



Computational study of the electronic, optical and photocatalytic properties of single-layer hexagonal zinc chalcogenides

Jiajun Wang^{a,*}, Xintong Yang^a, Jinrui Cao^a, Ying Wang^a, Qunxiang Li^{b,*}

^a Tianjin Key Laboratory of Structure and Performance for Functional Molecules, Key Laboratory of Inorganic-Organic Hybrid Functional Materials Chemistry, Ministry of Education, College of Chemistry, Tianjin Normal University, Tianjin 300387, China

^b Hefei National Laboratory for Physical Sciences at the Microscale & Synergetic Innovation Center of Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

ARTICLE INFO

Keywords:

Single-layer hexagonal zinc chalcogenides

Electronic structure

Band edge alignment

Optical absorption

Strain

2017 MSC:

00-01

99-00

ABSTRACT

Here, we investigate the stabilities, band structures and optical properties of single-layer hexagonal zinc chalcogenides (h-ZnX, X = S, Se, and Te) by performing first-principles calculations. Our results show that single-layer h-ZnX with relatively low formation energies (about 200 meV/atom) could be exfoliated from their bulk structures and stabilized on graphene substrate. All the single-layer h-ZnX are direct semiconductors with band gaps ranging from 2.75 eV (h-ZnTe) to 4.08 eV (h-ZnS). Calculations of the carrier effective mass indicate that single-layer h-ZnX has low recombination rate of the photogenerated electron-hole pairs. Furthermore, single-layer h-ZnTe is predicted to be a potential visible-light driven photocatalyst for water splitting since it possesses a suitable band gap and well-located band edge position. Moreover, introducing mild tensile strains can effectively tune the band gaps, optical performances and redox abilities of these single-layer h-ZnX, thus enable them to present excellent photocatalytic activity.

1. Introduction

Production of hydrogen from water splitting via semiconductor photocatalysts under sunlight has been deemed as one of the most promising solutions to solve the increasingly serious energy and environmental crises because hydrogen provides an alternative energy source, which promises to be clean, environmentally friendly, low cost, and renewable [1,2]. Since the pioneering work by Fujishima and Honda on photocatalytic splitting of water on TiO₂ electrodes in 1972, great effort has been paid for new photocatalysts with high performance [3]. So far, hundreds of semiconductor materials, including SrTiO₃, NaTaO₃, ZnO, Ag₃PO₄, BiVO₄, TaON, have been proposed as photocatalysts for water splitting [4]. Unfortunately, the productivity of current photocatalysts is too low to meet the requirement of practical application.

Photocatalytic reactions of overall water splitting proceed on photocatalyst as schematically shown in Fig. 1(a). When sunlight shines on a photocatalyst, the photons can be adsorbed to generate electrons in the conduction band (CB) and holes in the valence band (VB) once their energy greater than the band gap energy of the photocatalyst. Then, these photoexcited electrons and holes migrate to surface and give rise to water redox reaction [5]. To be promising photocatalysts for splitting

water to hydrogen using solar energy, two important conditions must be satisfied. First, the band gap of a photocatalyst should exceed the standard Gibbs free energy change of water splitting (1.23 eV) and be smaller than about 3.0 eV for effective utilization of solar energy. Usually, the optimal band gap should be approximately 2.0 eV [4]. Second, the water oxidation and reduction potentials should be straddled by the band edges of a suitable photocatalyst. That is to say, the conduction band minimum (CBM) must be located more negative than the hydrogen reduction potential of H⁺/H₂ (−4.44 eV at pH = 0), and the valence band maximum (VBM) energy should be lower than the water oxidation potential of O₂/H₂O (−5.67 eV at pH = 0) [6].

To fulfill the above requirement, two-dimensional (2D) material-based photocatalysts have attracted an intense research interest in the field of photocatalysis [7–9]. Over the past few years, a large variety of 2D materials, such as metal oxide, graphitic carbon nitride, chalcogenide nanosheets, MXenes, and black phosphorus have been proven to be potential photocatalysts [10–24]. Comparing with their corresponding bulk counterparts, these 2D material-based photocatalysts not only possess diverse and tunable electronic and optical properties, but also offer some intriguing features that can be utilized to improve the efficiency of solar water splitting. First, 2D materials have large lateral size with ultra-high specific surface area, which provides more

* Corresponding authors.

E-mail addresses: hxywj@tjnu.edu.cn (J. Wang), liqun@ustc.edu.cn (Q. Li).

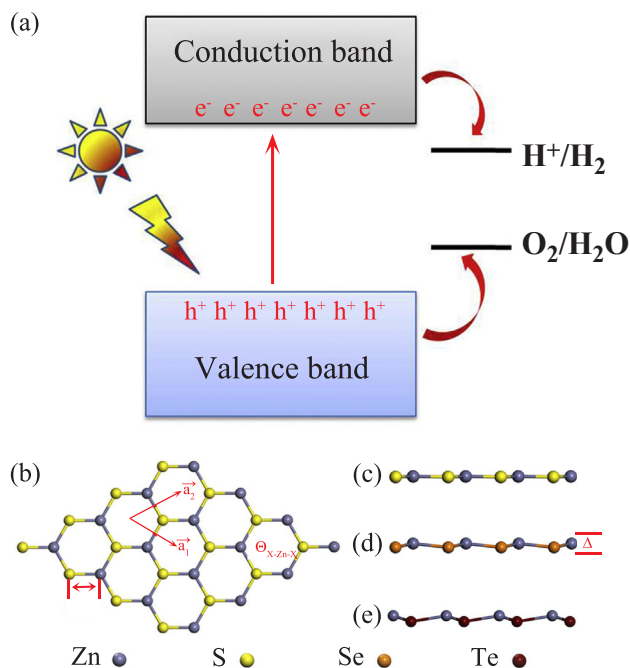


Fig. 1. (a) Illustration of water splitting for hydrogen production. Optimized single-layer h-ZnX (X = S, Se, and Te) sheets, (b) planar h-ZnS (top view), (c) planar h-ZnS (side view), (d) corrugated h-ZnSe (side view), and (e) corrugated h-ZnTe (side view). The top views of h-ZnSe and h-ZnTe are analogy to that of h-ZnS.

available active sites for photocatalytic reactions. Second, the 2D nature of these materials minimizes the migration distance for the photo-generated electrons and holes, thus decreasing the recombination rate of electrons and holes and then giving high quantum yields [25]. However, for most 2D materials, their electronic structures tend to be sensitive to the external factors, such as defects, dopants and environmental molecules, limiting their potential applications in the field of photocatalytic water splitting [26–28]. Therefore, designing and modifying new 2D material-based photocatalysts that exhibits desirable physical and chemical properties is urgently needed.

As an important binary II-VI semiconductor photocatalysts, Zinc chalcogenides (ZnX, X = S, Se, Te) have attracted significant research interest for degradation of organic pollutants and photocatalytic water splitting owing to rapid generation of photocarriers and strong reducing power of excited electrons [29,30]. However, bulk ZnX possess relatively wide band gap, so they are active only under ultraviolet irradiation, which accounts for less than 5% of solar energy [31–33]. Recently, 2D ZnX materials have been receiving more attention because of the fantastic electronic, optical, mechanical and photocatalytic properties compared with their corresponding bulk counterparts [34–36]. Xie and coworkers reported successful synthesis of freestanding four-atom-thick sheets of ZnSe. The as-synthesized ZnSe sheets give much enhanced photocurrent density, almost 200 times higher than that of the bulk counterpart [34]. Using DFT methods, Zhou et al. predicted a novel single-layer ZnSe sheet with three-atomic thickness, which is expected to exhibit a comparable behavior for photocatalytic water splitting [35,37]. Moreover, Li et al. [38] found that this type of ZnSe sheet exhibits highly tunable band gap under the biaxial strains.

Inspired by these exciting progressive achievements of ZnSe sheet, it is worthwhile to explore whether the single-layer hexagonal zinc chalcogenides (h-ZnX, X = S, Se, and Te) correspond to (001) plane cleavage of the bulk wurtzite phase could be achieved in experiments and whether they could exhibit interesting electronic, optical, and photocatalytic properties for water splitting reaction. In this study, we systematically investigate the single-layer hexagonal zinc chalcogenides

(h-ZnX, X = S, Se, and Te) as potential candidates for solar hydrogen production based on first principles calculations. First, we examine the stabilities of these novel 2D materials on the basis of the calculated formation energy and phonon spectra. Next, we investigate the practicability of the single-layer ZnX sheets for future application in the photocatalysis based on the calculated electronic structures, band edge alignments and optical absorptions. Finally, we discuss the methods of optimizing the band edge positions of ZnX sheets, and then make them meeting the requirements for water splitting.

2. Computational methods

We perform first-principles calculations using the frozen-core projector augmented wave approach [39] as implemented in the Vienna Ab initio Simulation Package (VASP) [40]. The Perdew-Burke-Ernzerhof generalized gradient approximation (GGA-PBE) is chosen to describe the exchange and correlation effects [41]. A 520 eV energy cutoff for plane wave basis set is adopted. The 2D Brillouin zone is sampled with a $21 \times 21 \times 1$ k-points mesh according to Monkhorst-Pack scheme [42]. To avoid interactions between neighbor layers, the vacuum spacing perpendicular to the sheets is at least 15.0 Å. The geometry optimization is stopped until total energy and residual forces are less than 10^{-5} eV and 0.01 eV/Å, respectively.

In order to overcome the shortcomings of GGA-PBE in predicting the band gap, we further calculate the electronic structures of h-ZnX sheets using the HSE06 hybrid functional [43,44]. The exchange–correlation contribution employed in the HSE06 functional is divided into short- and long-range parts. The 25% Hartree–Fock (HF) exchange is mixed with PBE exchange in the short-ranged part, and the expression for exchange–correlation in HSE06 is given by

$$E_{XC}^{HSE} = \frac{1}{4}E_X^{HF,SR}(\mu) + \frac{3}{4}E_X^{PBE,SR}(\mu) + E_X^{PBE,LR}(\mu) + E_C^{PBE}, \quad (1)$$

where SR and LR represent the short- and long-range parts of the exchange interaction, respectively. μ is the parameter that defines the range-separation of Coulomb kernel and $\mu = 0.2 \text{ \AA}^{-1}$.

Here, we determine the VBM and CBM energy levels of single-layer h-ZnX from the band gap center energy (E_{BGC}) and the band gap energy E_g as

$$\begin{aligned} E_{VBM} &= E_{BGC} - 1/2E_g, \\ E_{CBM} &= E_{BGC} + 1/2E_g. \end{aligned} \quad (2)$$

Comparing to the band gap, the energy of band gap center is almost independent of the selection of exchange–correlation functional. Thus, the E_{BGC} is calculated by the less computationally expensive PBE functional and the more accurate HSE06 functional is employed to calculate band gaps. The vacuum energy level is set to 0 for aligning the energy levels of different single-layer sheets.

To determine the optical absorption properties of h-ZnX sheets, we simulate the optical absorbance spectrum through converting the complex dielectric function to optical absorption coefficient α_{abs} according to the below expression [45],

$$\alpha_{abs} = \sqrt{2}\omega(\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega))^{\frac{1}{2}}, \quad (3)$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of frequency dependent complex dielectric function $\varepsilon(\omega)$, respectively. Considering the appropriate transition momentum matrix elements, the imaginary part of the dielectric function, $\varepsilon_2(\omega)$ is calculated by summing all possible transitions from the unoccupied to the occupied wave functions within the selection rules. The real part of the dielectric function, $\varepsilon_1(\omega)$ can be derived from $\varepsilon_2(\omega)$ using the Kramer-Kronig relationship.

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