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# Strain engineering and photocatalytic application of single-layer ReS<sub>2</sub>

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## ABSTRACT

We present a theoretical study on the electronic, dynamical, and photocatalytic properties of single-layer ReS<sub>2</sub> under uniaxial and shear strains. The single-layer ReS<sub>2</sub> shows strong anisotropic responses to straining. It remains dynamically stable for a wide range of *x*-axial strain, but becomes unstable for 2% *y*-axial compressive strain. The single-layer ReS<sub>2</sub> is calculated to be an indirect bandgap semiconductor, and there is an indirect–direct bandgap transition under 1–5% *x*-axial tensile straining. The single-layer ReS<sub>2</sub> is predicted incapable of catalyzing the water oxidation reaction. However, 1–5% *y*-axial tensile strain can enable the single-layer ReS<sub>2</sub> for overall photocatalytic water splitting. Besides, the single-layer ReS<sub>2</sub> can also catalyze the overall water splitting and be most efficient under acidic water solutions with pH = 3.8.

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## Introduction

Hydrogen, sourced from photocatalytic water splitting, is one of the most promising methods to provide energy for the sustainable development of our economy and society. Qualified photocatalysts have the bandgap over 1.23 eV. The conduction band minimum (CBM) should be more negative than the H<sup>+</sup>/H<sub>2</sub> water reduction potential, while the valence band maximum (VBM) should be more positive than the OH<sup>-</sup>/O<sub>2</sub> water oxidation potential [1].

Nanostructured materials have shown their advantages in photocatalytic applications [2–4]. Bandgap can be opened up due to the quantum confinement effect in nano-sized materials, and the increased surface-to-volume ratio provides more chemical-active sites [2,5]. These can effectively

improve the photocatalytic efficiency. Besides, nanostructured materials coupled with traditional or other nanostructured materials, can further enhance the catalytic properties via the mechanisms of Z-scheme, plasmonic resonance effect and so on [6,7]. Among the nanostructured materials, two-dimensional (2D) materials is more efficient because of the best surface-to-volume ratio and abundant chemical-active sites [5].

The single-layer MX<sub>2</sub> (M = Mo, W, Nb; X = S, Se, Te) is a series of typical 2D materials that have promising applications in photocatalytic water splitting. The bulk MX<sub>2</sub> is usually indirect bandgap semiconductor [8]. There is an indirect–direct bandgap transition and improved light absorption when thinning the bulk MX<sub>2</sub> into single layers [9,10]. Some of the single layers are semiconductors with the bandgap between 1.1 eV and 2.1 eV [8]. MoS<sub>2</sub>, MoSe<sub>2</sub>, and WS<sub>2</sub> have been shown

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to produce high yields of H<sub>2</sub> [2,4,11]. Three types of structure have been observed among the MX<sub>2</sub> single layers: 1H-MX<sub>2</sub> (space group  $P\bar{6}m2$ ), 1T-MX<sub>2</sub> (space group  $P\bar{3}m1$ ), and distorted 1T-MX<sub>2</sub> (space group  $P-1$ ). The metal atoms are trigonal prismatically coordinated in the 1H-MX<sub>2</sub> structure, and octahedrally coordinated in the 1T-MX<sub>2</sub> structure. The distorted 1T-MX<sub>2</sub> is a triclinic structure with distorted X octahedron. It was recently found that the single-layer ReS<sub>2</sub> keeps the distorted 1T-MX<sub>2</sub> structure as in the bulk ReS<sub>2</sub> [12]. It was proved that the ReS<sub>2</sub> layers are electronically and dynamically decoupled in the bulk with very weak van der Waals forces. The bulk and single layer possess nearly identical band structure and Raman active modes [12,13]. This unique character makes the bulk ReS<sub>2</sub> a pseudo single-layer material. This also creates great advantage for ReS<sub>2</sub> if it can be engineered for photocatalytic applications. The weak coupling between single layers in ReS<sub>2</sub> allows for easy preparation of nanosheets that can provide abundant surfaces and can be easily co-catalyzed with other materials.

However, the potential photocatalytic application of the two-dimensional ReS<sub>2</sub> has not been comprehensively investigated. In this paper, we explore the photocatalytic application of the single-layer ReS<sub>2</sub> by using density functional theory (DFT) based calculations. First, we present the electronic and optical properties of the pristine single-layer ReS<sub>2</sub>; Then we investigate the variations of the dynamic, electronic, and photocatalytic properties of the strained single-layer ReS<sub>2</sub>. At last, we discuss the potential application of the single-layer ReS<sub>2</sub> as a photocatalyst.

## Methodology

The present calculations are based on DFT and use a plane-wave basis set, as implemented in the Vienna Ab initio Simulation Package (VASP) [14,15]. The interaction between the ions and valence electrons is described by the projector augmented wave (PAW) method [16–18]. Most of the calculations, including structural relaxations and phonon spectra calculations, are done on the level of generalized gradient approximation (GGA), employing the exchange-correlation functional by Perdew, Burke and Ernzerhof (PBE) [19]. In general, semi-local GGA functionals are known to underestimate the electronic bandgap of semiconductors and insulators, while providing good structural accuracy [10,20,21]. The S-3s<sup>2</sup> 3p<sup>4</sup> and Re-5d<sup>5</sup> 6s<sup>2</sup> are treated as valence electrons. The convergence criteria is  $1 \times 10^{-6}$  eV/atom for the total energy and  $1 \times 10^{-5}$  eV/Å for the force on atoms. We performed tests to find suitable cut-off energy and **k**-mesh. A plane-wave cut-off energy of 500 eV and a **k**-mesh of  $16 \times 16 \times 1$  were enough to reach convergence and used in the calculations.

The phonon dispersions were calculated by means of PHONOPY code [22], which is an implementation of post-process phonon analyzer, from the Hessian matrix calculated using density functional perturbation theory (DFPT) and PBE functional implemented in VASP. We used a  $2 \times 2 \times 1$  supercell to calculate the eigenvalues of the Hessian matrix. The phonon-related thermal properties of these compounds were then derived from the calculated phonon spectra.

The bulk ReS<sub>2</sub> corresponds to a triclinic structure, which can be considered as a transformed structure from the hexagonal lattice via Peierls distortion. The single layers in ReS<sub>2</sub> keeps the distorted 1T-MX<sub>2</sub> structure. To facilitate the simulation, we adopted an orthorhombic unitcell for the single layer. Fig. 1 shows the structures of the bulk and single-layer ReS<sub>2</sub>.

The x-axial strain ( $\epsilon(x)$ ), y-axial strain ( $\epsilon(y)$ ), and shear strain ( $\epsilon(\text{shear})$ ) were applied upon the relaxed ground-state structure, respectively. The transform matrix is

$$\begin{pmatrix} 1 + \epsilon(x) & \epsilon(\text{shear})/2 & 0 \\ \epsilon(\text{shear})/2 & 1 + \epsilon(y) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The internal atomic coordinates were fully relaxed for the strained structures, but the lattice vectors were not allowed to relax. This mostly resembles the case that single layers are located on substrates, where the lattice vectors of the single layer are locked respectively.

To better describe the changes of the structure, we labeled the atoms and the angles in the single-layer ReS<sub>2</sub> as depicted in Fig. 2.

## Results and discussion

### Ground-state single-layer ReS<sub>2</sub>

Table 1 shows the calculated lattice parameters of the single-layer ReS<sub>2</sub> in comparison with the bulk. The calculated lateral area of the single-layer ReS<sub>2</sub> is very close to that of bulk. Besides, the calculated Re–S bond length (2.33–2.44 Å) matches with that of experimental data and that of LDA (local density approximation) data [13].

Besides, the calculated bandgap of the single-layer ReS<sub>2</sub> is 1.43 eV. This value is close to the experimental value (1.55 eV) and agrees with other calculations (1.43 eV) [12]. It suggests the good choice of our method. The bandgap calculated using HSE06 is 2.00 eV, which is highly overestimated. Such a phenomenon is usually seen in 2D semiconductors [10]. Hybrid functionals usually overestimate the bandgap of single layers, while the semi-local functionals can provide closer values to the experimental data. This can be attributed to the weak non-local correlations in 2D semiconductors. Besides, there is no sharp cutoff of the charge density on the surface and thus can be accurately described by the generalized gradient approximation. We also calculated the band structures of the bulk, four-layer, and two-layer ReS<sub>2</sub>. They share much the same band structure. The calculated bandgap of the bulk ReS<sub>2</sub> is 1.36 eV, which is also very close to that of the single layer.

Our calculations show that both the single-layer and bulk ReS<sub>2</sub> are indirect bandgap semiconductors. The single-layer and bulk ReS<sub>2</sub> share a very similar band structure [12]. Fig. 3 shows the band structure of the single-layer ReS<sub>2</sub>. It was claimed that the single-layer and bulk ReS<sub>2</sub> are direct bandgap semiconductors, however, some recent high-quality experiments proved that the bulk ReS<sub>2</sub> is an indirect bandgap semiconductor [25,26]. It is reasonable to expect an indirect bandgap character for the single-layer ReS<sub>2</sub>, which is shown by our calculations and needs to be confirmed by experiments.

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