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Influences of vacancies on the structural, electronic and optical properties of monoclinic $BiVO_4$

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ABSTRACT

Monoclinic $BiVO_4$ (m-$BiVO_4$) is a potential photocatalyst for environmental protection. Based on density functional theory (DFT) calculations, the influences of vacancies on the structural, electronic and optical properties of $2 \times 2 \times 2$ $BiVO_4$ are investigated. The results indicate that the lattice parameters of $BiVO_4$ change with vacancy types slightly. The formation energies of four different types of O vacant $BiVO_4$ (denote as V_O) are smaller than those of the other two types of Bi and V vacant $BiVO_4$ (denote as V_{Bi} and V_v) respectively, and V_{1O} $BiVO_4$ is most easily formed. The indirect band gaps of V_{1Bi}, V_{2Bi}, V_{1V}, V_{2V}, V_{1O}, V_{2O}, V_{3O} and V_{4O} $BiVO_4$ are 1.994 eV, 1.989 eV, 1.792 eV, 1.793 eV, 0.465 eV, 0.521 eV, 0.515 eV and 0.465 eV, respectively, while the direct band gap of ideal $BiVO_4$ is 2.108 eV. Theoretical calculated band gaps are slightly smaller than experimental values owing to the well-known limitation of DFT method. Taking V_{1Bi}, V_{1V} and V_{1O} $BiVO_4$ as an example, the calculated optical properties show that the static dielectric, refractive index and reflectivity of defective $BiVO_4$ are larger than those of ideal crystal. In the low energy range, ε_1, n and R increase with increasing energy for ideal and V_{1O} $BiVO_4$, while they decrease for V_{1Bi} and V_{1V} $BiVO_4$. Moreover, compared with ideal $BiVO_4$, defective $BiVO_4$ will absorb more energy, while V_{1O} and V_{1V} $BiVO_4$ dissipate the highest and lowest energy respectively. The optical absorption spectra indicate that the optical band gaps of defective $BiVO_4$ are reduced and will effectively enhance the optical absorption in visible light range.

1. Introduction

Environmental pollution and energy crisis are two important issues which should be overcome for the sustainable development of human society [1]. Photodegradation and photoelectrocatalytic water splitting can immediately capture solar energy from sunlight, and they are believed to be the ideal solution to environmental and energy problems, respectively [2–5]. As the photocatalysts, ZnO, SnO_2 and TiO_2 have been widely studied in the past few years because of non-toxicity, high oxidation, chemical stability and low cost. Nevertheless, due to their large band gaps (≥ 3.2 eV), they can only respond to UV light irradiation, and only 4–5% of the solar energy might be adopted. Therefore, it is urgent to develop photocatalysts which can respond to visible light [6].

$BiVO_4$ is a prospective photocatalyst with a narrow band gap, and has been extensively studied for photocatalytic degradation of harmful organic pollutants and photoelectrochemical water splitting under visible light illumination [6]. $BiVO_4$ has four crystalline phases: tetragonal-1, tetragonal-2, orthogonal and monoclinic. Among them, monoclinic $BiVO_4$ (m-$BiVO_4$) has a band gap of 2.4 eV and a valence band (VB) edge at about 2.5 V vs. NHE, and the photocatalytic activity under visible light irradiation is the highest [7–10]. Theoretical works have been conducted to understand the excellent photocatalytic activity of m-$BiVO_4$. Walsh et al. [11] elucidated that the Bi-6s and V-3d orbitals affect the band edge of m-$BiVO_4$, and Zhao et al. [12] analyzed the adsorption spectrum and the molecular orbital hybridization in m-$BiVO_4$. Kweon et al. [13] investigated the effect of hybrid density functionals on the structural and electronic properties of m-$BiVO_4$. However, ideal $BiVO_4$ usually exhibits a lower separation of photo-excited electron-hole pairs and thus has low photocatalytic performance [14]. Doping and heterojunction have been proposed to improve the optical absorption and promote the separation of photo-generated electron and hole pairs [15]. For instance, doping $BiVO_4$ with cerium species can improve the separation of photogenerated electron-hole pairs and thus the photocatalytic performance. The difference of band edges in heterojunction can be used to separate the photo-generated electron-hole pairs. The composite structures of $BiVO_4/TiO_2$ [16], graphene/$BiVO_4$ [17], Ag/$BiVO_4$ [18], Au/$BiVO_4$ [19] and $Cu_2O/BiVO_4$ [20] have been widely studied. Furthermore, the influences of defects on the physical properties are

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significant. For vacancies, Li et al. [21] found that vacancy can trap photo-generated electrons and thus control the electron-hole recombination. Yin et al. [22] investigated the influences of intrinsic defects in m-$BiVO_4$ including Bi interstitial (Bi_{int}), V interstitial (V_{int}), and O interstitial (O_{int}) in their study. Besides, Yuan et al. [1] reported the photocatalytic activity of m-$BiVO_4$ can be improved effectively by introducing O vacancy. However, whether the optical properties and photocatalytic properties are sensitive to the vacancy types has not been systematically investigated. In this paper, first-principle calculations are performed to systematically study the influences of Bi, V and O vacancies on structural stability, electronic states and optical properties of $2 \times 2 \times 2$ $BiVO_4$.

2. Computational methods

All the calculations are performed using the Cambridge Sequential Total Energy Package (CASTEP) software [23] based on the density functional theory (DFT) [24]. The geometrical optimization is carried out by using the Broyden-Fletcher-Goldfrab-Shanno (BFGS) method [25]. Exchange and correlation interactions are described by the generalized gradient approximation (GGA) functional developed by Perdew-Burke-Ernzerhof (PBE) [26]. $2 \times 2 \times 2$ supercells are adopted for ideal and defective $BiVO_4$. The total energy convergence is tested with respect to the cut-off energy of plane-waves and K points. The cut-off energy is tested from 300 eV to 500 eV with an interval energy of 40 eV and the corresponding calculated final energies are −124076.630 eV, −124102.746 eV, −124107.941 eV, −124108.526 eV, −124109.189 eV and −124110.599 eV. Therefore, the energy differences of adjacent cut-off energy can be easily obtained, which are 26.117 eV, 5.195 eV, 0.585 eV, 0.663 eV and 1.411 eV. Balancing the computational cost and calculation precision, 380 eV is chosen as cut-off energy. K-point samplings of $2 \times 2 \times 1$, $3 \times 3 \times 1$ and $4 \times 4 \times 1$ are also tested and similar final energies are obtained. In this paper, $2 \times 2 \times 1$ Monkhorst-Pack k-point mesh is adopted. All the atoms are fully relaxed to their equilibrium positions with energy convergence of 5×10^{-6} eV, force convergence of 0.01 eV/Å, and stress convergence of 0.02 GPa. In addition, the atomic displacement is less than 5×10^{-4} Å and the self-consistent field (SCF) tolerance is 5×10^{-7} eV. The valence electron configurations of Bi $6s^26p^3$, V $3s^23p^63d^34s^2$ and O $2s^22p^4$ are involved. Ultrasoft pseudopotential is adopted in the reciprocal space. Since we mainly focus on the effects of various types of vacancies on the physical properties and make a relative qualitative comparison, furthermore, experimental data for some defective systems are unavailable, therefore scissors operator is not adopted in the calculation.

3. Results and discussion

3.1. Geometrical optimization and defect formation energy

Fig. 1 shows the crystal structures of $2 \times 2 \times 2$ ideal $BiVO_4$ as well as that with Bi, V and O vacancies. The integral structural formula of $2 \times 2 \times 2$ $BiVO_4$ is $Bi_{32}V_{32}O_{128}$, from which the vacancy concentration of Bi, V and O can be easily obtained as 3.125%, 3.125% and 0.781%. Due to the centrosymmetry, m-$BiVO_4$ is a nonpolar oxide. However, supercells might induce the transformation of monoclinic $BiVO_4$ into triclinic one. For simplicity, $BiVO_4$ with Bi, V or O vacancy located at different site are labeled as V_{1Bi}, V_{2Bi}, V_{1V}, V_{2V}, V_{1O}, V_{2O}, V_{3O} and V_{4O}. The optimized lattice parameters and unit-cell volumes of ideal, V_{1Bi}, V_{2Bi}, V_{1V}, V_{2V}, V_{1O}, V_{2O}, V_{3O} and V_{4O} $BiVO_4$ are calculated and listed in Table 1. It can be seen that the lattice parameters a, b and c change slightly while the corresponding volumes decrease for defective $BiVO_4$ compared with ideal $BiVO_4$. Actually, if the interaction between atoms along one direction is weakened, the lattice constant along that direction will become larger correspondingly, and vice versa. Due to different types of vacancies, the lattice parameters will change differently along each direction, the total effect of lattice change will result in the variation of corresponding volumes.

Besides, in order to study the relative energy stability of different vacancies in $BiVO_4$, the formation energies E_f of vacancy X (herein, X denotes Bi, V or O atom, respectively) in charge state q are calculated by the following equation [27]:

$$E_f[X^q] = E_{tot}[X^q] - E_{tot}[Bi_{32}V_{32}O_{128}, bulk] + \mu_X + q[E_F + E_v + \Delta V] \quad (1)$$

where $E_{tot}[X]$ is the total energy of different type of V_{Bi}, V_V or V_O $BiVO_4$, $E_{tot}[Bi_{32}V_{32}O_{128}, bulk]$ is the total energy of ideal bulk $BiVO_4$, μ_X is the corresponding chemical potentials of Bi, V and O atoms, among which μ_{Bi}, μ_V and μ_O are obtained by calculating the free energy of metallic bulk Bi, V and that of an O atom in one O_2 molecule: $\mu_O = \frac{1}{2}\mu(O_2)$. E_F is the Fermi level which is referenced to the valence band maximum (VBM) in the bulk, E_v is formation energies of charged states, and ΔV is correction term to align the reference potential in all considered materials above.

Herein, the considered defective $BiVO_4$ are all electrically neutral ($q = 0$). Therefore, the equation of formation energy is rewritten as:

$$E_f[X^0] = E_{tot}[X^0] - E_{tot}[Bi_{32}V_{32}O_{128}, bulk] + \mu_X \quad (2)$$

The formation energy of different defective $BiVO_4$ are calculated by Eq. (2) and the corresponding results are listed in Table 1. It can be observed that the formation energies of the same defective atom at different position show little difference, while they are in the order of V_V, V_{Bi}, V_O $BiVO_4$ from high to low. It is well known that the smaller value E_f of a defective system has, the higher thermal stability it possesses. Therefore, the calculated results indicate that V_{1O} $BiVO_4$ is most easily formed and stably existed among all types of defective $BiVO_4$.

3.2. Energy band structure

The conductivity and photocatalytic performance of semiconductors depend on the energy band structures. An appropriate band gap is required to improve the absorption of visible light and photocatalytic efficiency [28]. Fig. 2(a)-2(i) show the calculated energy band structures of ideal, V_{1Bi}, V_{2Bi}, V_{1V}, V_{2V}, V_{1O}, V_{2O}, V_{3O} and V_{4O} $BiVO_4$, respectively, where reciprocal k-point coordinates are G (0,0,0), F (0,0.5,0), Q (0,0.5,0.5), Z (0,0,0.5) for ideal and all types of defective $BiVO_4$. The Fermi level (E_F) is set at zero, as marked by the horizontal red dashed lines.

As for ideal $BiVO_4$, it can be seen that both the valence band maximum (VBM) and the conduction band minimum (CBM) are between G and F points, indicating ideal $BiVO_4$ is a direct band gap semiconductor. The calculated band gap is 2.108 eV which is consistent with the reported theoretical results [29,30]. However, due to the well-known limitation of DFT method, the calculated result is slightly smaller than experimental value of 2.4 eV [31].

The band gap is reduced as a vacancy is introduced in ideal $BiVO_4$. For V_{1Bi} or V_{2Bi} $BiVO_4$, the VBM is across the Fermi level (E_F) showing a p type semiconductor. The VBM is located at F point while CBM is located at a point between Q and Z, and the calculated indirect band gaps are reduced down to 1.994 eV and 1.989 eV, respectively. Compared with ideal $BiVO_4$, the bottom of conduction band shifts downwards by 0.095 eV, which favors the migration of photo-generated electrons. V_{1V} or V_{2V} $BiVO_4$ is also a p type semiconductor, the VBM is located at Q point while CBM is located at a point between G and F. Moreover, the calculated indirect band gaps are 1.792 eV and 1.793 eV, respectively. As for V_{1O}, V_{2O}, V_{3O} or V_{4O} $BiVO_4$, the band gaps are in the range of 0.465 eV–0.521 eV depending on the configuration of O vacancy. From Fig. 2(f)-2(i), it can be easily seen that the VBM of V_{1O}, V_{2O}, V_{3O} or V_{4O} is located at Z point and CBM is located at a point between G and F, showing indirect band gap. In indirect band gap materials, electrons will travel a certain longer distance in the k-space which make the recombination of photo-generated electrons and holes difficult, and thus it is helpful to improve the photocatalytic performances [32]. All the above mentioned band gaps are underestimated due to the limitation of DFT theory, however, they do not affect the relative variation