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Enhanced photocatalytic activity of nonmetal doped monolayer MoSe₂ by hydrogen passivation: First-principles study

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ABSTRACT

Using first-principle calculations, we have systematically investigated the enhancement of photocatalytic activity in nonmetal (NM) (B, C, Si, N, P and As) doped monolayer MoSe₂ after hydrogen (H) passivation. We have found that incorporation of the NM atoms into MoSe₂ will be easier in the presence of H. Moreover, H-passivation can enhance the photocatalytic activity of doped MoSe₂ by suppressing the recombination of photo-generated electron/hole pairs and increasing the reduction ability of photogenerated electrons, especially in C-2H doped MoSe₂. This work provides a useful guidance of H passivation, since H is abundant in the processing or application environment and its interaction with NM acceptors is inevitable.

1. Introduction

The unique electronic properties and potential photocatalyst applications of transition metal dichalcogenides (TMDCs) have recently stimulated considerable worldwide attention [1–6]. Doping is considered as a promising method to enhance the photocatalytic properties of MoS₂ and MoSe₂ [7–10]. Such as, a series of works have reported that ultrathin C-, N- and P-doped MoS₂ nanosheets have demonstrated enhanced oxygen reduction reaction (ORR) and efficient degradation of organic pollutants, respectively [11–16].

In addition, many researchers have confirmed that H atoms in SnO₂ and TiO₂ are highly mobile shallow donor, and have strongly interacted with negatively ionized acceptors [17–22]. Thus, H will interact with the NM dopants and affect the photocatalytic efficiency dramatically, since H is usually present in the processing or application environment. But neither theoretical nor experimental studies have reported relating work so far [23–27]. Therefore, knowledge about the interactions between H and NM acceptors (B, C, Si, N, P and As) in monolayer TMDCs is crucial.

In this work, using first-principle calculations we have systematically studied the geometrical structure, formation energy, electronic and photocatalytic properties of H-passivated NM (B, C, Si, N, P and As) doped monolayer MoSe₂. We found that that incorporation of the NM atoms into MoSe₂ will be easier in the presence of H. Moreover, H-passivation can further enhance the photocatalytic activity of doped

MoSe₂ by suppressing the recombination of photogenerated electron/hole pairs and increasing the reduction activity of photogenerated electrons; especially C-2H doped system.

2. Computational methods

First-principles study was performed within the framework of density functional theory (DFT) by using the Vienna Ab-initio Simulation Package (VASP). Projected augmented wave (PAW) and Perdew-Burke-Ernzerhof (PBE) function of the generalized gradient approximation (GGA) are used for the electron-ion interactions and exchange–correlation potential, respectively [28,29].

All simulations are carried out for a 4 × 4 × 1 monolayer MoSe₂ supercell with 16 Mo atoms and 32 Se atoms (Fig. 1a). In H-passivated NM doped systems, one NM atom substitute a Se atom and H atoms are adsorbed on the surface. Meanwhile, we have considered all 13 possible H-passivation configurations (based on the distance between NM and H atom), as shown in Fig. 1b. For each H-passivated case, the most stable configuration is when the H atoms directly bond to the substitutional NM atom, as shown in Fig. 1c–l. The reason is that the H atom has an unpaired electron, and it presents in the nearest position can neutralize the holes introduced by substitutional NM atom. Thus, the total formation energy is lowered with H-passivation.

The high cutoff energy for the plane-wave basis was set at 500 eV and a 8 × 8 × 1 k-point sampling grid is applied to integrate over the

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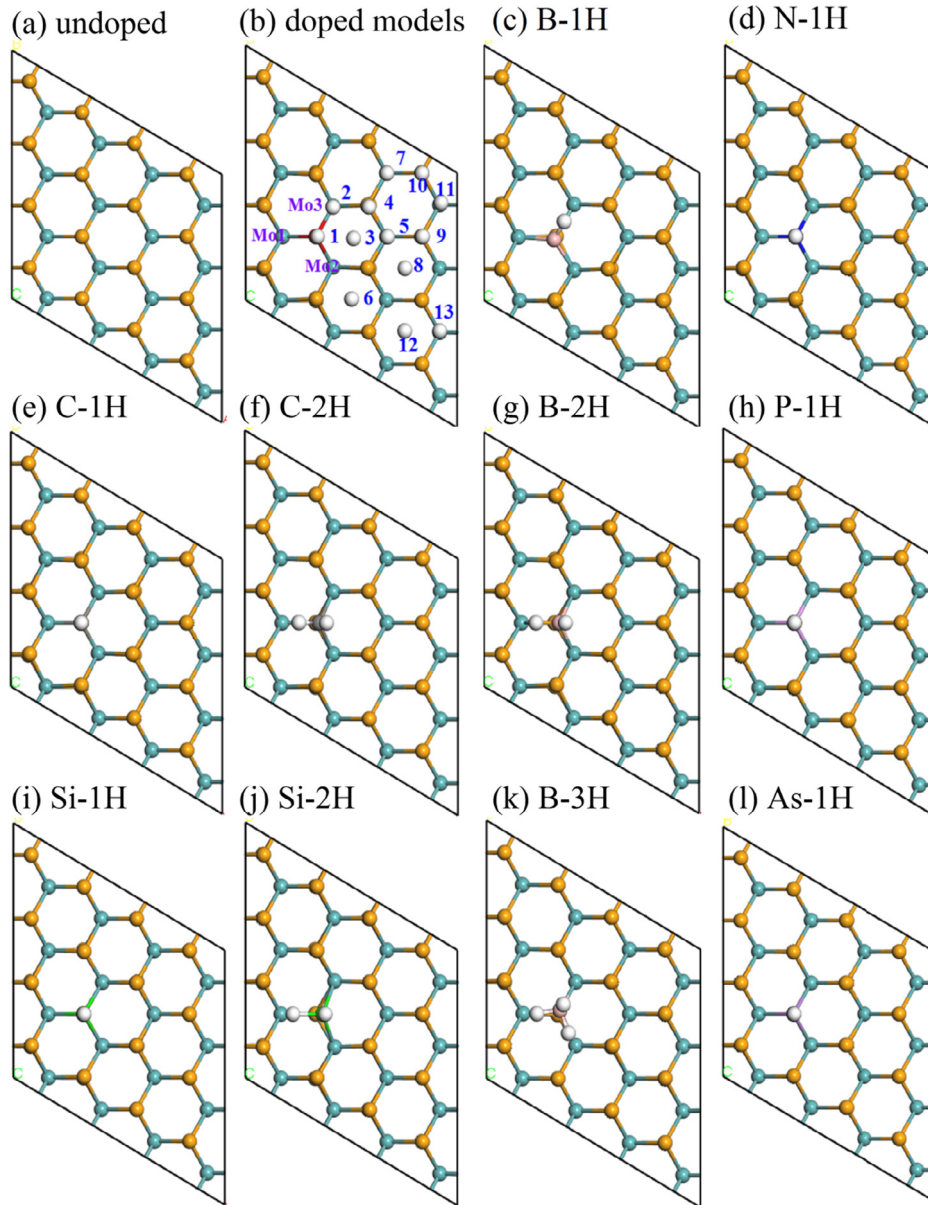


Fig. 1. Top view of the crystal structure of undoped (a), B-1H- (b), B-2H- (c), B-3H- (d), C-1H- (e), C-2H- (f), Si-1H- (g), Si-2H- (h), N-1H- (i), P-1H- (j), As-1H- (k), and all possible H-passivation models of NM-doped (l) $4 \times 4 \times 1$ supercell monolayer MoSe_2 , respectively. The blue, yellow and white spheres are denote the Mo, Se and H atoms, respectively. The numbers represent the possible positions of H atoms.

first Brillouin zone. A vacuum layer of 15 \AA is adopted along the z-direction to avoid the interactions between periodic slabs. The structural optimization is continued until the convergence tolerance of energy and maximum force was less than $1.0 \times 10^{-5} \text{ eV/atom}$ and 10^{-3} eV/\AA , respectively. All the calculations are performed under same relaxation criteria.

We have calculated the formation energy (E_f) of all the doped systems to assess the stability of different NM dopants:

$$E_f = E_{\text{doped}} - E_{\text{undoped}} + \mu_{\text{Se}} - \mu_{\text{NM}} - n\mu_{\text{H}} \quad (1)$$

where E_{doped} and E_{undoped} are the total energy of the monolayer MoSe_2 with and without dopants atoms, μ_{NM} and μ_{H} are the chemical potential of the dopant and is calculated with respect to the elemental bulk or gas in nature. The n denotes the number of H atoms adsorbed on the surface of a MoSe_2 monolayer. In view of the growth of MoSe_2 being a dynamic process, the E_f is unfixed and depends on the growth condition (changing from Mo-rich condition to Se-rich condition). The chemical potentials of Mo and Se atoms satisfy the equations:

$$\mu_{\text{Mo}} + 2\mu_{\text{Se}} = \mu(\text{MoSe}_2) \quad (2)$$

Under Se-rich condition, μ_{Se} is the chemical potential of bulk Se in its reference phase, and μ_{Mo} is obtained by Eq. (2). On the contrary, under Mo-rich condition, μ_{Mo} is the chemical potential of bulk Mo, and μ_{Se} is calculated by Eq. (2). Negative E_f suggests that dopants atoms are very easily to enter the MoSe_2 lattice.

3. Results and discussions

3.1. Formation energies and optimized structures

Tables 1 and S1 lists the E_f of the NM-doped MoSe_2 with and without (w/o) H-passivation. For all of them, the E_f obtained under the Mo-rich condition is smaller than that under the Se-rich condition, which indicates that the NM atoms prefer to substitute the Se atoms under Mo-rich conditions, since more Se vacancies are present in this case. Thus, only the E_f under Mo-rich conditions will be discussed in the

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