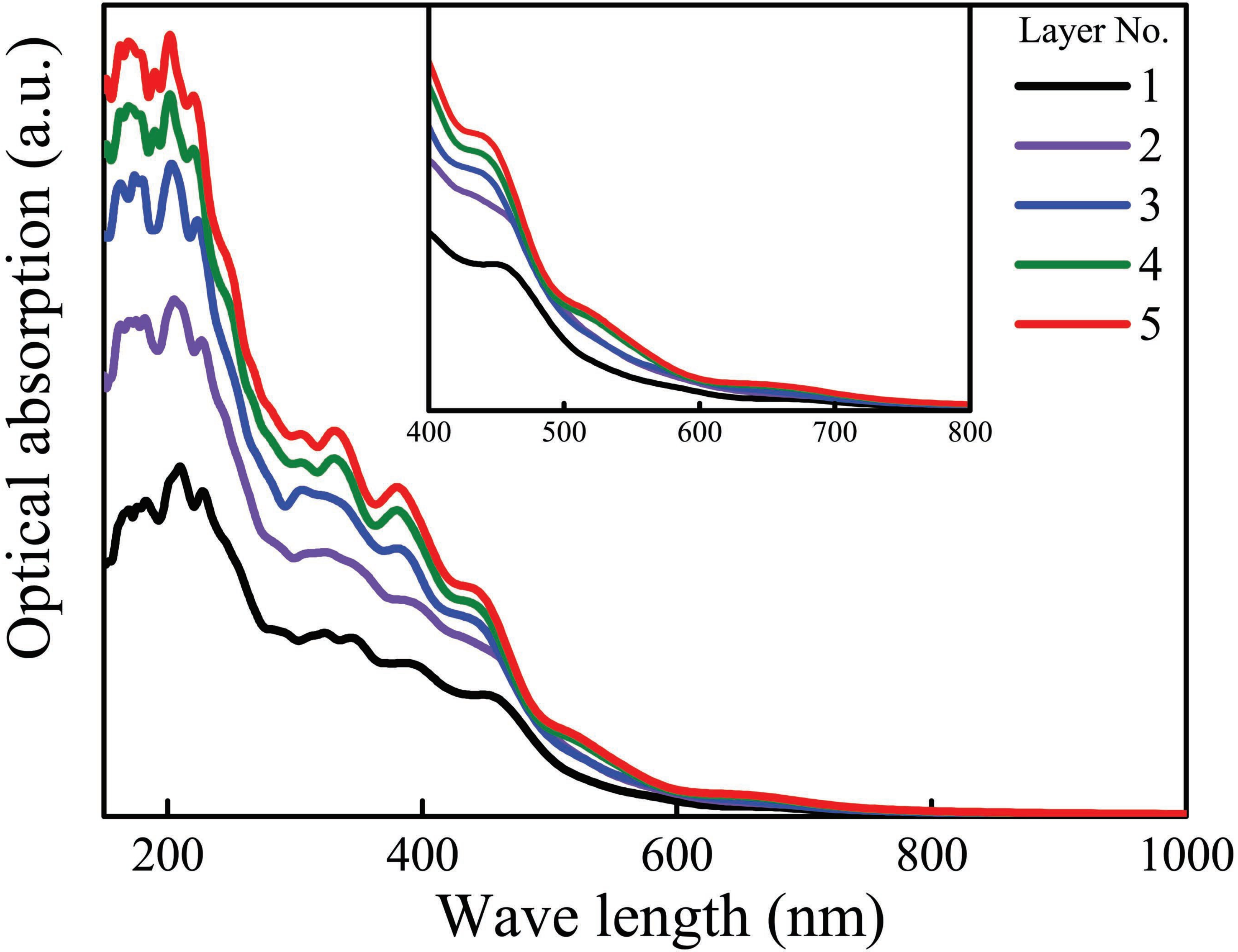
Method	Band gap (eV)
PBE	1.41
HSE03	1.89
HSE06	2.20
GW	1.87
Experimental result	1.55

Table 1 Calculated Band Gap for monolayer ReS_2


(a)
(b)
band gap of multilayer ReS$_2$
band gap of multilayer MoS$_2$
Gap (eV)
1.95
1.80
1.65
1.50
1.35
1.20
Bulk
1
2
3
4
5
Layer No.
(c)
Energy (eV)
2
1
0
-1
-2
E_F
K
Γ
M
(d)
DOS (states/ev*u.c.)
30
20
10
0
Total
S_s
S_p
Re_S
Re_p
Re_d
1-layer
E_F
-6
-4
-2
0
2
4
Energy (eV)


(a)
(b)
S
Re
Layer 1
Layer 2
c
b


-4.0
-4.5
-5.0
-5.5
-6.0
Energy level (eV)
H^+/H_2O
-4.44eV
O_2/H_2O
-5.67eV
1.89eV
1.80eV
1.76eV
1-layer
2-layer
3-layer
4-layer
5-layer
Bulk


Optical absorption (a.u.)
Wave length (nm)
200
400
600
800
1000
400
500
600
700
800
Layer No.
1
2
3
4
5