

Two-dimensional metallic MoS₂: A DFT study



Xinyue Lin, Wentong Li, Yingying Dong, Chen Wang, Qi Chen, Hui Zhang*

Normal College, Shenyang University, Shenyang 110044, China

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ABSTRACT

The single-layer MoS₂ has drawn extensive attention due to its appealing properties for device applications. In this paper, a new porous MoS₂ (so-called as P-MoS₂) is theoretically explored. Compared with conventional H-MoS₂, P-MoS₂ has quite different crystal structure, and more importantly, it possess 27% larger specific surface area, making it superior candidates in energy industry and catalysts. Furthermore, P-MoS₂ becomes metallic from semiconducting H-MoS₂. Finally, P-MoS₂ transforms back to a semiconductor with tunable band gap by changing applied strains. Our studies enrich the family of MoS₂ nanostructures, and also extend the application range. More interestingly, it also provides a platform of exploring other porous TMDs with diverse electronic structures.

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1. Introduction

The absence of a pristine band gap of graphene [1,2] has stimulated exploration of many 2D nanomaterials, such as *h*-BN, C₃N₄, black phosphorus and transition metal dichalcogenides [3–8]. Furthermore, some nano-scale materials containing tetraoxa[8]circulene core units have been theoretically predicted [9–11]. Transition metal dichalcogenides (TMDs), which are layered materials similar to graphite, provide interesting candidates of electronic device [12]. Single-layer MoS₂, which is usually represented as H-MoS₂, attracted special interest. Upon thinning from the bulk, H-MoS₂ becomes a direct-gap semiconductor with gap of 1.8 eV [13]. A recent experiment further demonstrated that single-layer MoS₂ has high intrinsic electron mobility and high on/off ratios [14]. These superior optical and electronic properties make MoS₂ attractive for low power optoelectronic applications [15].

Many 2D materials can exhibit distinct electronic phenomena dominated by the different 2D structure units, which have been demonstrated by tremendous studies. For the case of MoS₂, single-layers of the 1T polytype of MoS₂ become metallic and show extraordinary hydrogen evolution reaction (HER) activity [16]. Consequently, undiscovered polytypes of MoS₂ may possess different electronic structure from known ones.

The 2D materials have extreme specific surface area, which is a major reason why they are expected as promising good catalysts. Recently many porous MoS₂ thin films have been prepared as high electrocatalysts and visible light photocatalysts for HER due to higher surface area by many experimental works [17–25]. Those

porous MoS₂ films preserve the crystal structure of H-MoS₂, and their higher surface area originates from their polycrystalline structures. Actually, people more expect to fabricate another kind of porous MoS₂ films, which can possess both higher surface area and distinct crystal structure from H-MoS₂. However, fabrication of this kind of porous MoS₂ films has seldom been declared. In theoretical side, porous allotropes of graphene and BN have also been proposed [26–31]. Gapless so-MoS₂ has been reported by theoretical works [32]. Thus, it is of great interest and also significance to explore more stable porous MoS₂ allotropes and possible fantastic characters.

In this paper, based on theoretical calculations, one special porous P-MoS₂ is proposed. The structure stability has been confirmed by phonon calculations. The specific surface area of P-MoS₂ is 27% enlarged compared with H-MoS₂, which enables the former potential candidates in many fields, such as hydrogen storage and catalysts. Furthermore, P-MoS₂ shows a metallic behavior, but a metal-semiconductor transition occurs when strains are applied. In addition, the band gaps can also be modulated by different strains. Our results predict a new stable MoS₂ nanocrystals that have considerable specific surface area and tunable electronic structure for possible applications in electronics and catalysts. Besides, considering the structure similarity, it can be expected that this classic structure will occur for other TMDs, such as MoSe₂ and WTe₂, which stimulates future investigations.

2. Methodology

The first-principles calculations were performed based on the density functional theory (DFT), as implemented in the Vienna Ab Initio Simulation Package (VASP) [33,34]. The generalized

* Corresponding author.

E-mail address: huizhangsy@outlook.com (H. Zhang).

gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional [35] was used to treat the electron exchange correlation interactions with Projector-augmented-wave (PAW) potentials [36]. To remove spurious interactions between neighboring structures due to periodic calculations, a vacuum layer of no less than 12 Å was taken in the perpendicular direction. The energy cutoff was set to 400 eV and the $9 \times 9 \times 1$ Monkhorst-Pack k -mesh were used to sample the Brillouin zone (BZ) [37].

The equilibrium geometries were fully optimized with both the 2D lattice vectors and atom coordinates. Force tolerance on each atom is less than 0.01 eV/Å. The real-space force constants were calculated from the Hellmann-Feynman forces by introducing displacements to supercells based on finite displacement method [38]. Then, the dynamical matrices and phonon frequencies were obtained via the force constants, as implemented in Phonopy package [39].

3. Results and discussion

3.1. Structure stability

The story begins with our previous work [30]. In that work, a periodic porous p-BN structure was designed based on a defective h-BN with one third of the atoms being occupied by vacancies via a dramatic reconstruction during structure optimization. The usual H-MoS₂ also forms a honeycomb hexagonal lattice like h-BN, but the effort on finding porous MoS₂ via the similar route failed. In usual H-MoS₂, one third of the Mo/S atoms were replaced by vacancies. Unfortunately, the above defective MoS₂ was destroyed by structure optimization. It is not surprising because H-MoS₂ is quite different from h-BN due to the three-layered structure containing one Mo layer sandwiched by two S layers.

To avoiding great atom reconstruction, fictional structure of porous MoS₂ was artificially constructed based on the previous p-BN, where B atoms are replaced by Mo atoms, and N atoms are replaced by sandwiching S atoms. The perpendicular distance of two S layers and Mo–S bond length are set the same as in perfect H-MoS₂ by changing the lattice constants. Interestingly, the fictional structure finally brings us an unfamiliar single-layer MoS₂ after fully structure optimization.

Similar as H-MoS₂, the new structure of P-MoS₂ also contains sandwiched three layers, as shown in Fig. 1(a) and (b). H-MoS₂ forms honeycomb periodic hexagons. Interestingly, present MoS₂ is constructed by alternatively repeated quadrangles and hexagons, as shown in Fig. 1(a). In other words, present MoS₂ contains porous dodecagons, and that's why it is named as P-MoS₂.

P-MoS₂ belongs to P6/M (175) point group symmetry with the lattice constant of 8.77 Å. Mo atoms lie in the Wyckoff site 6(k) at (0.87053, 0.53168, 0.50000) and S atoms lie in the 12(l) sites at (0.43693, 0.11889, $0.5 \pm z$), where the value of z is about 0.104 when lattice vector c with vacuum layer is set as 15 Å. The covalent bonds in P-MoS₂ preserve the character of H-MoS₂. For example, the distance of two S layers perpendicular to MoS₂ plane is about 1.56 Å, and the average length of Mo–S bonds in P-MoS₂ is about 2.41 Å.

For one primitive cell, the H-MoS₂ contains one MoS₂ unit, while the P-MoS₂ has six ones. Besides, the lattice constant of H-MoS₂ and P-MoS₂ are 3.18 Å and 8.77 Å, respectively. Thus, it is easy to derive that the present P-MoS₂ possesses a 27% higher specific surface area than conventional H-MoS₂. Such a large specific surface area makes P-MoS₂ promising candidates of hydrogen storage and catalysts.

Although the crystal structure has been fully optimized, the structure stability of P-MoS₂ could not be decided yet. The formation energy, E_f , is a good criterion to evaluate the phase stability in many conditions. Herein, the formation energy of MoS₂ is calculated by $E_f = E_{\text{bulk}}(\text{Mo}) + 2E_{\text{bulk}}(\text{S}) - E(\text{MoS}_2)$, where $E_{\text{bulk}}(\text{Mo})$, $E_{\text{bulk}}(\text{S})$ and $E(\text{MoS}_2)$ represent the total energy per formula of equilibrium bulk Mo, bulk S, and MoS₂, respectively. The present formation energy of H-MoS₂ is 2.59 eV, which agrees well with the value of 2.49 eV with local density approximation (LDA) [40]. The formation energy of P-MoS₂ is 1.69 eV, which is 0.9 eV lower than that of H-MoS₂ [40]. The lower formation energy of P-MoS₂ suggest that it is less stable than pristine H-MoS₂. It is reasonable because P-MoS₂ originates from a defective H-MoS₂. However, the formation energy of P-MoS₂ is comparable with that of WSe₂ (1.86 eV) by LDA [40], which has been prepared by experiments [41,42]. The moderate formation indicates that P-MoS₂ may be fabricated, but its stability need to be further confirmed.

Besides formation energy, the phonon dispersion spectrum analysis usually provides a reliable tool to confirm structure stability. A structure can be considered as stable, when phonon frequencies on the k -points all over the Brillouin zone are positive [43,44]. Actually, lattice dynamics is a basic property of solids. For example, phonon instability and phonon-limited mobility have been reported in MoS₂ [45,46].

Herein, we performed accurate phonon calculations to check the structure stabilities of designed P-MoS₂. In this paper, 2×2 supercells are employed and the first BZ is sampled by 4×4 k -meshes when making phonon calculations. The full phonon dispersion spectra is shown in Fig. 2. Clearly, no imaginary vibration frequency

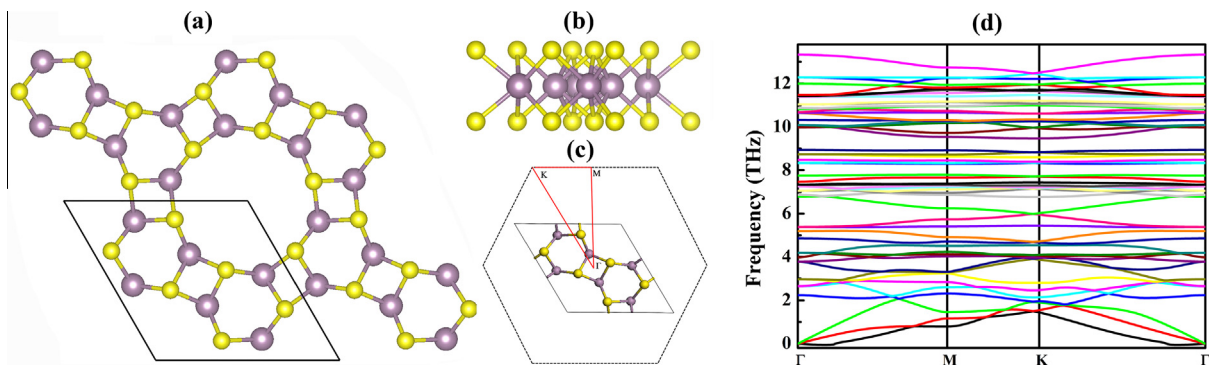


Fig. 1. The (a) top and (b) side view, (c) first Brillouin zone, and phonon spectrum of P-MoS₂. The purple and yellow balls represent Mo and S atoms, respectively. The figure (a) shows a 4×4 supercell, where primitive cell is depicted by black lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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