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Adsorption of 3*d* transition-metal atom on InSe monolayer: A first-principles study

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ABSTRACT

The adsorption of 3*d* transition metal (TM) atoms (from Sc to Zn) on the InSe monolayer is studied by using density functional theory. The most preferable adsorption site is on top of In atoms for Sc, Ti, and V atoms, while the other seven 3*d* TM atoms (from Cr to Zn) are found to prefer the hollow adsorption site of InSe monolayer. The sizable adsorption energies are obtained for these systems except Zn-InSe system. The electrons are transferred from the adsorbed TM atoms to the support, thus a *n*-doping effect is achieved in the InSe monolayer by the TM atoms adsorption. The interesting magnetic properties are exhibited in those TM-InSe systems for TM from Sc to Co, which can be understood based on the orbital alignments and occupations of adsorbed TM atoms. The spin configurations are listed for each system. Our results indicate that great potential exists in these systems for 2D InSe utilization in nanoelectronics and spintronics.

1. Introduction

The discovery of graphene has intrigued strong interest in two-dimensional (2D) materials, including graphene itself [1], transition metal dichalcogenides (TMDCs) [2], hexagonal boron nitride [3,4], silicene [5,6], germanane [7], and phosphorene [8,9]. However, some intrinsic deficiencies, such as the lack of a band-gap in graphene or relatively low mobility in MoS_2, limit their successful applications in electronic devices [10,11]. Thus, the continuous search for other 2D materials with desired properties is very necessary. Very recently, another group layered materials, Group III-VI chalcogenides, such as GaSe, GaS, and InSe, etc., have drawn lots of attention [12–16]. Bulk InSe is an important layered semiconductor with direct band-gap of ~1.2 eV [17,18]. Each of its layers has a honeycomb lattice that consists of four covalently bonded Se-In-In-Se atomic planes. Similar to the graphite, the layers are bonded together by van der Waals (vdW) interactions at an interlayer distance of ~0.8 nm [13]. Importantly, the multilayer InSe is stable under ambient conditions, which is very valuable for the flexible nanoelectronics application [19].

The mobility of few-layer InSe could reach 10^3 $cm^2/(Vs)$ at room temperature and exceed 10^4 $cm^2/(Vs)$ at low temperature [13,20]. Thus the few-layer 2D InSe will be a promising candidate for the next generation high performance 2D semiconductor devices. The 2D InSe has been synthesized by several research groups by mechanical exfoliation from bulk InSe [15,21]. Lauth et al. also obtained ultrathin InSe nanosheets by a colloidal ligand template method [16]. The field effect transistor (FET) based on multilayer InSe has been fabricated by several groups, and a high room temperature electron mobility up to 10^3 $cm^2/(Vs)$ and a high current on/off ratio of ~10^8 are exhibited in these FETs, suggesting the huge potential of 2D InSe as a new material for high performance electronics [20,22,23]. Analysis of photoconductivity spectra performed by Lei et al. suggested that few-layer InSe had an indirect band-gap of 1.4 eV [24]. Their band-gaps depend on the layer numbers, and the huge band-gap tuning of around 1 eV is demonstrated in InSe as its thickness decreases from bulk to single layer [24–26]. Moreover, the density functional theory (DFT) calculations suggested InSe could transform from a direct to an indirect band-gap semiconductor when the layer number decreased [27]. Also, the band-gap of InSe monolayer could also be switched from indirect to direct through the application of an electric field perpendicular to the 2D plane. When the strength of the electric field is enough large (~1.0 V/Å), the band-gap of InSe monolayer is closed, resulting in a semiconductor to metal transition [17]. Few-layer InSe has exhibited promising characteristics for the application in nanoelectronics, sensors, optoelectronics, and photodetectors field.

Tunable electronic and magnetic properties of 2D materials are crucial, which can facilitate the application of these materials in spintronic devices. The pristine InSe, however, is in itself nonmagnetic. Decoration of transition metal (TM) atoms is a simple and natural way to induce magnetism in the nonmagnetic 2D materials. The TM-

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decorated graphene can serve as very potential materials in nanoelectronics and spintronics [28,29]. For example, Fe or Co atoms adsorbed graphene was predicted as a half-metal, which could be used as a spin-filtering material [30]. Also, the electronic and magnetic properties of graphene nanoribbon and nanotube could be strongly modified through the adsorption of 3*d* TM atoms [31,32]. TM-decorated 2D TMDCs were also widely investigated. Based on DFT calculations, Ramasubramaniam and Mishra et al. found the Mn-doped TMDCs were promising candidates for 2D dilute magnetic semiconductors, respectively [33,34]. The experimental investigation performed by Xiang et al. suggested the magnetic moments of Co-doped MoS_2 decreased with the increase of Co atoms concentrations [35]. Moreover, TM decoration also endowed silicene, phosphorene, and antimonene with the potential for utilization in innovative spintronic devices [36–38].

In this work, we investigate the adsorption of 3*d* TM atoms (from Sc to Zn) on InSe monolayer. The most stable adsorption sites for TM atoms on InSe monolayer are identified. Only Zn atom is physically adsorbed on InSe monolayer. The direction of charge transfer is from TM atoms to the support, meaning *n*-type doping of InSe monolayer. The former seven TM atoms (from Sc to Co) can induce magnetism into InSe monolayer, and the magnetic behavior of these systems can be understood based on the orbital alignments and occupations of adsorbed TM atoms. No magnetic moments are obtained in the Ni-, Cu-, Zn-InSe systems.

2. Method and models

Our results are based on first-principles plane-wave calculations within DFT using projector-augmented wave potentials, as implemented in the Vienna *ab initio* simulation program (VASP) [39,40]. The Perdew-Burke-Ernzerhof (PBE) form of the Generalized-Gradient Approximation is used to describe the exchange and correlation functional [41]. The spin-polarized DFT was adopted in the calculations of InSe monolayers with the adsorption of TM atoms. The Se 4*s* 4*p*, In 5*s* 5*p*, and TM 3*d* 4*s* electrons are treated as valence electrons. The long-range Van der Waals interactions are included using Grimme's DFT-D3 method [42]. Since the PBE exchange correlation often underestimates the band gap, the more accurate hybrid functional (HSE06) [43] was also used to correct the PBE results. Note that all results and discussions in this paper are based on the HSE06 method, unless otherwise mentioned. The valence electrons are described by a plane wave basis set with an energy cutoff energy of 400 eV and the convergence criterion on the total energy is 10^{-6} eV. The monolayer hexagonal InSe consists of planar quaternary layers, in which closed-packed Se-In-In-Se monatomic sheets pile up along *c*-axis. There is strong covalent bonding within each layer. The optimized lattice constant is 4.052 Å for the primitive cell, containing two In and two Se atoms, which is in good agreement with the previous reports [44,45]. The optimized lengths of Se-In and In-In bonds are 2.68 Å and 2.79 Å, respectively. In order to model a TM atom adsorbed on InSe monolayer, we choose a 4×4 supercell of InSe monolayer (see Fig. 1(a)), i.e., 32 In and 32 Se atoms plus one TM adatom. The vacuum thickness along the *z* axis is no less than 16 Å to avoid artifacts due to periodic boundary conductions. For geometry optimization, the internal coordinates are allowed to relax with the fixed lattice constants until the Hellmann-Feynman forces are less than 0.01 eV/Å. The first Brillouin zone is sampled with a $3 \times 3 \times 1$ Γ-centered special grid for relaxation calculations and $9 \times 9 \times 1$ for static calculations based on PBE method. Due to the high computational consumption, a $5 \times 5 \times 1$ grid is used for the HSE06 hybrid functional method [46].

For the adsorption of TM atoms, five possible adsorption positions are considered on 4×4 supercell of InSe monolayer, i.e., H site (above the center of the hexagonal ring of Se-In), T_{In} site (on top of In atom), T_{Se} site (on top of Se atom), $B_{Se\text{-}Se}$ site (above the middle of Se-Se bond), and $B_{Se\text{-}In}$ site (above the middle of Se-In bond) as represented by five red triangles in Fig. 1. The relative stabilities of these configurations are measured by their adsorption energy E_{ad}, defined as $E_{ad} = E_{InSe} + E_{TM} - E_{total}$, where E_{InSe} represent the total energies of the pristine InSe monolayer, E_{TM} is corresponding to the total energy of single TM atoms, and E_{total} represents the total energy of the InSe monolayer with the adsorbed TM atoms. According to this definition, the positive values mean an exothermic process. The 5×5 supercell of InSe monolayer is also employed to check the convergence of E_{ad} with respect to supercell size. The results show the change of E_{ad} is less than 1%, suggesting 4×4 supercell is enough large to avoid the interactions between the TM atoms images.

3. Results and discussion

The band structure and electronic densities of states (DOS) of the unit cell of the pristine InSe monolayer are plotted in Fig. 1(b) and (c), respectively. Obviously, InSe monolayer is an indirect band-gap semiconductor. The valence band maximum lies between Γ and K points, and the conduction band minimum is at Γ point [17,27,44]. The partial densities of states (PDOS) in Fig. 1(c) show that valence band is mainly contributed by the *p* states of Se and In atoms, while the components of conduction band are different. Except for the *p* states, the *s* and *d* states of In atoms also make the contribution to the conduction band. The obtained PBE band-gap is 1.575 eV and the HSE band-gap is 2.326 eV, which is in good agreement with the previous PBE (1.44 eV) and HSE06 (2.16 eV) results, respectively [44,47].

3.1. Geometrical structures and stability

The obtained results of InSe monolayer with ten kinds of 3*d* TM atoms are given in Table 1. For each TM atom, five adsorption sites are all considered, including 'H', 'T_{In}', 'T_{Se}', '$B_{Se\text{-}Se}$', and '$B_{Se\text{-}In}$' sites. The relative stabilities of these sites are judged by comparing their adsorption energies E_{ad}. Upon full geometry optimization, Sc, Ti, and V atoms prefer to bond at the 'T_{In}' site, as shown in Fig. 2(a). For the other TM atoms (from Cr to Zn), the 'H' site is found to be the most stable, as shown in Fig. 2(b). The adsorption energies of all stable TM-InSe systems are listed in Table 1. Except Zn-InSe system, the adsorption energies of TM-InSe systems are quite sizable, ranging from 1.1 eV to 2.9 eV based on HSE method (1.4–3.7 eV based on PBE method), which are much larger than those in the systems of graphene with TM atoms, about or much less than 1.0 eV [48]. For example, the adsorption energy of Mn atom on graphene is only 0.42 eV [29], while the adsorption energy of 1.42 eV (HSE) is obtained in Mn-InSe system. It can be found from Table 1 that there are four systems whose adsorption energies are less than 1.5 eV (HSE), that is, Cr-InSe, Mn-InSe, Cu-InSe and Zn-InSe systems. We know that the 3*d* orbital of free Cr, Mn atoms are half-filled, and the 3*d* orbital of free Cu, Zn atoms are full-filled. The full-filled or half-filled *d* orbitals weaken the interaction between TM atoms and InSe monolayer, reducing the adsorption energies of these systems. Especially in Zn-InSe system, both 3*d* and 4*s* orbitals are full-filled, leading to closed-shell structure. Thus Zn atom is physically adsorbed on InSe monolayer, with the smallest adsorption energy of 0.23 eV (HSE) and the largest Zn-Se and Zn-In bond lengths of 3.47 Å and 4.48 Å, respectively. The scenario is similar for the adsorption of Zn atom on the other 2D material, for example phosphorene [49].

3.2. Electronic structures

In order to understand the influence of 3*d* TM atoms on the electronic structures of InSe monolayer, the total DOS (TDOS) of all TM-InSe systems are shown in Fig. 3. Obviously, the former seven TM atoms induce the asymmetric distribution between spin-up and spin-down states, meaning the adsorption of those atoms from Sc to Co can induce effectively the magnetism in InSe monolayer. The spin-polarized states mainly lie around the Fermi level (E_F). Obviously, these states are mid-gap states in the band-gap of InSe monolayer, which are introduced by