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Effects of natural and thermal oxidation on electronic and optical properties of monolayer WS_2: a theoretical study

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Abstract

Tungsten disulfide (WS_2) has recently attracted considerable attention owing to its excellent physical, chemical, electronic, and optical properties, leading to increased research into its applications in electronic and optoelectronic devices. However, the oxidation of 2D material affects significantly its optical and electronic properties during storage or processing. This study employs density functional theory (DFT) to analyze the effects of natural and thermal oxidation on the optical and electronic properties of WS_2 monolayer. First, the climbing-image nudged elastic band (cNEB) method is applied to analyze transitional states and the potential barriers of WS_2 oxidation. It reveals that primarily involves the bonding of oxygen atoms with sulfur atoms, whereas thermal oxidation introduces both oxygen substitutions and generates oxygen vacancies. Second, the electron band structures after natural and thermal oxidation are comparably analyzed, which reveals that natural and thermal oxidation both can narrow the bandgap. Lastly, we investigate the optical properties of WS_2 monolayer under different oxidation conditions. The results demonstrate that natural oxidation results in weakened light absorption and a blue shift relative to the pristine WS_2, whereas thermal oxidation enhances absorption and induces a red shift. These findings underscore the importance of carefully managing oxidation conditions to effectively modulate the optoelectronic properties of WS_2.

1. Introduction

Two-dimensional transition metal dichalcogenides (TMDCs) are extensively utilized in various applications such as electrocatalysis, photovoltaics, photocatalysis, optoelectronics, and due to their exceptional electronic, mechanical, and optical attributes. [1, 2]. However, the stability of TMDCs in atmospheric conditions poses challenges for practical applications. The oxidation during storage and processing can affect its photoelectric properties, including light absorptance, dielectric function, electronic structure, etc[3]. WS_2 stands out among TMDCs materials for its superior properties, including high carrier mobility, significant spin-orbit coupling, and enhanced photoluminescence, making it a material of interest for advanced technological applications[4-6].

Despite its promising properties, the WS_2 monolayer has been observed to degrade over time even at room temperature. For instance, after just one month exposed to ambient air, the current of the WS_2-based transistor declined by nearly two orders of magnitude[7]. Pető *et al.*[8] found that oxidation can affect the catalytic activity of MoS_2 and WS_2. Kang *et al.*[9] revealed that oxidation can induce different doping effects on the WS_2 and further influence the electronic transport properties of the devices. Additionally, Lu *et al.*[10] emphasized the significance of understanding size-dependent surface oxidation for the nonlinear optical properties of WS_2, advocating that controlled oxidation could enhance the efficiency of WS_2 in electronic and optical applications. However, a comprehensive theoretical analysis regarding the impact of various oxidation levels on the electronic and optical properties of WS_2 remains lacking.

This study utilizes first-principles calculations to systematically investigate the optical and electronic properties of monolayer WS_2 across different oxidation states. It is found that oxygen atoms will replace sulfur atoms on the surface under natural oxidation, so the optical electronic properties change with the increase of replacement sites. In the thermal oxidation reaction, the surface vacancy appears, and the optical electronic properties change into this. The results of density functional theory (DFT) show that the controlled oxidation method can effectively control the optical and electronic properties of WS_2, thereby offering valuable insights for the strategic design of electronic and optical devices incorporating WS_2.

2. Computational methods

All first-principles calculations of structural relaxation, electronic and optical properties of pristine and oxidized WS_2 are carried out using DFT as implemented in the plane-wave code CASTEP (see Figure 1). The exchange and correlation energies in our calculations are implemented using generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) functionals. Double numerical atomic orbital plus polarization (DNP) is selected as the base set, and the global orbital cut-off is set at 5.0 A. A 12×12×1 k-points mesh is used for geometric optimization and accurate calculation of electronic properties. The maximum energy force and convergence tolerance settings are 0.002 Ha A^{-1} and 1.0×10^{-5} Ha, respectively. In terms of optical properties, the plane wave energy cut-off value is set to 450 eV. Considering the limited computing resources, the 12×12×1 k-points mesh Monkhorst-Pack grid is adopted.

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The absorption energy E_{ads} of an oxygen molecule on a sulfur vacancy of the WS_2 monolayer is defined as follows:

$$E_{\mathrm{ads}} = E_{\mathrm{SV}} + E_{\mathrm{O2}} - E_{\mathrm{SV+O2}} \tag{1}$$

where $E_{\mathrm{SV+O2}}$ is the energy of the WS_2 adsorb O_2 molecule and E_{O2} is the energy of an isolated O_2 molecule in the gas phase.

In addition, we calculated the imaginary part of the dielectric function (ε_2) of monolayer WS_2 under different oxidation conditions, which relates to its optical properties and is defined as follows,

$$\varepsilon_2(\omega) = \frac{8\pi^2 e^2}{L\cdot A\cdot m^2\omega^2}\sum_{c,\mathrm{v}}\sum_{K}|\langle \mathrm{v},\mathrm{K}|p_\alpha|c,K\rangle|^2\delta(E_c(K) - E_{\mathrm{v}}(K) - \hbar\omega) \tag{2}$$

where c and v represent the conduction and valance states associated with the energies $E_c(K)$ and $E_v(K)$, delta function δ ensures the conversation of energy, A is the sheet area, L is the vertical height between the sheets in the periodic supercell, <> is the momentum transition matrix, e is the charge of electron, m and $\hbar$ are the effective mass and Planck constantly, respectively. The absorption coefficient α can be calculated as:

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

3. Results and Discussion

3.1 Oxygen adsorption and dissociation

First, the perfect WS_2 monolayer is fully relaxed along with the lattice constants. The calculated 2D lattice constant is 3.242 Å for the WS_2 monolayer, in agreement with the reported values of ref.[11]. To understand the oxygen absorption on the top of perfect and defected WS_2 monolayers, we calculate different adsorption configurations. The most stable adsorption configurations are shown in Figure1. The E_{ads} of perfect and defected WS_2 monolayers are 40.8 meV and 2.746 eV, respectively. After optimization, no chemical bond was ever formed between O_2 and the perfect WS_2 layer, with the nearest distance between O atom and S atom of about 2.959 Å. Such weak vdW interactions clearly indicate that a perfect WS_2 monolayer cannot be oxidized owing to the chemically inert surface with saturated sulfur ions.

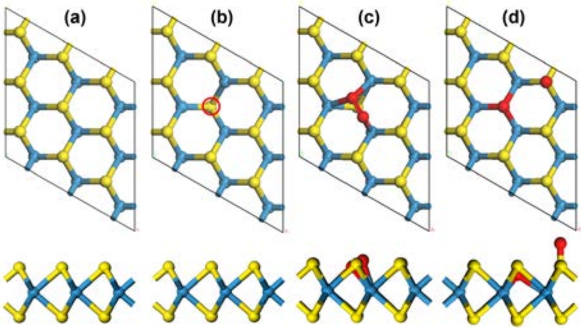

Figure 1: Top views (upper) and side views (lower) of the atomic configurations of (a) perfect WS_2 monolayer, (b) WS_2 monolayer with one SV; (c) WS_2 monolayer with O_2 adsorption on SV; (c) oxidized WS_2 monolayer after O_2 dissociation. The red circle in (a) represents SV.

For WS_2 monolayer with sulfur vacancies (SVs), the adsorbed O_2 molecules form covalent bonds at the vacancy sites with three surrounding W atoms. The O-W bond length of the oxidized WS_2 monolayer is 1.496 Å, which is a typical bond length for transition metal oxide covalent bonds. After the adsorption of the O_2 molecule on the WS_2, the O-O bond length is elongated by 0.24 Å. The weakening of O-O bond is caused by the formation of O-W bond, which will affect the electronic and optical properties of WS_2 to a certain extent. The E_{ads} of WS_2 is 2.746 eV, and the positive value indicates that the oxidation of defected WS_2 monolayer is an exothermic process. It corresponds to the weakest interaction between oxygen and the vacancies. According to the ref. [8], when WS_2 is oxidized, an O_2 molecule bonds with unsaturated W atoms at the vacancy sit and obtains electrons from W atom. As the electronegativity of S atoms decreases, more electrons are transferred from W to O, thus forming stronger W-O bonds.

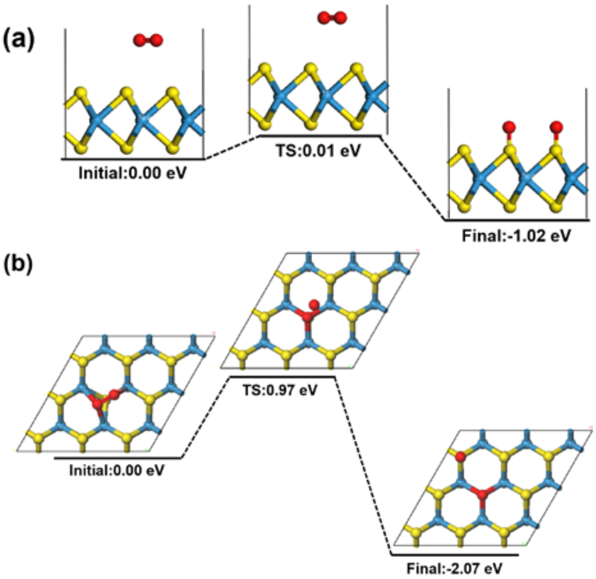

Figure 2: Dissociation process of O_2 on (a) perfect and (b)sulfur SV of an WS_2 monolayer.

By studying the thermodynamic stability of perfect and defected WS_2 monolayers during oxygen adsorption, we further clarified the oxidation mechanism and identified the kinetic barriers associated with the dissociative adsorption process of O_2 molecule through the climbing-image nudged elastic band (cNEB) method. The initial and final configurations vary with the barrier energy, as shown in Figure 2. The kinetic barrier is approximately 1.57 eV, which is relatively high, indicating that the WS_2 surface maintains chemical stability under low temperatures in the atmosphere. However, when SVs are present on the surface, the kinetic barrier for oxygen adsorption and subsequent dissociation is halved (approximately 0.97 eV), suggesting that SVs can be easily passivated by O_2 molecule. Also, an oxygen atom at the vacancy position replaces the original missing sulfur, while the other one at the top of the adjacent sulfur atom bonds with a sulfur atom perpendicular to the monolayer sheet. This observation illustrates the ease with which oxygen can saturate sulfur-deficient WS_2 surfaces upon exposure to atmospheric conditions.

The dissociation of an O_2 molecule at a sulfur vacancy is found to be an exothermic reaction with a reaction energy of 2.70 eV. After the dissociated O_2 molecule adsorbs on the defected WS_2 monolayer, one O atom remains at the original vacancy position to saturate the dangling bonds, while the other O atom may stay or move to nearby regions of the WS_2 monolayer. Overall, the perfect WS_2 monolayer is difficult to oxidize in air, while oxidation occurs easier for the defected WS_2. Since the oxidation process is exothermic, heating can provide an external driving force for the oxidation, resulting in several SVs on the WS_2 monolayer. Experimental evidence from Ref. [8] suggested that natural oxidation makes oxygen atoms replace part of sulfur atoms, while the thermal oxidation process not only creates oxygen substitution but also produces oxygen vacancies. Accordingly, we analyze the oxidation effects on the electronic and optical properties of the WS_2 monolayer.

3.2 Oxidation effect on electronic band structures

We first investigate the impact of oxygen substitution (OS) and adsorption (O_{ads}) complex processes on the electronic structure of WS_2 monolayers. Figure 3a depicts the atomic structure of WS_2 with substituted O atoms and adsorbed O atoms. At low oxygen concentrations, these defects minimally affect the electronic properties as evidenced by the density of states (DOS) shown in Figure 3b. When the concentration of these substituted and adsorbed species is high, the evolution of SOx compounds on the surface can cause damage to WS_2 due to surface reactions. The oxygen atoms adsorbed on the sulfur sites do not exhibit a noticeable interaction with the oxygen atoms used to passivate S vacancies; only minor changes in the DOS can be observed, leading to the superposition of the DOS.

Next, we discuss the electronic properties of WS_2 monolayers including pristine sheets, naturally oxidized WS_2 with oxygen-substitution, and thermally oxidized WS_2 with SV, and analyze models of oxidation at different levels. As shown in Figure 4a, the perfect WS_2 monolayer is an indirect-gap semiconductor with a bandgap of 1.976 eV, which aligns well with the theoretical values from previous studies[12]. As depicted in Figures 4b-e, oxidation leads to narrowing of the WS_2 bandgap. At lower concentrations, OS does not significantly alter the electronic properties. These results suggest that defect sites on the surface exhibit higher reactivity. Vacancy sites are responsible for the catalytic activity and chemical adsorption of oxygen on WS_2 because W sites are partially or fully exposed to the atmosphere due to sulfur vacancies, depending on the defect concentration. The greater the number of substitution sites, the more substantial the change in the bandgap. The thermal oxidation induced SVs resulting in the significant bandgap change. For defected WS_2 monolayers, SVs introduce impurity states within the bandgap. The SVs interfere with the top of the valence band, transforming the defected WS_2 monolayer into a deep p-type doped semiconductor. Notably, the SV-induced impurity states in the gap are completely removed under the adsorption of an oxygen molecule, due to the saturation effect caused by the formation of a W-O bond at the vacancy site.

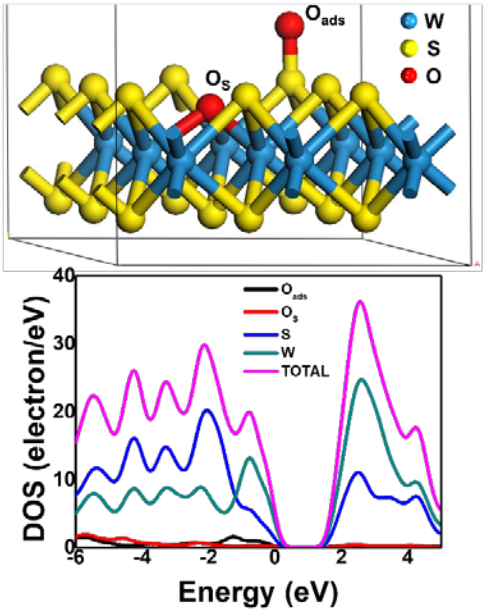

Figure 3: (a) Atomic positions of substitutional and adsorbed O atoms on WS_2 monolayer as indicated by arrows, and (b) local DOS of selected atoms (O_S, O_{ads}, bulk S and bulk W atoms).

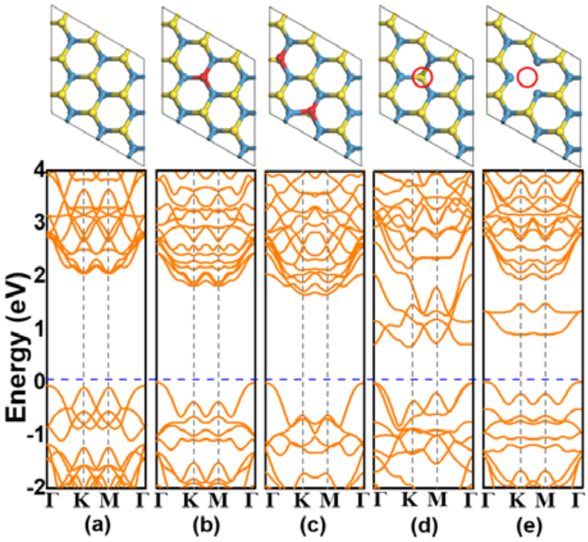

Figure 4: Band structures of (a) perfect WS_2, (b) one and (c) two S atom substitutes S of WS_2 monolayer, WS_2 monolayer with (d) one and (e) two SVs.

3.3 Oxidation effect on optical properties

Since the dielectric function and absorption coefficient play a crucial role in characterizing 2D materials and their optical applications, we discussed the optical properties of WS_2 monolayers, including pristine sheets, naturally and thermally oxidized WS_2. calculated imaginary part (ε_2) of the dielectric function and adsorption coefficient (α) of the WS_2 monolayer are similar to the calculated result of Wei *et al.*,[13], indicating that our calculations are reasonable.

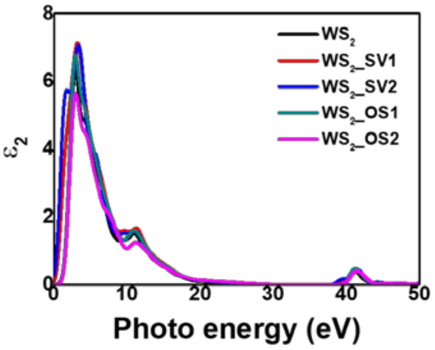

Figure 5: Imaginary part of the dielectric function (ε_2) of perfect WS_2, one and two S atom substitutes S of WS_2 monolayer, WS_2 monolayer with one and two SVs.

As shown in Figure 5, the $\varepsilon_2(\omega)$ spectrum of the WS_2 monolayer is nearly zero below 1.2 eV due to the prohibition of transitions between the valence band maximum (VBM) and the conduction band minimum (CBM). The first peak is located around 2.9 eV and extends to 1.5 eV, suggesting that WS_2 can absorb visible light. Moreover, there are two prominent peaks beyond the ultraviolet range at >3 eV. Upon exposure to natural oxidation, oxygen substitution causes the ε_2 to shift towards the ultraviolet region, and the $\varepsilon_2(\omega)$ spectrum below 1.2 eV remains close to zero. However, after thermal oxidation that creates oxygen vacancies, the spectrum shifts towards the infrared, and the transition between the valence and conduction bands becomes active. Following oxidation, the main peaks of all materials are near 2.9 eV, confirming their ability to absorb visible light. Nevertheless, after oxidation, the main peaks all exhibit a blue shift, with the shift due to oxygen vacancies being greater than that from oxygen substitution. Additionally, Additionally, when oxygen vacancies are pronounced, a secondary peak appears at 1.55 eV. Moreover, the ε_2 values of oxidized models are higher than that of WS_2 monolayer, showing remarkably enhanced absorption of photons.

Importantly, oxidized WS_2 exhibits a broad photoresponse spectrum ranging from visible to deep ultraviolet light. It is evident that natural oxidation leads to weakened light absorption and a blue shift relative to the pristine WS_2, whereas thermal oxidation boosts light absorption and induces a red shift. Consequently, meticulous control over the oxidation environment can effectively modulate the optoelectronic properties, offering substantial potential for applications in optical communication and photoelectric technologies.

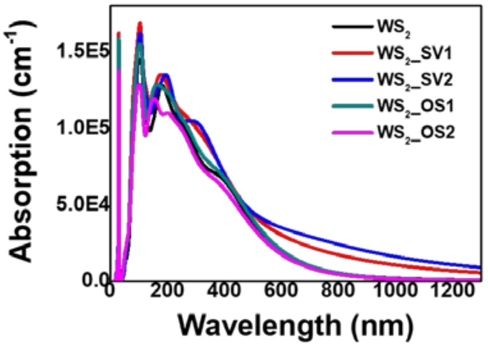

Figure 6: The adsorption coefficient of perfect WS_2, one and two S atom substitutes S of WS_2 monolayer, WS_2 monolayer with one and two SVs.

4. Conclusions

This study employs DFT to explore the effects of natural and thermal oxidation on the optical and electronic properties of WS_2 monolayer. Using the cNEB method, the study analyzes the transition states and potential barriers involved in the oxidation process. It reveals that the WS_2 monolayer with SVs possesses significantly lower kinetic barrier, indicating that the oxidation process is both thermodynamically and kinetically favorable, leading to structural and electronic passivation of the WS2 surface. Band structure analysis indicates that both natural and thermal oxidizations both contribute to narrowing the bandgap of the WS_2 with thermal oxidation inducing SVs and causing a substantial change in the bandgap. Furthermore, the optical properties of pristine and oxidized WS_2 monolayer under various oxidation conditions are compared. It shows that natural oxidation results in weaker light absorption and a blue shift in the absorption spectrum relative to the unoxidized WS_2. Conversely, thermal oxidation enhances light absorption and causes a red shift. In conclusion, controlling the oxidation conditions can effectively fine-tune the electronic and optical properties of the WS_2 monolayer. This finding is particularly significant for enhancing the performance of WS_2-based devices and for customizing their attributes for sensor applications.

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