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Electronic and optical properties of O-doped monolayer MoS_2 ☆

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ABSTRACT

The O-doping effects for monolayer molybdenum disulfide (MoS_2) are systematically investigated by first-principle calculations. It is shown that the geometrical, electronic and optical properties are affected distinctively by the oxygen dopant. Structural analysis reveals a local contraction along c axis in the substituted cases. The substitution of oxygen for a sulfur atom in monolayer MoS_2 leads to a transition from a direct K–K band gap to an indirect Γ–K band gap. And, the value of band gap decreases with increasing doping concentration. In addition, for the pure MoS_2, strong covalent chemical bonds are formed on the Mo–S bonds, which is ascribed to the strong hybridization between Mo-4d and S-3p orbitals. After oxygen doping, the covalent bonding of Mo–S is distinctively weakened. More electrons are transferred from Mo to O because of the larger electronegativity of O, and the atomic populations of O atoms become larger than that of S atoms. Optical properties are also found to be affected distinctively by the oxygen dopant. An interesting blue-shift of the absorption threshold is observed in the O-doped systems.

1. Introduction

Since the breakthrough in the fabrication of monolayered graphene from bulk graphite, it has triggered an extensive investigation because of its exceptional physical and chemical properties [1–5]. Much of the enthusiasm which surrounds graphene can be attributed to its two dimensional (2D) nature. 2D geometry is compatible with the established manufacturing techniques used in the semiconductor industry. However, the pristine graphene does not possess a nonzero band gap in its electronic structure, which is deemed as a considerable drawback for realizing application in electronic and optical devices. Even though the band gap of graphene can be opened up by applying the electronic field [6] or fabricating nanostructures [7], the possibilities for engineering the desired structure of energy levels in graphene-based materials are limited. The intrinsic limitations of graphene prompt researchers to investigate alternate materials that are similar to graphene and distinct in their electronic properties. In this regard, transition metal dichalcogenides (TMDs) have attracted huge interest in recent years due to their novel physical phenomena in reduced dimension and the spatially confined electronic and optical properties [8,9]. Among them, monolayer molybdenum disulfide (MoS_2), as a kind of prototypical 2D TMDs, has emerged as a semiconducting alternative to gapless graphene owing to its intrinsic direct band gap. Monolayer MoS_2 contains hexagonal planes of Mo atoms lying between two hexagonal planes of S atoms, forming a sheet of S–Mo–S. Each Mo atom interacts with six neighboring S atoms through covalent bonds. A rather large band gap makes monolayer MoS_2 favorable for nanoelectronic applications [10], field-effect transistors [11], and photovoltaic cells [12]. In addition, due to the strong spin–orbit interaction and broken inversion symmetry, monolayer MoS_2 also exhibits novel valley and spin physics [13–17]. Consequently, monolayer MoS_2 becomes a promising material for spintronic and nanoelectronic devices.

These applications of monolayer MoS_2 have triggered research that aims at understanding as well as modifying the physical and chemical properties under diverse conditions and requirements. To achieve this goal, defects and strain are expected to modify the electronic and magnetic properties of single-layer MoS_2 [18–23]. For example, Yue et al. [24] investigated the nonmetal and transition-metal atoms doped monolayer MoS_2 by first-principle calculations and found that all dopants are strongly bound, inducing interesting magnetic behaviors. Via density functional theory computations, Hu et al. [25] also calculated the electronic structure and magnetic properties of nonmetallic elements (B, C, N, O, F, Cl, Br, and I) doped monolayer MoS_2. The main conclusion of this investigation is that all the doped systems, expect for C- and O-doped cases, exhibit half-metallic characters with a total magnetic moment $\sim 1.0\ \mu_B$. In addition, using first-principle calculations, Lin et al. [26] evidenced that the Mn, Fe, and Co

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dopants substituting for a Mo atom in monolayer MoS_2 are all magnetic in their neutral and charge states. The electronic structure and optical properties of Mn and B, C, N co-doped monolayer MoS_2 have been studied by Xu et al. [27]. They suggested that the band gaps of the co-doped systems are smaller than those of the corresponding pristine forms and the optical absorption edges exhibit redshift phenomena.

Although simulations of the electronic, magnetic and optical properties of monolayer MoS_2 containing various dopants have been carried out [24–29], to the best of our knowledge, comprehensive and systematical understanding of the 2D MoS_2 substitutionally doped with oxygen atom is still lack. In this paper, by means of first-principle calculations, we would like to perform a systematically study on the geometrical, electronic and optical properties of O-doped monolayer MoS_2. In order to make it clear how doping O atom affects the properties of 2D MoS_2, we will perform geometrical and electronic structure analysis. Then, the optical properties affected by doping O atom will be discussed.

2. Method of calculation

Geometry relaxation, electronic structure and optical properties will be investigated by using the plane-wave-based density functional theory (DFT), as implemented in the CASTEP program [30]. Electron–electron exchange correlations are treated by the generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) function [31]. Ultrasoft pseudo-potentials [32], known for their high efficiency in calculating the structural and electronic properties, are used for the electron–ion interactions. To ensure the convergence of the calculation, the cutoff energy is set to be 400 eV, which corresponds to a criterion of convergence of 1.0×10^{-6} eV/atom. The geometric structures are shown in Fig. 1. Doping effects are considered by varying the supercell size. We deal with 48-, 27-, 12-atom supercells doped by a single oxygen dopant to simulate three cases with O-doping concentrations 2.08%, 3.70%, and 8.33% (see Fig. 1(b), (c), and (d)), respectively. Pure monolayer MoS_2 as shown in Fig. 1(a) is also calculated for comparison. A vacuum space of 20 Å between adjacent single layers is adopted to prevent interlayer interactions. Previously, it was already reported that no noticeable van der Waals (vdW) interlayer interaction is present in monolayer MoS_2 [33]. It means that the vdW interactions does not play an important role in monolayer MoS_2. Therefore, the vdW correction is not included in the following calculations. The Monkhorst–Pack [34] k-point sampling is set as $15 \times 15 \times 1$, $5 \times 5 \times 1$, $7 \times 7 \times 1$, and $9 \times 9 \times 1$ for structures shown in Fig. 1(a)–(d), respectively. Structural optimization is continued until the magnitude of force on each atoms converges to less than 0.02 eV/Å and the total energy to less than 1.0×10^{-5} eV. All the electronic structures and optical properties are calculated based on the corresponding optimized crystal geometries.

Optical properties can be described by the frequency-dependent dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, which is mainly contributed from the electronic structures. The imaginary part of the dielectric constant $\varepsilon_2(\omega)$ is calculated by the momentum matrix elements between the occupied and unoccupied electronic states, and is defined as [35]

$$\varepsilon_2 = \frac{2\pi e^2}{\Omega\varepsilon_0}\sum_{k,v,c}|\langle\psi_k^c|\hat{u}\cdot r|\psi_k^v\rangle|^2\delta[E_k^c - E_k^v - \hbar\omega], \tag{1}$$

where Ω is the volume of the elementary cell, and ω is the light frequency. ψ_k^c and ψ_k^v are the conduction band and valence band wave functions at k point, respectively. $\hat{u}$ is the vector defining the polarization of the electric field of the incident light, which is averaged over all spatial directions in the polycrystalline case. The real part $\varepsilon_1(\omega)$ can be evaluated by $\varepsilon_2(\omega)$ using the Kramer–Kronig relations [36]

$$\varepsilon_1(\omega) = 1 + \left(\frac{2}{\pi}\right)\int_0^\infty d\omega'\frac{(\omega')^2\varepsilon_2(\omega)}{(\omega')^2 - \omega^2}. \tag{2}$$

Then the expression for absorption coefficient $\alpha_{(}\omega)$ can be gained by $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ [35]

$$\alpha_{(\omega)} = \sqrt{2}\omega[\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega)]^{1/2}. \tag{3}$$

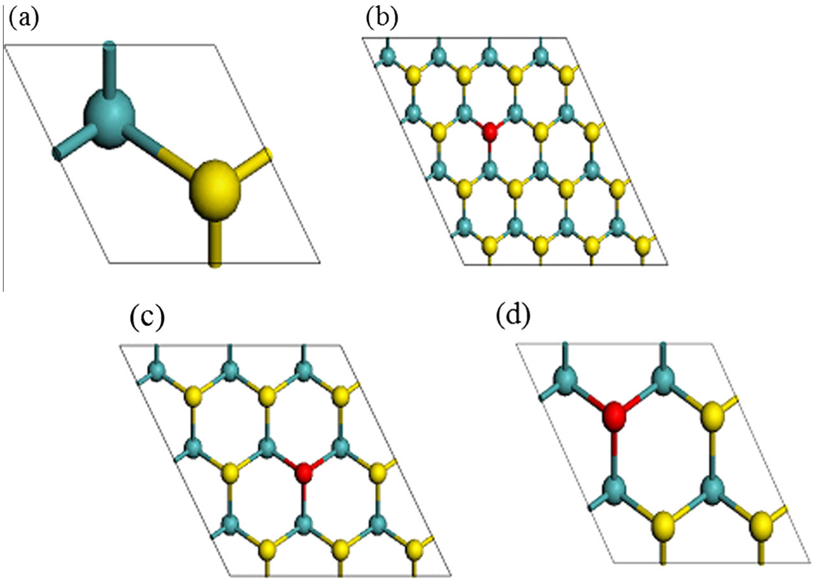

Fig. 1. Geometric structures of monolayer MoS_2 with O-doping concentration: (a) 0.00%; (b) 2.08%; (c) 3.70%; (d) 8.33%. The light blue, yellow, and red balls are Mo, S, and O atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)