

Van Der Waals Forces, Electronic Structure and Photocatalytic Properties of Layered MoO₃

Qian Qu

Guangdong University of Science & Technology, Dongguan, 523083, China

Abstract

Based on first-principles density functional theory, orthorhombic and monoclinic layered-MoO₃ have been investigated systemically. The structure, electronic structure, optical properties and photocatalytic properties have been given in details. Our results indicate that PBE overestimated the interlayer distance. While the optB88-vdW, which considers the vdW interaction reasonably, can give a quite satisfied crystal structure. In addition, PBE also underestimates the band gap seriously, while the HSE06 functional can give consistent results with experiment. The calculated imaginary part of the dielectric function suggest that the two structures have a efficient absorption for ultraviolet sunlight. Finally we also calculated the band-edge of the two structures and found the band-edge of MoO₃-II exclusive redox potential range, while the band-edge of layered α -MoO₃ contains water reduction and oxidation potentials. This suggests that α -MoO₃ is a potential photocatalysis of water-splitting.

Keywords

First-principles; MoO₃; Van der Waals forces; Electronic structure; Photocatalytic properties.

1. Introduction

Molybdenum trioxide has a unique layered structure and optical properties, and has broad application prospects in many fields, such as gas sensors, photochromic and electrochromic devices, display materials, storage materials and catalysts, etc. [1]. Its band gap is about 2.75~3.2eV (different crystal types have different band gap widths), and it belongs to N-type wide band gap semiconductor. There are three common phase structures of MoO₃: the thermodynamically stable orthogonalized phase (α -MoO₃), the thermodynamically metastable monoclinic phase (MoO₃-II) and the hexagonal phase (h-MoO₃). Octahedron (MoO₆) is used as the basic construction unit of the orthogonality phase. Octahedron of the same layer shares edges and vertex angles, and layer to layer is bound by weaker van der Waals force. Hexagonal h-MoO₃ and monoclinic MoO₃-II basic building units are also octahedral (MoO₆). Hexagonal h-MoO₃ is formed by octahedral concordant angles to form a chain-like structure. Octahedral octahedrons in monoclinic phase share all vertical angles to form a twisted cube. Regardless of the crystal structure of MoO₃, there are a large number of tetrahedral and octahedral holes in its structure. These holes are not only ideal embedding locations for small ions, but also provide convenient channels for the transport of substances in the photocatalytic reaction process [1-6]. So molybdenum trioxide has an attractive application prospect in the field of photocatalysis. At present, the photocatalytic performance of MoO₃ has attracted extensive attention. A. Chithambararaj et al. [7] took advantage of the fact that h-MoO₃ band gap is located in visible light region and it is an appropriate candidate material for photocatalyze to successfully synthesize floral layered h-MoO₃, and experimental observation proved that h-MoO₃ completely degrades methylene blue (MB) in 120 minutes under visible light irradiation. It shows excellent photocatalytic performance. Huang et al. [8] covered the surface of MoO₃ with

g-C₃N₄ material, and found that g-C₃N₄ could help reduce the recombination probability of the electron-hole pair of MoO₃. The degradation of methylene blue showed that g-C₃N₄ was beneficial to improve the photocatalytic activity of MoO₃ under visible light and contribute to charge transfer at the heterogeneous interface. M. B. Sreedhara and his colleagues [9] studied the degradation kinetics of methylene blue (MB) by bulk MoO₃ and multilayer MoO₃ under UV irradiation, and compared the photocatalytic activities of bulk and multilayer MoO₃. It was found that the degradation rate of multilayer MoO₃ was faster than that of bulk MoO₃ by detecting the concentration change of Mb at 664 nm over time.

A large number of experimental studies have proved that MoO₃ has certain feasibility in photocatalysis, but there are relatively few theoretical studies. In particular, the vdW forces between laminated MoO₃ layers and the electronic association effects of transition metals greatly challenge the widely used LDA/GGA calculations. In this paper, optB88-vdW functional was used to consider the interlayer vdW forces, and hybrid functional (HSE06) was used to accurately calculate the material band gap. The structure, electronic structure, optical properties and photocatalytic performance of layered MoO₃ were systematically studied to explore the feasibility of using it as a photocatalytic catalyst for water degradation.

2. Calculation Method

In this paper, based on the first-principles calculation method of density functional theory, the electronic structure, optical properties and photocatalytic performance of bulk MoO₃ compounds were studied by using the plane-wave code VASP (Vienna AB-initio Simulation Package) [10]. Among them, the form of exchange correlation functional is PBE (Perdew-Burke-Ernzerhof), which is a widely used exchange correlation functional at present. A large number of calculations show that the PBE can not accurately consider the vdW force of interlayer bonding, and the band gap obtained is too small. In order to accurately consider the vdW forces between layers of layered MoO₃, optB88-vdW functional is also used in this paper. At the same time, in order to calculate the energy band structure and spectrum of the material more accurately, we also use HSE06 functional for calculation. OptB88-vdW functionals introduce nonlocal correlation terms, which can well describe systems in which vdW forces are dominant. We also used the hybrid functional method to calculate the band gaps of the two structures. In the HSE06 functional, a certain proportion of Hartree-Fock (HF) exchange was mixed, which proved to be able to study the electronic structure and optical properties of the material more accurately.

In this paper, two kinds of layered MoO₃ structures are studied. α -MoO₃ belongs to the orthogonal crystal system, the space group is pnma (62), the lattice constants $a=13.8221$, $b=3.6954$, $c=3.9522$, $\alpha=\beta=\gamma=90^\circ$ [3], and the plane wave truncation energy and k-point obtained by the convergence test are 650 eV and $3\times 10\times 9$, respectively. The convergence accuracy is up to 1 MeV/Atom. MoO₃-II belongs to monoclinic system, space group p21/m (11), lattice parameters $a=3.9451$, $b=3.6872$, $c=7.0954$, $\alpha=\gamma=90^\circ$, $\beta=103.745^\circ$ [11], cutoff energy 650 eV, K point is $13\times 14\times 7$.

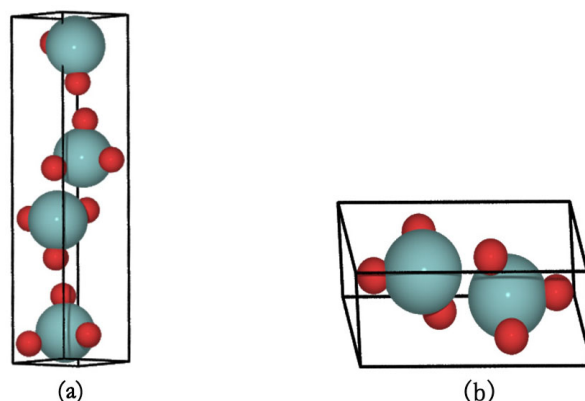


Figure 1. α -MoO₃ structural model (a) and MoO₃-II structural model (b)

Firstly, we use two different methods PBE and optB88 to optimize the structure. As shown in Table 1, we can see that PBE greatly overestimates layer spacing. For α -MoO₃ and MoO₃-II, the errors calculated by PBE are 16.36% and 13.58%, and after considering the vdW force through the optB88-vdW functional, the calculated results are in good agreement with the experimental results, and the errors are reduced to 0.75% and 1.10%, respectively. These results indicate that optB88-vdW can handle the interlayer vdW forces very well. Meanwhile, our calculation results are reasonable and reliable, which can be used for the subsequent calculation of electronic structure, optical properties and photocatalytic performance.

Table 1. Experimental parameters and optimized parameters of the block model

structure	lattice parameter	experiment value	PBE optimize	optB88 optimize	PBE error	optB88 error
α -MoO ₃	a(Å)	13.8221	16.0832	13.9256	16.36%	0.75%
	b(Å)	3.6950	3.7079	3.7377	0.35%	1.16%
	c(Å)	3.9522	3.9566	3.9420	0.11%	0.26%
	a(Å)	3.9541	3.9535	3.9391	0.02%	0.38%
MoO ₃ -II	b(Å)	3.6872	3.7089	3.7378	0.59%	1.37%
	c(Å)	7.0954	8.0590	7.1736	13.58%	1.10%
	$\beta(^{\circ})$	103.754	102.095	103.649	1.60%	0.10%

3. Results and Discussion

3.1. Electronic Structure

Based on the crystal structure optimized by optB88 method, the band structure of the block was calculated by using PBE and HSE06 functional respectively. Calculation selection of brillouin zone high symmetry photograph for $\Gamma \rightarrow X \rightarrow S \rightarrow R \rightarrow T \rightarrow Z \rightarrow \Gamma$, monoclinic phase for $\Gamma \rightarrow B \rightarrow A_0 \rightarrow E_0 \rightarrow C \rightarrow Z \rightarrow \Gamma$. Except for the difference in band gap size, the PBE and HSE06 calculation results in similar band structures. As can be seen from Figure 2(a), the bottom of the orthogonal conduction band is located at the origin Γ of the Brillouin region, and the top of the valence band is located at point R. The bottom of the conduction band and the top of the valence band are not located at the same K point in the Brillouin region. Similarly, according to Figure B, the base of conduction band of monoclinic phase is located at point B, and the top of valence band is located at point C. The monoclinic phase MoO₃-II also belongs to the indirect transition type energy band structure.

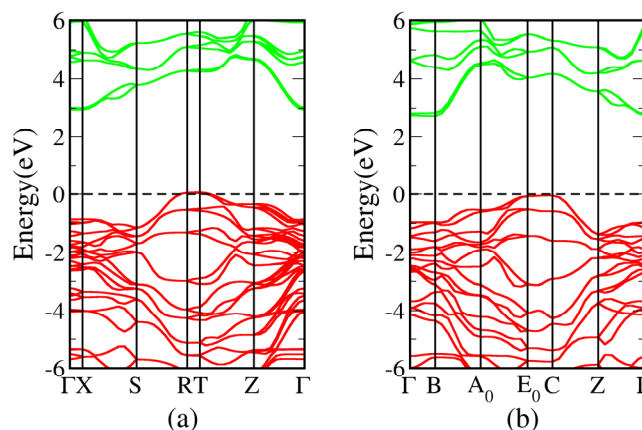


Figure 2. Energy band structures of α - MoO_3 (a) and MoO_3 -II (b) calculated by HSE06 functional

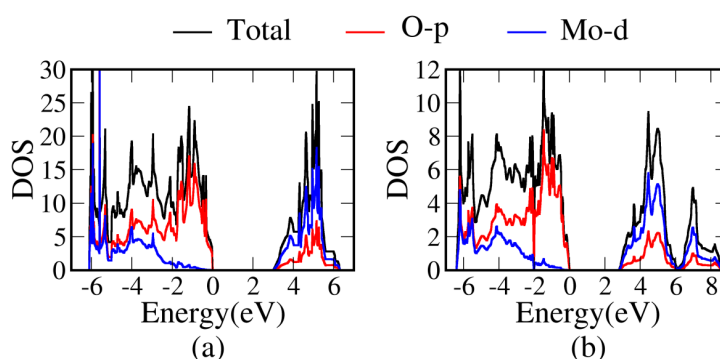


Figure 3. The densities of states of α - MoO_3 (a) and MoO_3 -II (b) calculated by HSE06 functional

According to the density of state diagram calculated by HSE06 method, it can be clearly known that the band gap width of α - MoO_3 block is 3.001 eV. The valence band of α - MoO_3 can be basically divided into two regions, namely the lower valence band from -6 eV to -4 eV, and the upper valence band from -4 eV to 0 eV. Obviously, the upper valence band region of α - MoO_3 is mainly formed by O 2p state. The lower valence band region is mainly contributed by Mo 4d state. The conduction band is mainly derived from the contribution of O 2p and Mo 4d states. According to the state density map of MoO_3 -II block, the band gap is 2.794 eV. Similarly, the above-ground valence band region is mainly formed by O 2p state, the lower valence band region is mainly contributed by Mo 4d state, and the conduction band is mainly contributed by Mo 4d state. The band gaps of the orthogonalized phase (α - MoO_3) and monoclinic phase (MoO_3 -II) calculated by PBE are 1.714 eV and 1.703 eV, respectively. In the experiment, the experimental band gap of the orthogonal phase is 3.2 eV [12], which is in excellent agreement with our HSE06 calculation, indicating that the current HSE06 calculation can perfectly describe the electronic structure and optical properties of layered MoO_3 .

3.2. Optical Properties

Whether a material can effectively absorb the visible light band of sunlight is also one of the key factors affecting whether it can be used as a photocatalyst. Based on this, HSE06 functional was also used to calculate the optical dielectric function of the block. From the imaginary part of the dielectric function, we can see that there are two obvious absorption peaks in the vicinity of 5.559 eV and 8.723 eV in the orthogonality phase, and there are two absorption peaks in the vicinity of 5.559 eV and 8.868 eV in the monoclinic phase, both of which belong to the ultraviolet light band, indicating that the two kinds of block materials can effectively absorb the ultraviolet band under the solar radiation.

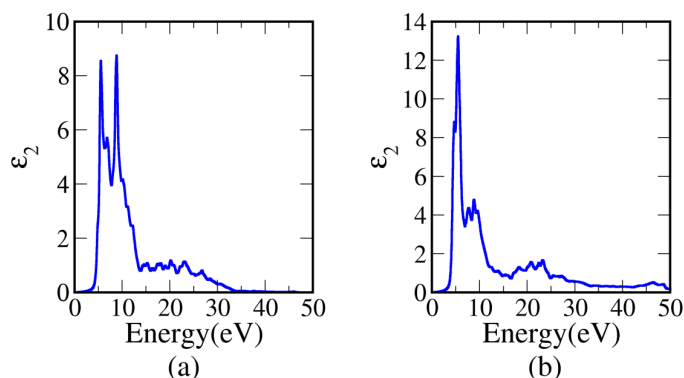


Figure 4. The imaginary part of the dielectric function of α -MoO₃ (a) and MoO₃-II (b) calculated by HSE06 functional

3.3. Photocatalytic Properties

The working principle of semiconductor photocatalysis technology is that the photon energy generated by illumination is used to excite the electrons in the semiconductor to generate the transition phenomenon, and the generated electrons and holes are separated to the solid-liquid interface and become unbound electrons and holes, and the redox reaction occurs with degradable materials [2]. Electrons excited by photons promote the reduction reaction to produce hydrogen: $2H^+ + e^- \rightarrow H_2$; The holes are involved in the oxidation reaction of water to produce O₂: $H_2O + 2h^+ \rightarrow 1/2O_2 + 2H^+$. Catalytic materials for photodegradation of water should meet at least the following four necessary conditions: (1) relatively low synthesis energy; (2) Appropriate band gap; (3) The band edge of the semiconductor material must contain the redox potential interval of water [-5.67eV, -4.44eV]; (4) Semiconductor materials are insoluble in water [13].

In order to further evaluate the photocatalytic performance of the two layered materials, the optimized block model was used to establish the surface structures of the two crystal systems along the Z-axis of the cell (Figure 5,6), and a 15Å vacuum layer was added to the surface structures. The orthogonal phase and monoclinic phase both contain 6 MoO₃-MoO₃ units for the calculation of the vacuum electrostatic potential of the surface. Combined with the previously obtained band gap E_g , we can calculate the absolute band edges of two different layered structures. The calculation formula is as follows [14]:

$$E_{CBM}^* = (E_{CBM} + E_{VBM})/2 - V_{vacuum} + 1/2E_g$$

$$E_{VBM}^* = (E_{CBM} + E_{VBM})/2 - V_{vacuum} - 1/2E_g$$

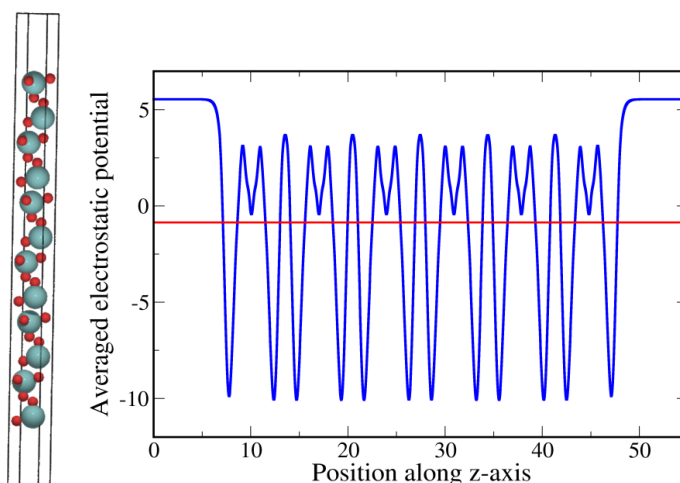


Figure 5. Layered structure and vacuum electrostatic potential of α -MoO₃

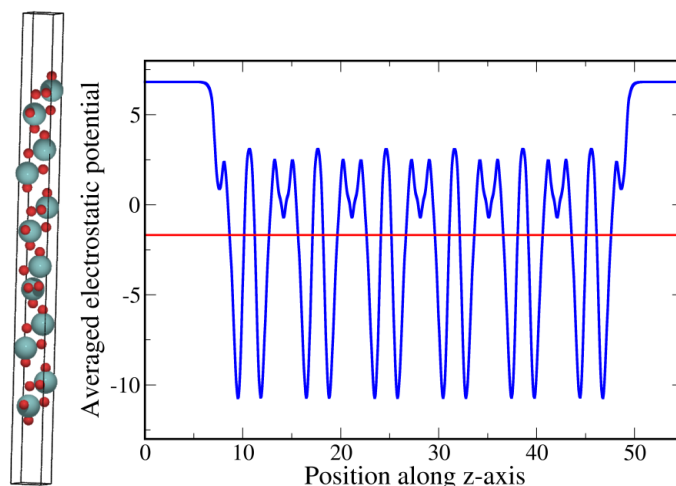


Figure 6. MoO₃-II layered structure and vacuum electrostatic potential diagram

Considering the hybrid functional calculation of surface structure, it requires a large amount of computation. In this paper, we only use PBE functional to calculate the electrostatic potential of the surface. Perdew and Levy [15] calculated that, although different functionals give different absolute band edges, the absolute band gap center is not sensitive to different functionals, and the band gap center obtained by different functionals is basically constant. Therefore, the absolute band gap center obtained by PBE calculation can be approximately the absolute band gap center of the material. It can be seen from the figure that the average electrostatic potential of vacuum on the surface of the orthogonalized and monoclinic phase blocks is $V_{\text{vacuum}}=5.54\text{eV}$ and 6.83 eV , respectively. Accordingly, we can also read the values of the top and bottom of the valence band from the static calculation of the layered structure. The orthogonalized phase: $E_{\text{VBM}}=-0.861\text{ eV}$, $E_{\text{CBM}}=0.592\text{eV}$. Monoclinic phase: $E_{\text{VBM}}=-1.680\text{ eV}$, $E_{\text{CBM}}=-0.045\text{ eV}$. Therefore, the absolute band gap center values of the two layered materials are -5.675eV (orthogonalized phase) and -7.692eV (monoclinic phase), respectively. Using the band gap obtained by HSE06, the absolute band edges of the materials can be obtained. It can be seen from the figure that the absolute band edge of $\alpha\text{-MoO}_3$ contains the potential needed for photocatalytic oxidation and reduction reactions $[-5.67, -4.44]$ [13], indicating that $\alpha\text{-MoO}_3$ is a potential photocatalytic water catalyst, while the absolute band edge calculated by monoclinical phase is not within the range of photocatalysis.

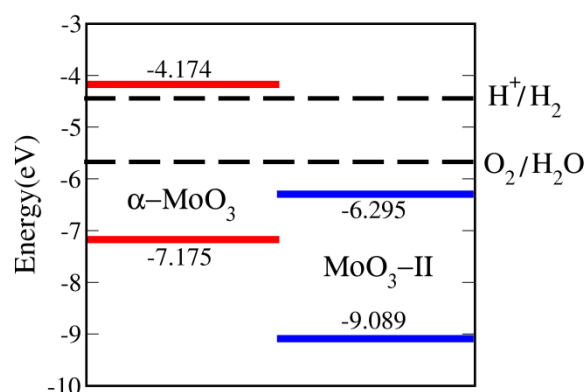


Figure 7. Comparison of absolute band edge positions of two layered compounds

4. Conclusion

Based on density functional theory, the structures, electronic structures, optical properties and photocatalytic properties of the orthogonal and monoclinic phases of MoO_3 have been calculated theoretically. Our results show that optB88-vdW functional can take the van der Waals forces between layers into account to optimize the block structure reasonably, and the HSE06 method can obtain the band gaps in accordance with the experimental results. In addition, we also calculated the dielectric functions and band-edges of the two structures by HSE06 method, and found that the layered $\alpha\text{-MoO}_3$ meets the necessary conditions for the photohydrolysis of water catalyst: the absolute band-edge energy containing the redox potential of water. Considering that MoO_3 is insoluble in water, the formation energy is low and easy to synthesize, and has a suitable band gap, we suggest that $\alpha\text{-MoO}_3$ is a potential photocatalytic agent for water degradation. In spite of this, its absorption peaks all fall in the ultraviolet band, and the absorption efficiency of visible light is not high. In the future, we will improve the photocatalytic efficiency of MoO_3 materials by some means such as doping and constructing van der Waals heterojunction [16].

References

- [1] Sivacarendran Balendhran. Devices and systems based on two dimensional MoO_3 and MoS_2 [D]. RMIT University. School of Electrical and Computer Engineering, 2013.
- [2] Chenggong Wang, Irfan Irfan et al. Role of molybdenum oxide for organic electronics: Surface analytic-al studies[J]. J. Vac. Sci. Technol. B. 2014, 32:040801.
- [3] D. Liu, W. W. Lei, J. Hao, D. D. Liu, B. B. Liu, X. Wang, X. H. Chen, Q. L. Cui, G. T. Zou, J. Liu, and S. Jiang. High-Raman scattering and x-ray diffraction of phase transitions MoO_3 [J]. J. Appl. Phys., 2009, 105(2), 023513.
- [4] Fengyu Li and Zhongfang Chen. Tuning electronic and magnetic properties of MoO_3 sheets by cutting, Hydrogenation, and external strain: a computational investigation [J]. Nanoscale, 2013, 5(12): 5321.
- [5] A. D. Sayede, T. Amriou, M. Pernisek, B. K. helifa, C. Mathieu. An ab initio LAPW study of the α and β phases of bulk molybdenum trioxide, MoO_3 [J]. Chem Phys, 2005, 316(1-3): 72-82.
- [6] Hong Ding, Keith G. Ray, Vidvuds Ozolins and Mark Asta. Structural and vibrational properties of $\alpha\text{-MoO}_3$ from van der Waals corrected density functional theory calculations[J]. Phys. Rev. B. 2012, 85:012104.
- [7] A. Chithambararaj, N. S. Sanjini, A. Chandra Bose and S. Velmathi. Flower-like hierarchical h- MoO_3 : New findings of efficient visible light driven nano photocatalyst for methylene blue degradation[J]. Cat. al. Sci. Technol. 2013, 3(5): 1405.
- [8] Liying Huang, Hui Xu et al. Synthesis and characterization of g-C $_3$ N $_4$ / MoO_3 photocatalyst with improved visible-light photoactivity[J]. Appl. Surf. Sci. 2013, 283: 25-32.
- [9] M. B. Sreedhara et al. Synthesis, Characterization, and Properties of Few-Layer MoO_3 [J]. Chemistry - An Asian Journal. 2013, 8(10): 2430-2435.
- [10] G. Kresse and J. Furthmüller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set[J]. Phys. Rev. B. 1996, 54(16): 11169.
- [11] E. M. McCarron III and J. C. Calabrese. The Growth and Single Crystal Structure of a High Pressure Phase of Molybdenum Trioxide $\text{MoO}_3\text{-II}$ [J]. Solid State Chemistry. 1991, 91(1): 121-125.
- [12] Ioannis Kostis, Nicolaos Vourdas et al. Effect of the Oxygen Sub-Stoichiometry and of Hydrogen Intermediate Bands within the Gap of Disordered Molybdenum Oxide Films[J]. J. Phys. Chem. C. 2013, 117: 18013-18020.
- [13] Arunima K. Singh, Kiran Mathew et al. Computational Screening of 2D Materials for Photocatalysis [J]. J. Phys. Chem. Lett. 2015, 6(6): 1087-1098.

- [14] Maytal Caspary Toroker et al. First principles scheme to evaluate band edge positions in potential transition metal oxide photocatalysts and photoelectrodes[J]. Phys. Chem. Phys. 2011, 113:16644-16654.
- [15] J.P. Perdew and M. Levy. Physical Content of the Exact Kohn-Sham Orbital Energies: Band Gaps and Derivative Discontinuities[J]. Phys. Rev. Lett. 1983, 51, 1884-1887.
- [16] A.K. Geim et al. Van der Waals heterostructures[J]. Nature. 2013, 499(7495):419-425.