Hybrid Density Functional Theory Study of Native Defects and Nonmetal (C, N, S, and P) Doping in a Bi$_2$WO$_6$ Photocatalyst

Jihua Zhang,§ Panluo Deng,§ Mingsen Deng, Hujun Shen, Zhenzhen Feng, and Hang Li*

ABSTRACT: Native defects and nonmetal doping have been shown to be an effective way to optimize the photocatalytic properties of Bi$_2$WO$_6$. However, a detailed understanding of defect physics in Bi$_2$WO$_6$ has been lacking. Here, using the Heyd–Scuseria–Ernzerhof hybrid functional defect calculations, we study the formation energies, electronic structures, and optical properties of native defects and nonmetal element (C, N, S, and P) doping into Bi$_2$WO$_6$. We find that the Bi vacancy (Bivac), O vacancy (Ovac), S doping on the O site (SO), and N doping on the O site (NO) defects in the Bi$_2$WO$_6$ can be stable depending on the Fermi level and chemical potentials. By contrast, the substitution of an O atom by a C or P atom (CO, PO) has high formation energy and is unlikely to form. The calculated electronic structures of the Bivac, Ovac, SO, and NO defects indicate that the band-gap reduction of Ovac$^{2+}$, Bivac$^{3-}$, and SO defects is mainly due to forming shallow impurity levels within the band gap. The calculated absorption coefficients of Ovac$^{2+}$, Bivac$^{3-}$, and SO show strong absorption in the visible light region, which is in good agreement with the experimental results. Hence, Ovac$^{2+}$, Bivac$^{3-}$, and SO defects can improve the adsorption capacity of Bi$_2$WO$_6$, which helps enhance its photocatalytic performance. Our results provide insights into how to enhance the photocatalytic activity of Bi$_2$WO$_6$ for energy and environmental applications through the rational design of defect-controlled synthesis conditions.

1. INTRODUCTION

Visible-light-driven photocatalysts are promising candidates for solving the energy crisis and environmental pollution problems because of their high efficiency and clean and renewable characteristics. Recently, Bi$^{3+}$-based oxides such as BiOCl$^{16-19}$, Bi$_2$MoO$_6$,$^{10}$ and Bi$_2$WO$_6$,$^{11-13}$ are fascinating and of practical importance for visible-light-driven photocatalysts. Among these materials, Bi$_2$WO$_6$ as an n-type semiconductor with a 2.80 eV$^{13}$ band gap, is an interesting Aurivillius phase of perovskite layers inserted between Bi$_2$O$_2$ layers. Its potential applications, including solar cells, electrode materials, an excellent photocatalyst for water splitting, and photodegradation of organic pollutants$^{11,14,15,17,18}$.

However, the visible-light-responsive photocatalytic application of Bi$_2$WO$_6$ is limited by rapid recombination of exciplex pairs, ineffective charge separation, and poor visible-light absorption. Various improvement methods have been developed to improve the photocatalytic activity, for example, semiconductor coupling$^{20}$, morphology control,$^{21,22}$ noble metal deposition,$^{23}$ and metal or nonmetal ion doping.$^{24-33}$ All these methods can improve the photocatalytic activity of Bi$_2$WO$_6$. Nonmetallic element doping is regarded as an efficient approach to enhance the activity. For example, Hoang et al.$^{30}$ synthesized N-doped Bi$_2$WO$_6$ by using a two-step microwave-assisted and hydrothermal method. It was found that 0.25% (atomic ratio) N-doped Bi$_2$WO$_6$ exhibited the best photocatalytic activity. This is due to the most significant decrease in the recombination rate of photo-generated electron•hole pairs. Fu et al.$^{29}$ reported that doping Bi$_2$WO$_6$ with 0.5% B displayed the highest photocatalytic...

Received: July 31, 2020
Accepted: October 26, 2020
Published: November 5, 2020
activity under visible-light irradiation. This is because the doped B atoms could act as electron traps and facilitate the separation of photogenerated electron−hole pairs. Shang et al.31 demonstrated that doping Bi₂WO⁶ with N could significantly enhance photocatalytic activities. The reasons are that N doped into Bi₂WO⁶ not only broadens the range of light absorption in the visible region but also inhibits the photogenerated electron−hole recombination losses and increases the transfer rate. However, the nature of the promoting effects remains elusive. A complete understanding of the nonmetallic-induced photocatalytic activity of Bi₂WO⁶ is still lacking.

The formation of intrinsic defects (such as Bi vacancy, W vacancy, O vacancy, and so on) may compensate the extrinsic nonmetallic doping into Bi₂WO⁶. Therefore, the intrinsic defects of Bi₂WO⁶ had been studied both theoretically and experimentally. For example, Huo et al.34 showed that the photocatalytic NO oxidation activity was enhanced by introducing oxygen vacancy defects into Bi₂WO⁶. Using the GGA (generalized gradient approximation) + U method, they reported that oxygen vacancies narrow band gaps compared with perfect Bi₂WO⁶. Di et al.15 had engineered bismuth vacancies into Bi₂WO⁶ using a highly efficient template-directed strategy. They found that bismuth vacancies favor water oxidation reactions. Their PBE (Perdew−Burke−Ernzerhof) calculations suggest that bismuth vacancies in Bi₂WO⁶ would induce new energy levels in the band gap, increasing its conductivity.

Theoretically, intrinsic defects and nonmetallic doping in Bi₂WO⁶ have been calculated with the GGA-PBE and DFT + U method.15,28,34−36 However, they only focus on neutral impurities and their electronic properties. Note that the formation energy of a neutral defect is independent of the position of the Fermi level. Whether an impurity or defect becomes electrically active or instead remains inactive often depends on the growth conditions (e.g., the presence of native defects) and cannot directly be inferred from a DFT calculation on a neutral defect alone.37 In addition, GGA-PBE yield significantly underestimated band gaps, i.e., 1.85−1.95 eV, compared to the experimental value of 2.80 eV.13 Moreover, the GGA + U correction was only employed for W's d electrons, whereas all other components were treated within GGA. Hence, quantitatively more reliable calculations are required. As proposed by Heyd, Scuseria, and Ernzerhof (HSE06),38,39 it provides the best overall performance compared to GGA-PBE and GGA + U. More importantly, previous results have shown that the HSE06 hybrid functional is a reliable method to calculate transition levels and formation energies of defects.40

This paper systematically studies the doping properties for both intrinsic and nonmetal (C, N, S, and P) doping of Bi₂WO⁶ and understands how they can change the electronic structure of Bi₂WO⁶.
structure and optical absorption properties using the HSE06 hybrid approach. We calculate the transition energies and formation energies of intrinsic and impurity defects and Fermi-level pinning positions. The Bivac, Ovac, S O, and NO have rather low formation energies. Due to CO and PO having higher formation energies, they are unlikely to form. The calculated electronic structures of Bivac, Ovac, S O, and NO defects implied that Ovac²⁺, Bivac³⁻, and SO defects can narrow the band gap of Bi₂WO₆, and no recombination centers occurred, which can improve photocatalysis of Bi₂WO₆. The calculated absorption coefficients of Ovac²⁺, Bivac³⁻, and SO show strong absorption in the visible region. Our results suggest that O vac²⁺, Bivac³⁻, and SO doping is able to narrow the band gap, and thus these defects are good dopant candidates to tailor the visible light absorption property of Bi₂WO₆ photocatalysts.

2. RESULTS AND DISCUSSION

2.1. Formation Energy. For vacancy calculations, one atom is removed from the supercell, and the remaining atoms are allowed to relax. Here, we consider three types of intrinsic defects in the Bi₂WO₆ lattice for various possible charge states, including Bivac, W vac, and Ovac. The substitutional defect XO is created by replacing a lattice O by X (X = C, N, S, and P). The defect formation energies for various charge states in Bi₂WO₆ are plotted as a function of the electronic Fermi energy for five representative chemical potential conditions with the finite size corrections in Figure 1. As shown in Figure 1, all the defects’ formation energies depend on the growth condition and the Fermi level. The energy of a defect with a charge state is only shown for the range of Fermi levels where the charge state has the lowest energy. In Figure 1, the line’s slope is associated with the most stable charge state of a defect, and the transition levels lie where the slopes change. Moreover, Figure 1 depicts that the formation energies of intrinsic defects and nonmetal-doped (C, N, S, and P) defects in the charge-neutral charge states are constant regardless of the variations in Fermi energy.

In Figure 1a,c,e, at chemical potentials C, E, and M, the results show that the dominant native acceptor is Bivac, while the primary native donor is Ovac. The Fermi level is pinned (where the formation energy lines cross the energy overlap of the lowest-energy donor and acceptor) by Bi vac and Ovac. However, the position of the Fermi level pinning is different. At chemical potentials C, the Fermi level is pinned to be at ∼1.1 eV above VBM, showing a p-type conductivity. At chemical potential E, as Ovac is positively charged and Bivac is negatively charged for Fermi level within the band gap, these defects self-compensate, and the Fermi level is pinned roughly around the midgap, resulting in the intrinsically insulating property. At chemical potentials M, the Fermi level is pinned to be at ∼0.75 eV below CBM within the n-type region. These results imply that it is possible to control the growth condition to obtain the conductivity from p-type to good n-type. At chemical potentials C and E, the formation energy of the W vac defect is similar to that of O₃ and O₅. Whereas, at chemical potential M, the formation energy of the W vac defect significantly increased. These results indicated that the
oxygen-rich environment could promote the formation of \( W \) vacancies. Moreover, under these conditions (chemical potentials \( C \), \( E \), and \( M \)), the formation energy of \( O_p \) and \( O_c \) is very high, > 9 eV, which means that it is difficult to dope \( C \) and \( P \) into \( \text{Bi}_2\text{WO}_6 \). For PBE results, as shown in Figure S2 of the Supporting Information, the transition trends of formation energy as a function of the Fermi level are almost identical with the transition trends calculated by the HSE method. However, the energy of the pinned Fermi level is different. This is because the PBE method underestimates the band gap of \( \text{Bi}_2\text{WO}_6 \).

However, in Figure 1b,d, under the oxygen-poor/bismuth-rich conditions (chemical potentials \( D \) and \( F \)), we find that the formation energy of \( \text{Bi}_{\text{vac}} \) increases evidently when the formation energy of \( \text{ON} \) and \( \text{OS} \) both decrease. Thus, the lowest-formation energy defects are \( \text{VO} \) as \( \varepsilon < 1.55 \text{ eV} \). When \( \varepsilon > 1.55 \text{ eV} \) formation energies of \( \text{O}_{\text{vac}} \) and \( \text{OS} \) are almost identical, which is the lowest-formation energy defects between these ranges. We notice that the formation energy of \( \text{ON} \) is also low in the same range of \( \varepsilon \). Therefore, it is easy to synthesize \( N \)-doped bismuth tungstate experimentally.30,31,41 Under these conditions, the Fermi level is pinned by \( \text{O}_{\text{vac}} \) and \( \text{ON} \), which is to be at \( \sim 0.79 \text{ eV} \) below CBM, within the n-type region. Meanwhile, the formation energy of the \( \text{W}_{\text{vac}} \) defect is the highest than others for the Fermi level within the band gap. Moreover, \( O_p \)'s and \( O_c \)'s formation energies both decrease, but the value is about 6 eV, which is still very high. These results suggested that \( \text{W}_{\text{vac}} \), \( O_p \), and \( O_c \) defects are unlikely to form.

The transition (ionization) levels of low-energy defects depend on free carrier generation and its contribution to the electrical conductivity,42 which can be derived according to the turning points in Figure 1. We are concerned about the transition level of \( \text{Bi}_{\text{vac}}, \text{O}_{\text{vac}}, \) and \( \text{ON} \) defects due to lower formation energy compared with the other defects. The \( e^-(/+0) \) thermodynamic transition level (ionized from neutral to \(-1/0 \) charged) of \( \text{Bi}_{\text{vac}} \) is located at 0.17 \text{ eV} above VBM, thereby demonstrating its shallow donor character, which agrees with the experimental observation.15 For \( \text{O}_{\text{vac}} \), the donor \(+2/+1\) transition level is observed at 0.45 \text{ eV} above VBM, while \(+1/0\) donor levels appear to be localized deep into the band gap 1.50 \text{ eV} above VBM. Unlike the \( \text{O}_{\text{vac}} \) the density of states (DOS) for \( \text{O}_{\text{vac}}^2+ \) show delocalized distribution (we will address this issue in Section 2.2). This suggests that the \( \text{O}_{\text{vac}}^2+ \) acceptor state is not a deep, localized state. Such shallow levels not only extend the absorption spectra of \( \text{O}_{\text{vac}}^2+ \) in \( \text{Bi}_2\text{WO}_6 \) but also play a role as trap levels, which increase the carrier lifetime.43,44 For all the chemical potentials, the formation energy of the donor \( \text{O}_{\text{vac}}^2+ \) is the lowest when the conductivity is p-type. Therefore, the ionization of the dominant \( \text{O}_{\text{vac}}^2+ \) with a high concentration can produce an evident amount of hole carriers, resulting in good p-type conductivity. Moreover, the acceptor \((-1/0\) level associated with \( \text{ON} \) appears to be localized deep at 1.38 \text{ eV} above VBM, which may act as recombination centers.

2.2. Electronic Structure with HSE06. In Figure 2, we present the total density of states (TDOS) and partial density of states (PDOS) for different native defects of \( \text{Bi}_2\text{WO}_6 \) between \(-5 \) and 6 \text{ eV} using the HSE06 functional. We focus on the defects \( \text{O}_{\text{vac}}, \text{O}_{\text{vac}}^+, \text{O}_{\text{vac}}^{2+}, \text{Bi}_{\text{vac}}, \text{Bi}_{\text{vac}}^+, \text{N}_{\text{O}}, \text{N}_{\text{O}}^-, \) and \( \text{SO} \). This is because these defects have the lowest formation energies under different chemical conditions for a certain range of Fermi level. The electronic properties of pure \( \text{Bi}_2\text{WO}_6 \) were also calculated to compare with native defects of \( \text{Bi}_2\text{WO}_6 \) as shown in Figure 2a. For pure \( \text{Bi}_2\text{WO}_6 \) the valence band maximum (VBM) of \( \text{Bi}_2\text{WO}_6 \) is predominantly composed of \( O_2p \) states, which hybridize with the \( Bi_6s \) \& \( W_5d \) states of relatively lower density. Unlike the VBM, the

Figure 3. Spin-polarized DOS for the (a) \( \text{N}_{\text{O}} \), (b) \( \text{N}_{\text{O}}^+ \), and (c) \( \text{SO} \) defects using the HSE06 functional. The red dotted lines indicate the Fermi level. Positive (negative) values of the DOS denote spin up (down).
conduction band minimum (CBM) has nearly identical contributions from the O 2p orbitals and the W 5d orbitals. These results are in good agreement with previous theoretical results.\textsuperscript{15,36,45}

For the Bivac\textsuperscript{2+} defect, as shown in Figure 2b, we find that an occupied state in the gap (at about 0.1 eV below the Fermi level) and an isolated empty band (at about 0.9 eV above the Fermi level). These two states are mainly composed of O 2p orbitals, which may act as recombination centers when electron–hole pairs are generated. This is consistent with a previous theoretical result,\textsuperscript{15} where they only focus on the neutral bismuth vacancy. Moreover, there is a shallow defect level underneath the CBM concerning that of the pure Bi\textsubscript{2}WO\textsubscript{6}. An attempt to add an electron, for the Bivac\textsuperscript{2+} defect, we observe from Figure 2c that the Fermi level is at the edge of the conduction band, which exhibits typical n-type characteristics. There are two occupied states (one is spin up, and another is spin down) near the Fermi level. Its localization character is fragile. This suggests that the band gap of Bi\textsubscript{2}WO\textsubscript{6}/Bi\textsubscript{2}WO\textsubscript{6} is narrower than the gap of undoped Bi\textsubscript{2}WO\textsubscript{6}, and thus the photoabsorption probability increases.

In addition, these delocalization characters of the defect level and enhanced DOS will favor the electron transition into the conduction band under the irradiation, leading to a higher carrier concentration and an increasing electronic conductivity.\textsuperscript{46,47} It has been reported that bismuth vacancy-rich Bi\textsubscript{2}WO\textsubscript{6} exhibits significantly increased visible-light photocatalytic oxygen evolution activity than that of pristine Bi\textsubscript{2}WO\textsubscript{6}.\textsuperscript{15} This activity can be explained by the formation of the Bivac\textsuperscript{2+} defect. This is because not only the formation energy of Bivac\textsuperscript{2+} is the lowest under oxygen-rich conditions when \( E_F > 2.31 \text{ eV} \), but also it has a narrow band gap, such that its absorption is increased. More importantly, there is no recombination centers that occurred.

For the neutral oxygen vacancy, as shown in Figure 2d, there are two spin-degenerated occupied states (the positive is spin up, and the negative is spin down) in the vicinity of midgap. These two states are dominated by Bi 6p orbitals, serving as a recombination center, which decreases the efficiency of charge separation. As shown in Figure 2e, the DOS of Ovac\textsuperscript{−} is similar to the DOS of Bi\textsuperscript{2+}. There is an occupied state in the gap (at about 0.1 eV below the Fermi level) and an isolated empty band (at about 0.9 eV above the Fermi level), which also act as recombination centers. However, as shown in Figure 2f, for Ovac\textsuperscript{−}, the Fermi level is at the edge of the valence band, which exhibits typical p-type characteristics. There are two empty states (one is spin up, and another is spin down) near the Fermi level, which shows the delocalization character. This suggests that the band gap of Ovac\textsuperscript{−}/Bi\textsubscript{2}WO\textsubscript{6} is narrower than the band gap of pristine Bi\textsubscript{2}WO\textsubscript{6} and its absorption is increased. The Ovac\textsuperscript{−} defect can enhance the photocatalytic activity, while Ovac\textsuperscript{−} degrades, and it is desirable to induce the former one as much as possible and suppress the latter. This can be achieved by controlling \( E_F < 0.45 \text{ eV} \) under any environment (Figure 2), as discussed in the previous section.

In Figure 3, we plot the TDOS and PDOS for different nonmetal elements (N and S) doping into Bi\textsubscript{2}WO\textsubscript{6} between −5 and 6 eV using the HSE06 functional. For the N\textsubscript{3}\textsuperscript{−} defect, as shown in Figure 3a, we found an isolated empty band (at about 1.0 eV above the Fermi level). This state is mainly composed of N 2p orbitals, which may act as recombination centers when electron–hole pairs are generated. This is consistent with the localized deep (−1/0) transition level of O\textsubscript{3}\textsuperscript{−} that appears to be at 1.38 eV above VBM. Based on the previous analysis, this defect is not natural to be formed because the formation energy of N\textsubscript{3}\textsuperscript{−} is higher than that of compensated defect Ovac\textsuperscript{−} under any conditions. When one more electron is injected, the empty band of O\textsubscript{3}\textsuperscript{−} is occupied by the extra electron (Figure 3b). The occupied states are moved below the Fermi level. These states are mainly composed of N 2p orbitals, which results in a higher degree of delocalization and a correspondingly reduced band gap of pure Bi\textsubscript{2}WO\textsubscript{6}. As shown in Figure 2, under the oxygen-poor/bismuth-rich conditions, the formation energy of N\textsubscript{3}\textsuperscript{−} is almost the same as the lowest formation energy (Ovac\textsuperscript{−} and O\textsubscript{3}\textsuperscript{−}). Therefore, experimentally synthesized N-doped Bi\textsubscript{2}WO\textsubscript{6} samples\textsuperscript{30,31,41} may be N\textsubscript{3}\textsuperscript{−}. This explains the experimental observations of a better photocatalysts efficiency performance of N-doped Bi\textsubscript{2}WO\textsubscript{6}.

It is shown that the band gap of S-doped Bi\textsubscript{2}WO\textsubscript{6} is about 2.33 eV in Figure 4c, which is reduced by 0.46 eV comparing with pure Bi\textsubscript{2}WO\textsubscript{6}. The substitution S mainly modifies the valence band edge and forms the O 2p and S 2p hybridization states on the valence band’s band edge. Thus, the S doping narrows the band gap of Bi\textsubscript{2}WO\textsubscript{6} without localized gap states, which yields a clean band gap by maintaining the stability of the photocatalyst and avoids the formation of the recombina-
tion centers, leading to better photocatalytic performance. Therefore, the S–Bi2WO6 may be good candidates for visible-light photocatalysis.

It is known that the shallow levels have delocalized wave functions. On the other hand, deep levels have localized ones.48–50 As shown in Figure 4, we have plotted the wave-function squares of the Bivac−, Ovac−, Ovac2+ defects near the Fermi level in the band gap. Figure 4a,b,h plots the wave-function square of the Bivac− and Ovac− defect states. The wave function of the defect states distributes not only around the defects but also around O atoms away from the W atom, indicating a delocalized feature, which is consistent with the result that Bi3+ vac, O2− vac, and S0 defects narrow the band gap, respectively. It is seen that the wave function is localized around defects, consistent with the deep-level feature.

Generally, the conduction band (CB) and valence band (VB) edge potentials of a semiconductor play a vital role in the photocatalysis process. The Mulliken electronegativity theory51 can predict the conduction band and valence band potentials of Bi2WO6: CB = \( E_C = E^0 - 0.5E_F \) (or VB = \( E^0 + 0.5E_F \)), where \( E_C \) (VB) is the conduction (valence) band potential, \( E_F \) is the energy of the free electron in the hydrogen scale (approximately 4.5 eV),52 and \( E_F \) is the band gap energy of the Bi2WO6 (2.79 eV). Using the Mulliken electronegativities, the band position and photoelectric thresholds for many compounds have been calculated.53–55

For the Mulliken electronegativity (\( \chi \)) of compound A_{a,b,c} can be calculated according to the following equation:56–58

\[
\chi(A_{a,b,c}) = (\chi(A)^a(\chi(B)^b(\chi(C)^c)^{1/a+b+c}, \text{ where } \chi(A), \chi(B), \text{ and } \chi(C) \text{ are the absolute electronegativity of the A atoms, B atoms, and C atoms respectively; the } a, b, c \text{ are the number of A atoms, B atoms, C atoms in an } A_{a,b,c} \text{ compound, respectively. According to the Mulliken definition, per atom’s absolute electronegativity is equal to the arithmetic mean of the atomic electron affinity (A) and the first ionization energy (I).}59 \text{ From these data, we obtained the Mulliken electronegativity of Bi, W, O, N, and S that are 4.12, 4.40, 7.54, 7.24, and 6.22 eV, respectively.}60 \text{ The } \chi \text{ value for Bi2WO6 is 6.2 eV. Hence, the } E_C \text{ value of Bi2WO6 was calculated to be +0.31 eV, and the } E_V \text{ value was estimated to be } +3.10 \text{ eV, which agreed well with the previous calculation.}60

To evaluate the defects’ influence on the photocatalytic activity of Bi2WO6, the CBM and VBM of the Bi3+ vac, O2− vac, and S0 defects concerning the Bi2WO6 are presented in Figure 5. As shown in Figure 5, for the Bi3+ vac defect, the VBM is raised by 0.25 eV relative to that of the pure Bi2WO6. This result indicated that the oxidizing capacity of the VB and the reducing capacity of the CB are reduced. Meanwhile, some defect states are introduced in the band gap, and the electron transition among the VB, CB, and these gap states leads to the visible-light absorption. For O2− vac defects, the CBM does not change, and the VBM is reduced by 0.24 eV relative to that of the pure Bi2WO6, which suggests that the oxidizing capacity of VB will decrease. This is due to the band gap is reduced to 2.84 eV. Only one spin up and one spin down defect states appear in the band gap. Immensely, for the S0 defect, the CBM does not change, and the VBM is raised by 0.25 eV relative to that of the pure Bi2WO6. This result suggested that the oxidizing capacity of the VB is improved. One occupied state and one unoccupied state are introduced in the band gap, improving the visible-light absorption capacity of Bi2WO6.

2.3. Optical Properties. Generally, the optical absorption properties of photocatalytic semiconductor material are closely related to its electronic band structure. This is a significant factor affecting the photocatalytic activity.51 In this study, we focus on the Bi3+ vac, O2− vac, and S0 defects. This is because these defects narrow the band gap of Bi2WO6, and no recombination centers are formed. The calculated absorption coefficients along the [001] direction for Bi3+ vac, O2− vac, and S0 defects in Bi2WO6 are shown in Figure 6. For comparison, the absorption coefficient of Bi2WO6 was also calculated. Figure 6 indicates that pure Bi2WO6 cannot absorb the visible light effectively due to its wide band gap. After Bi3+ vac, O2− vac, and S0 doping, the absorption coefficients in the visible-light region are enhanced, and a redshift is observed on the absorption edge. The high optical absorption results from the narrow band gap and the weak electron–hole recombination, as mentioned already. In the energy region between 1.5 and 2.75 eV, the absorption coefficients of Bi3+ vac and O2− vac are more extensive than that of S0. When the energy is higher than 2.8 eV, the absorption coefficient is enhanced by about four times as compared with...
pure Bi$_2$WO$_6$. This is caused by absorption between the 2p orbital of O in the valence bands and the 5d orbital of W in the conduction bands according to the PDOS in Figures 2 and 3. Therefore, the enhanced absorption of incident photons will enhance the photocatalytic efficiency of Bi$_2$WO$_6$, O$_{vac}$, and S$_O$ doping Bi$_2$WO$_6$ in the near-ultraviolet region. These results are also in good agreement with the electronic properties mentioned above and previous experimental reports.

### 3. CONCLUSIONS

Using the HSE06 hybrid approach, we calculate the formation energies, electronic structure, and optical properties of native defects and nonmetals (C, N, S, and P) doping in a Bi$_2$WO$_6$ photocatalyst. We find that the formation energies strongly depend on the impurity charge states and Fermi level position. The calculated formation energies and transition levels demonstrate that Bi$_{vac}$, O$_{vac}$, S$_O$, and N$_O$ have relatively low formation energies. However, C$_O$ and P$_O$ are more challenging to form than S$_O$ and N$_O$ due to the higher formation energies. The calculated electronic structures of Bi$_{vac}$, O$_{vac}$, S$_O$, and N$_O$ defects reveal that the O$_{vac}$, Bi$_{vac}$, and S$_O$ defects facilitate the delocalization of electrons. This leads to narrow band gaps of Bi$_2$WO$_6$ and hinders the formation of recombination centers, which would improve the photocatalytic performance of Bi$_2$WO$_6$. We reveal that the semiconductor nature of Bi$_2$WO$_6$ can be tuned from p-type to n-type by changing the growth conditions. The calculated absorption coefficients of O$_{vac}$, Bi$_{vac}$, and S$_O$ show strong absorption in the visible region, which is in good agreement with the experimental results. Based on these results, we suggest that O$_{vac}$, Bi$_{vac}$, and S$_O$ doping are good dopant candidates to tailor the visible-light absorption property of Bi$_2$WO$_6$ photocatalysts. Our results provide a comprehensive investigation of the charged defect of the Bi$_2$WO$_6$, which provides a useful strategy for further optimizing the photocatalytic performance of Bi$_2$WO$_6$ and its future applications.

### 4. COMPUTATIONAL METHODS

First-principles calculations based on the density functional theory (DFT) were performed using the projected augmented wave (PAW) method implemented in the Vienna ab initio simulation package (VASP). The Kohn–Sham one-electron states are expanded using the plane-wave basis set with a kinetic energy cutoff of 500 eV. The Perdew–Burke–Ernzerhof (PBE) exchange-correlation (XC) functional within the GGA was employed for the geometrical optimization. Since the GGA approach usually underestimates the semiconductor nature of Bi$_2$WO$_6$, we used the hybrid exchange-correlation functional of Heyd, Scuseria, and Ernzerhof (HSE) for a more accurate description of the electronic structure. We tested the energy gap of pristine Bi$_2$WO$_6$ by adjusting the Hartree–Fock mixing parameter from 0.15 to 0.35. It was found that when $\alpha = 0.15$, the calculated band gap is 2.79 eV for Bi$_2$WO$_6$ closely to the experimental band gap 2.80 eV. Therefore, in our calculations, we chose the mixing parameter equals 0.15 for the short-range Hartree–Fock exchange instead of the commonly used value of 0.25. The PAW potentials with the valence electrons 6s$^2$6p$^6$ for Bi, 5d$^6$6s$^2$ for W, 2s$^2$2p$^4$ for O, 2s$^2$2p$^2$ for C, 2s$^2$2p$^2$ for N, 3s$^2$3p$^3$ for P, and 3s$^3$3p$^3$ for S have been employed. The Monkhorst–Pack $k$-point meshes for the 36-atom pure Bi$_2$WO$_6$ primitive cell is $6 \times 2 \times 6$. Vacancy and doping defects calculations were performed in a $2 \times 1 \times 2$ supercell (144 atoms). For these systems, we used a $2 \times 1 \times 2$ k-point, which was found to be sufficient to reach convergence for bulk calculations and used for geometry optimization and electronic property calculations. For defects calculations, the supercells’ sizes were kept, but the atomic positions were relaxed until forces were smaller than 0.03 eV/Å, corresponding to the energy convergence smaller than 0.0001 eV. For all calculations, spin polarization was taken into consideration. The experimental atomic positions were employed as the starting points of relaxation, and the following calculations were performed using the relaxed atomic positions.

The formation energy of a defect X in charge state $q$ is defined as

$$E_f(X^q) = E_{tot}(X^q) - E_{tot}(\text{bulk}) - \sum_i n_i \mu_i$$

$$+ q[E_F + E_V + \Delta V] + E_{corr}$$

(1)

where $E_{tot}(X^q)$ is the total energy of the Bi$_2$WO$_6$ in the presence of a defect X in charge state $q$ in the supercell, and $E_{tot}(\text{bulk})$ is the total energy of pristine Bi$_2$WO$_6$ in the absence of a defect in the supercell. For charged defects ($q \neq 0$), the formation energy depends on the Fermi level ($E_F$), which varies from the valence-band maximum (VBM) to the calculated conduction-band minimum (CBM). In this study, $E_F$ at the VBM is set to 0 eV, and CBM is set to 2.79 eV, respectively. $E_V$ is the energy cost in removing an electron from the pure supercell. $\Delta V$ is determined by aligning O atoms’ 1s core levels far away from the defect center in defective cells to the pure bulk. Additionally, $E_{corr}$ is a correction term to account for supercell errors such as image–charge interactions. This is because of the supercell and periodical boundary conditions used in the DFT calculations. Following the approach given by Lany and Zunger, the image–charge correction term is written as

$$E_{corr} = \left[1 + f \frac{q^2 \alpha}{2eL}\right]$$

(2)

where $f$ is a shape factor related to the supercell geometries, $q$ is the total charge, $\alpha$ is the Madelung constant, $e$ is the static dielectric constant of the pristine bulk, and $L$ is the linear dimension of the supercell ($L = V^{1/3}$, $V$ is the volume of the supercell). $n_i$ corresponds to the number of atoms added to ($n_i > 0$) or taken from ($n_i < 0$) the system to form the X. Defects with lower formation energies will form more easily and occur in higher concentrations. $\mu_i = E_i + \Delta \mu_i$ is the chemical potentials of the constituent i in the reservoir, where $E_i$ denotes the calculated standard state energies. The values of $\Delta \mu_i$ can vary depending on the environmental conditions in thermodynamic equilibrium but are restricted by the relation

$$2\Delta \mu_{Bi} + \Delta \mu_W + 6\Delta \mu_O = \Delta H_f(Bi_2WO_6),$$

(3)

where $\Delta H_f(Bi_2WO_6)$ is the formation enthalpy of per formula of Bi$_2$WO$_6$, which is equal to $-14.98$ eV according to our HSE06 calculations. This result is very close to previous $-15.50$ eV estimates using the PBE method but higher than the experimental value of $-11.52$ eV. The upper bound is $\Delta \mu_i \leq 0$ as, at this point, precipitation of element i to its standard state occurs. Thereby, the non-formation of the pure solids Bi and W or O$_2$ gas, requires

$$\Delta \mu_{Bi} < 0, \Delta \mu_W < 0, \Delta \mu_O < 0$$

(4)
The following relationships should be satisfied to avoid the formation of other oxide phases (such as WO₂, WO₃, and Bi₂O₃):

\[ \Delta \mu_\text{W} + 2\Delta \mu_\text{O} < \Delta H_i(\text{WO}_2) \]  
\[ \Delta \mu_\text{W} + 3\Delta \mu_\text{O} < \Delta H_i(\text{WO}_3) \]  
\[ 2\Delta \mu_\text{Bi} + 3\Delta \mu_\text{O} < \Delta H_i(\text{Bi}_2\text{O}_3) \] (1)-(7)

Eqs 3–7 determine the phase diagram of Bi₂WO₆ as a two-dimensional panel with two independent variables, \( \Delta \mu_\text{Bi} \) and \( \Delta \mu_\text{W} \). The PBE- and HSE06-calculated stable regions for Bi₂WO₆ in the phase diagram are shown as the light green and light blue shaded quadrilateral in Figure S1 and Figure 7.

![Figure 7. Ranges of chemical potentials showing the formation of different competing phases under thermodynamic equilibrium calculated by HSE06. The light-blue shaded quadrilateral CDEF is the region where Bi₂WO₆ is stable without forming other phases. Specific points C, D, E, F, and M are chosen as the representative chemical potentials for the following defect formation energy calculation.](image)

respectively. The values inside of these regions induce no precipitation of the second phase. Our PBE result is in excellent agreement with the previous theoretical studies. The stability regions are estimated by the PBE and HSE06 methods, having almost the same shape and size. Thus, the coordinates of C, D, E, F, and M in Figure S1 are not much different from those of C, D, E, F, and M in Figure 7. This indicates that the calculated results of the two methods agree with each other.

Five representative chemical potentials points C, D, E, F, and M were selected in the light-blue shaded regions to calculate defect formation energies. C and E represent oxygen-rich conditions, D and F indicate oxygen-poor and bismuth-rich conditions, and M in the stable region represents condition between O-rich conditions and O-poor/bi-rich conditions, respectively. Moreover, we obtained the values of \( \Delta \mu_\text{Bi} \), \( \Delta \mu_\text{W} \), and \( \Delta \mu_\text{O} \) and then calculated the values of corresponding chemical potentials using \( \mu_i = E_i + \Delta \mu_j \); the results are listed in Table 2.

When considering impurity (C, N, P, and S) doping, impurities' chemical potentials should also be considered. The following constraints are enforced to avoid the formation of impurity-related phases:

\[ \Delta \mu_\text{C} < 0, \Delta \mu_\text{N} < 0, \Delta \mu_\text{P} < 0, \Delta \mu_\text{S} < 0 \] (8)

\[ \Delta \mu_\text{C} + 2\Delta \mu_\text{O} < \Delta H_i(\text{CO}_2) \] (9)

\[ 2\Delta \mu_\text{N} + 5\Delta \mu_\text{O} < \Delta H_i(\text{N}_2\text{O}_5) \] (10)

\[ 2\Delta \mu_\text{P} + 5\Delta \mu_\text{O} < \Delta H_i(\text{P}_2\text{O}_5) \] (11)

\[ \Delta \mu_\text{S} + 3\Delta \mu_\text{O} < \Delta H_i(\text{SO}_3) \] (12)

\[ 2\Delta \mu_\text{Bi} + 3\Delta \mu_\text{S} < \Delta H_i(\text{Bi}_2\text{S}_3) \] (13)

For example, for N doping at C chemical potentials, \( \Delta \mu_\text{N} = -0.21 \text{ eV} \). In this case, the \( \mu_\text{N} = -9.68 \text{ eV} \) is used for the calculation of formation energy for N-doping defects. The derived upper-limit chemical potentials for C, N, P, and S by HSE06 are listed in Table 1, considering the special growth conditions.

The formation energy (given per formula unit) calculated by HSE06 for the various possible competing phases (Bi₂O₃, WO₂, WO₃, CO, CO₂, P₂O₅, SO₂, SO₃, and Bi₂S₃ WC N₂O₅) are shown in Table 1 together with the available experimental values. It is seen that the calculated values are in good agreement with the previous theoretical studies.

We further calculated the thermodynamic transition energy levels (\( \epsilon(q/q') \)) of the defect in Bi₂WO₆ using the following expression:

\[
\epsilon(q/q') = \frac{E_i(X^q) - E_i(X^{q'})}{q' - q}
\] (14)

where \( E_i(X^q) \) and \( E_i(X^{q'}) \) represent formation energies of the doped Bi₂WO₆ in the charge states \( q \) and \( q' \), respectively. \( \epsilon(q/q') \) refers to the Fermi level at which the formation energies of the defect in charge \( q \) and \( q' \) cross.

The imaginary part \( \epsilon_i(\omega) \) of the dielectric function \( \epsilon(\omega) \) is calculated using the standard formulation.
Table 2. Chemical Potentials Used to Represent Growth Conditions (C, D, E, F, and M) for Bi2WO6

| condition | μBι | μW | μO | μC | μBi | μS | μS |
|-----------|-----|----|----|----|-----|----|----|
| C         | −7.62 | −22.63 | −6.16 | −13.87 | −9.68 | −13.21 | −8.88 |
| D         | −4.29 | −15.97 | −8.38 | −9.96 | −9.47 | −7.66 | −5.34 |
| E         | −7.22 | −23.43 | −6.16 | −13.87 | −9.68 | −13.21 | −8.88 |
| F         | −4.29 | −17.59 | −8.11 | −9.97 | −9.47 | −8.34 | −5.34 |
| M         | −6.29 | −20.31 | −6.99 | −12.21 | −9.47 | −11.14 | −6.39 |

“M is one point in the Bi2WO6 stability region.

\[
\varepsilon_2(\omega) = \frac{V e^2}{2\pi \hbar m^* \omega^2} \int d^3k \sum_{n,\epsilon} |< nk| \tilde{p}| n'k > |^2
\]

\[
f_{n\epsilon}(1 - f_{n'\epsilon})\delta(E_{n\epsilon} - E_{n'\epsilon} - \hbar\omega),
\]

where \( V \) is the cell volume, \( \hbar\omega \) is the energy of the incident photon, \( p \rightarrow \) is the momentum operator, \( b_{n\epsilon} \rightarrow \) denotes the electronic state \( b_{n\epsilon} \) in band \( n \), and \( f_{n\epsilon} \rightarrow \) is the Fermi occupation function. The real part \( \varepsilon_1(\omega) \) is related to \( \varepsilon_2(\omega) \) from the Kramer–Krönig transformation. The absorption coefficient \( \alpha(\omega) \) can be derived from \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) as follows:77

\[
\alpha(\omega) = \frac{\sqrt{\omega}}{c}\frac{1}{\varepsilon} \left[ \varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) - \varepsilon_1(\omega) \right]^{1/2}
\]

It should be noted that many-body perturbation GW (“G” is the one-body Green’s function, which describes the propagation of a particle in an interacting system, and “W” is the linear response dynamically screened Coulomb interaction) approximation is used to calculate quasiparticle excitations in semiconductors and insulators, as measured by direct and inverse photoemission experiments.76 For the optical spectrum, the Bethe–Salpeter equation (BSE) is solved to include the effects of electron–hole interactions.79 However, more GW and BSE calculations for doped Bi2WO6 are limited by their expensive computational time in this paper.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03685.

Ranges of chemical potentials for Bi2WO6 under thermodynamic equilibrium calculated by PBE and defect formation energy calculations of Bi2WO6 supercells with various types of point defects in different charge states using the PBE-DFT method as a function of the Fermi level (PDF)

AUTHOR INFORMATION

Corresponding Author
Hang Li – Institute for Computational Materials Science, School of Physics and Electronics, Henan University, Kaifeng 475004, China; Email: hang.li@vip.henu.edu.cn

Authors
Jihua Zhang – Guizhou Provincial Key Laboratory of Computational Nano-Material Science, Guizhou Education University, Guiyang 550018, China; orcid.org/0000-0003-4308-3515
Panluo Deng – Institute for Computational Materials Science, School of Physics and Electronics, Henan University, Kaifeng 475004, China

Mingsen Deng – Guizhou Provincial Key Laboratory of Computational Nano-Material Science, Guizhou Education University, Guiyang 550018, China; orcid.org/0000-0002-3331-3850
Hujun Shen – Guizhou Provincial Key Laboratory of Computational Nano-Material Science, Guizhou Education University, Guiyang 550018, China; orcid.org/0000-0001-6117-0597
Zhenzhen Feng – Institute for Computational Materials Science, School of Physics and Electronics, Henan University, Kaifeng 475004, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c03685

Author Contributions
J.Z. and P.D. contributed equally to this paper.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the Natural Science Foundation of Guizhou Province (grant no. QHPT [2017] 5790-02), by the National Natural Science Foundation of China (grant no. 11804078), and support from Henan university (grant no. CJ3050A0240050). The Supercomputing Center of the University of Science and Technology of China is also acknowledged.

REFERENCES

(1) Ran, J.; Zhang, J.; Yu, J.; Jaroniec, M.; Qiao, S. Z. Earth-abundant cocatalysts for semiconductor-based photocatalytic water splitting. Chem. Soc. Rev. 2014, 43, 7787–7812.
(2) Chen, X.; Shen, S.; Guo, L.; Mao, S. S. Semiconductor-based Photocatalytic Hydrogen Generation. Chem. Rev. 2010, 110, 6503–6570.
(3) Chen, C.; Ma, W.; Zhao, J. Semiconductor-mediated photodegradation of pollutants under visible-light irradiation. Chem. Soc. Rev. 2010, 39, 4206–4219.
(4) Hisatomi, T.; Kubota, J.; Domen, K. Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting. Chem. Soc. Rev. 2014, 43, 7520–7535.
(5) Pan, H. Principles on design and fabrication of nanomaterials as photocatalysts for water-splitting. Renewable Sustainable Energy Rev. 2016, 57, 584–601.
(6) Jiang, J.; Zhao, K.; Xiao, X.; Zhang, L. Synthesis and Face-dependent Photoreactivity of BiOCl Single-crystalline Nanosheets. J. Am. Chem. Soc. 2012, 134, 4473–4476.
(7) Cheng, H.; Huang, B.; Dai, Y. Engineering BiOX (X = Cl, Br, I) Nanostructures for Highly Efficient Photocatalytic Applications. Nanoscale 2014, 6, 2009–2026.
(8) Di, J.; Xia, J.; Li, H.; Guo, S.; Dai, S. Bismuth oxyhalide layered materials for energy and environmental applications. Nano Energy 2017, 41, 172–192.

ACS Omega 2020, 5, 29081–29091

https://doi.org/10.1021/acsomega.0c03685

29089
(9) Yao, W.; Zhang, J.; Wang, Y.; Ren, F. Hybrid Density Functional Study on the Mechanism for the Enhanced Photocatalytic Properties of the Ultrathin Hybrid Layered Nanocomposite c-Ga2O3/β-Bi2O3. Appl. Surf. Sci. 2018, 435, 1531–1560.

(10) Liu, X.; Gu, S.; Zhao, Y.; Zhou, G.; Li, W. BiVO4, Bi2WO6, and Bi3Mo2O9 photocatalysis: A brief review. J. Mater. Sci. Technol. 2020, 56, 45–68.

(11) Zhang, N.; Ciriminna, R.; Pagni, M.; Xu, Y.-J. Nanochemistry-derived Bi2WO6 Nanostuctures: Towards Production of Sustainable Chemicals and Fuels Induced by Visible Light. Chem. Soc. Rev. 2014, 43, 5276–5287.

(12) Ren, F.; Zhang, J.; Wang, Y.; Yao, W. A Graphene-coupled Bi2WO6 Nanocomposite with Enhanced Photocatalytic Performance: a First-principles Study. Phys. Chem. Chem. Phys. 2016, 18, 14113–14121.

(13) Kado, A.; Hijiwi, S. H. or O2 Evolution from Aquous Solutions on Layered Oxide Photocatalysts Consisting of Bi3+ with 6s6 Configuration and d0 Transition Metal Ions. Chem. Lett. 1999, 28, 1103–1104.

(14) Li, C.; Chen, G.; Sun, J.; Rao, J.; Han, Z.; Hu, Y.; Zhou, Y. A Novel Mesoporous Single-Crystal-Like Bi2WO6 with Enhanced Photocatalytic Activity for Pollutants Degradation and Oxxygen Production. ACS Appl. Mater. Interfaces 2015, 7, 25716–25724.

(15) Di, J.; Chen, C.; Zhu, C.; Jì, M.; Xia, J.; Yan, C.; Hao, W.; Li, S.; Li, H.; Liu, Z. Bismuth vacancy mediated single unit cell Bi2WO6 nanosheets for boosting photocatalytic oxygen evolution. Appl. Catal. B 2018, 238, 119–125.

(16) Kang, D.; Park, Y.; Hill, J. C.; Choi, K. S. Preparation of Bi-Based Ternary Oxide Photoanodes Bi2VO4, Bi2WO6, and Bi3Mo2O9 Using Dendritic Bi Metal Electrodes. J. Phys. Chem. Lett. 2014, 5, 2994–2999.

(17) Zhou, Y.; Zhang, Y.; Lin, M.; Long, J.; Zhang, Z.; Lin, H.; Wu, J. C.-S.; Wang, X. Monolayered Bi2WO6 nanosheets mimicking heterojunction interface with open surfaces for photocatalysis. Nat. Commun. 2015, 6, 8340.

(18) Zhang, L.; Zhu, Y. A review of controllable synthesis and enhancement of performances of bismuth tungstate visible-light-driven photocatalysts. Catal. Sci. Technol. 2012, 2, 694.

(19) Zhang, L.; Wang, H.; Chen, Z.; Wong, P. K.; Liu, J. Bi2WO6 micro/nano-structures: Synthesis, modifications and visible-light-driven photocatalytic applications. Appl. Catal. B 2011, 106, 1–13.

(20) Tian, J.; Sang, Y.; Yu, G.; Jiang, H.; Mu, X.; Liu, H. A Bi2WO4-based hybrid photocatalyst with broad spectrum photocatalytic properties under UV, visible, and near-infrared irradiation. Adv. Mater. 2013, 25, 5075–5080.

(21) Huang, H.; Cao, R.; Yu, S.; Xu, K.; Hao, W.; Wang, Y.; Dong, F.; Zhang, T.; Zhang, Y. Single-unit-cell-layer established Bi2WO6 3D hierarchical architectures: Efficient adsorption, photocatalysis and dye-sensitized photovoltaic performance. Appl. Catal. B 2017, 219, 526–537.

(22) Shang, M.; Wang, W.; Zhang, L.; Liu, Z. Enhanced photocatalytic performance of boron doped Bi2WO6 nanosheets under simulated solar light irradiation. J. Hazard. Mater. 2013, 254–255, 185–192.

(23) Marschall, R.; Wang, L. Non-metal doping of transition metal oxides for visible-light photocatalysis. Catal. Today 2014, 225, 111–135.

(24) Hu, T.; Li, H.; Du, N.; Hou, W. Iron-Doped Bismuth Tungstate with an Excellent Photocatalytic Performance. ChemCatChem 2018, 10, 3040–3048.

(25) Li, K.; Zhu, Y.; Lu, J.; Dai, Y.; Huang, B. N- and Mo-doping Bi2WO6 in photocatalytic water splitting. Comput. Mater. Sci. 2013, 67, 88–92.

(26) Fu, Y.; Chang, C.; Chen, P.; Chu, X.; Zhu, L. Enhanced photocatalytic performance of boron doped Bi2WO6 nanosheets for promoted visible-light-assisted and hydrothermal synthesis. J. Alloys Compd. 2018, 744, 228–233.

(27) Shang, M.; Wang, W.; Zhang, L.; Xu, H. Bi2WO6 with significantly enhanced photocatalytic activities by nitrogen doping. Mater. Chem. Phys. 2010, 120, 155–159.

(28) Demurogrojthanan, P.; Phruangprar, A.; Thongtem, S.; Thongtem, T. Hydrothermal preparation of visible-light-driven Bi2WO6 photocatalyst. Mater. Lett. 2017, 209, 501–504.

(29) Kumar, B. V.; Prasad, M. D.; Vithal, M. Enhanced visible light photocatalytic activity of Sn doped Bi2WO6 nanocrystals. Mater. Lett. 2015, 152, 200–202.

(30) Huo, W. C.; Dong, X.; Li, J. Y.; Liu, M.; Liu, X. Y.; Zhang, Y. X.; Dong, F. Synthesis of Bi2WO6 with gradient oxygen vacancies for highly photocatalytic NO oxidation and mechanism study. Chem. Eng. J. 2019, 361, 129–138.

(31) Jiang, T.; Dai, Y.; Wei, W.; Ma, X.; Huang, B. Near-infrared photocatalytic activity induced by intrinsic defects in Bi2WO6 (M = W, Mo). Phys. Chem. Chem. Phys. 2014, 16, 18596–18604.

(32) Liu, K.; Wei, Y.; Zhu, Y.; Guo, M.; Dai, Y.; Huang, B. Effects of oxygen vacancy and N-doping on the electronic and photocatalytic properties of Bi2WO6 (M=Mo, W). J. Solid State Chem. 2012, 187, 103–108.

(33) Matsubara, M.; Saniz, R.; Partoons, B.; Lamoen, D. Doping anatase TiO2 with group V-B and VI-B transition metal atoms: a hybrid functional first-principles study. Phys. Chem. Chem. Phys. 2017, 19, 1945–1952.

(34) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid uncontracted Based on a Screened Coulomb Potential. J. Chem. Phys. 2003, 118, 8207–8215.

(35) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Erratum: "Hybrid Functionals Based on a Screened Coulomb Potential" [J. Chem. Phys. 2003, 118, 8207–8207 (2003)]. J. Chem. Phys. 2006, 124, 219906.

(36) Froyen, C.; Neugebauer, J.; Van de Walle, C. G. Electrostatic interactions between charged defects in supercells. Phys. Stat. Sol. B 2011, 248, 1067–1076.

(37) Tang, B.; Jiang, G.; Wei, Z.; Lu, X.; Zhang, Y.; Chen, W.; Wan, J. Preparation of N-Doped Bi2WO6 Microspheres for Efficient Visible-Light-Induced Photocatalysis. Acta Metall. Sin. 2014, 27, 124–130.

(38) Chen, S.; Walsh, A.; Gong, X.-G.; Wei, S.-H. Classification of Lattice Defects in the Kesterite Cu2ZnSnS4 and Cu2ZnSnSe4 Earth-Abundant Solar Cell Absorbers. Adv. Mater. 2013, 25, 1522–1539.

(39) Branco, J. J.; Bartlett, M. B. Challenges in Co-Alloyed Titanium Oxynitrides, a Promising Class of Photochemically Active Materials. Chem. Mater. 2015, 27, 7207–7217.

(40) Choi, H.; Shin, D.; Yeo, B. C.; Song, T.; Han, S. S.; Park, N.; Kim, S. Simultaneously Controllable Doping Sites and the Activity of a W–N Coproofed TiO2 Photocatalyst. ACS Catal. 2016, 6, 2745–2753.

(41) Liu, X.; Fan, H.-Q. Theoretical studies on electronic structure and optical properties of Bi2WO6. Optik 2018, 158, 962–969.

(42) Gao, S.; Gu, B.; Jiao, X.; Sun, Y.; Zuo, J.; Yang, F.; Zhu, W.; Wang, C.; Feng, Z.; Ye, B.; Xie, Y. Highly Efficient and Exceptionally Durable CO2 Photoxidation to Methanol over Freestanding Defective Single-Unit-Cell Bismuth Vanadate Layers. J. Am. Chem. Soc. 2017, 139, 3438–3445.

(43) Lei, F.; Sun, Y.; Liu, K.; Gao, S.; Liang, J.; Pan, B.; Xie, Y. Oxygen vacancies confined in ultrathin indium oxide porous sheets for promoted visible-light water splitting. J. Am. Chem. Soc. 2014, 136, 6826–6829.
(48) Segev, D.; Wei, S. H. Design of shallow donor levels in diamond by isovalent-donor coupling. Phys. Rev. Lett. 2003, 91, 126406.

(49) Yin, W.-J.; Wei, S.-H.; Al-Jassim, M. M.; Turner, J.; Yan, Y. Doping properties of monoclinic BiVO₄ studied by first-principles density-functional theory. Phys. Rev. B 2011, 83, 155102.

(50) Feng, C.; Yin, W.-J.; Nie, J.; Zu, X.; Huda, M. N.; Wei, S.-H.; Al-Jassim, M. M.; Turner, J. A.; Yan, Y. Strong asymmetrical doping properties of spinel Co₃Al₂O₆. J. Appl. Phys. 2012, 111, No. 093723.

(51) Butler, M. A. Prediction of Flatband Potentials at Semiconductor-Electrolyte Interfaces from Atomic Electronenegativities. J. Electrochem. Soc. 1978, 125, 228.

(52) Morrison, S. R. Electrochemistry at Semiconductor and Oxidized Metal Electrodes; Plenum Press: New York, NY, USA, 1980.

(53) Lim, Y. K.; Keong Koh, E. W.; Zhang, Y.-W.; Fan, H. Ab initio design of GaN-based photocatalyst: ZnO-codoped GaN nanotubes. J. Power Sources 2013, 232, 323–331.

(54) Zhang, J.; Ren, F.; Deng, M.; Wang, Y. Enhanced visible-light photocatalytic activity of a g-C₃N₄/BiVO₄ nanocomposite: a first-principles study. Phys. Chem. Chem. Phys. 2015, 17, 10218–10226.

(55) Zhang, J.; Deng, M.; Ren, F.; Wu, Y.; Wang, Y. Effects of Mo/W Codoping on the Visible-light Photocatalytic Activity of Monoclinic BiVO₄ within the GGA + U Framework. RSC Adv. 2016, 6, 12290–12297.

(56) El Halouani, F.; Deschanvres, A. Interfaces semi-conducteur-electrolyte: Correlations entre le potentiel de bande plate et les echelles d’elektronenegativite. Mater. Res. Bull. 1982, 17, 1045–1052.

(57) Gao, J.; Zeng, W.; Tang, B.; Zhong, M.; Liu, Q.-J. Density functional characterization of Bi-based photocatalysts: BiTaO₄, Bi₃Ta₃O₁₁ and Bi₂Ta₂O₁₈. Mater. Sci. Semicond. Process. 2021, 121, 105447.

(58) Andersen, T.; Haugen, H. K.; Hotop, H. Binding Energies in Atomic Negative Ions: III. J. Phys. Chem. Ref. Data 1999, 28, 1511–1533.

(59) Kittel, C. Introduction To Solid State Physics; 8th Edition Wiley India Pvt. Limited: 2005.

(60) Wang, B.; Yang, H.; Xian, T.; Di, L. J.; Li, R. S.; Wang, X. X. Synthesis of Spherical Bi₂WO₆ Nanoparticles by a Hydrothermal Route and Their Photocatalytic Properties. J. Nanomater. 2015, 2015, 1–7.

(61) Komsa, H.-P.; Rantala, T. T.; Pasquarello, A. Finite-size supercell correction schemes for charged defect calculations. Phys. Rev. B 2012, 86, No. 045112.

(62) Buckeridge, J.; Scanlon, D. O.; Walsh, A.; Catlow, C. R. A. Automated procedure to determine the thermodynamic stability of a material and the range of chemical potentials necessary for its formation relative to competing phases and compounds. Comput. Phys. Commun. 2014, 185, 330–338.

(63) Phapale, S.; Das, D.; Mishra, R. Standard molar enthalpy of formation of Bi₂WO₆(s) and Bi₂W₃O₁₀(s) compounds. J. Chem. Thermodyn. 2013, 63, 74–77.

(64) Jing, T.; Dai, Y.; Ma, X.; Wei, W.; Huang, B. The photocatalytic properties of ultrathin bismuth oxychloride nanosheets: a first-principles study. Phys. Chem. Chem. Phys. 2016, 18, 7261–7268.

(65) Moirera, K.; Park, J.-S.; Kima, S.; Yasuokac, K.; Walsh, A. Crystal Engineering of Bi₂WO₆ to Polar Aurivillius-Phase Oxyhalides. J. Phys. Chem. C 2019, 123, 29155–29161.

(66) Haynes, W. M.; Lide, D. R.; Bruno, T. J. CRC handbook of chemistry and physics; CRC Press: Boca Raton, Florida, 2014.

(67) Saha, S.; Sinha, T. P.; Mookerjee, A. Electronic Structure, Chemical Bonding, and Optical Properties of Paraelectric BaTiO₃. Phys. Rev. B 2000, 62, 8828.

(68) Reining, L. The GW approximation: content, successes and limitations. WIREs Comput. Mol. Sci. 2017, 8, No. e1344.

(69) Onida, G.; Reining, L.; Rubio, A. Electronic excitations: density-functional versus many-body Green’s-function approaches. Rev. Mod. Phys. 2002, 74, 601–659.