Investigation of the Optical and Excitonic Properties of the Visible Light-Driven Photocatalytic BiVO₄ Material

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Supporting Information

ABSTRACT: An investigation of the optical and excitonic properties of photocatalytic compounds based on both experimental and theoretical approaches is proposed. More specifically, this paper reports, for the first time, the local-field, optical anisotropy, and excitonic effects in BiVO₄, an active photocatalytic material in the visible range. The analyses are based on electron energy-loss spectroscopy measurements, ground-state density functional theory calculations, including crystal local-field effects, and many-body corrections using the Bethe–Salpeter equation. These results are supported by a comparison with two materials, namely, TiO₂ anatase and rutile, which are well-known to differ in their photocatalytic properties, those being important and negligible, respectively. The analogies found for these two categories of compounds allow the proposal of criteria that appear to be essential for producing an optimal photocatalytic material.

INTRODUCTION

In 1972, Honda and Fujishima first discovered that it was possible to promote the water splitting reaction, i.e., the decomposition of water into oxygen and hydrogen, by using an electrochemical device based on a TiO₂ anode and a platinum counter electrode exposed to ultraviolet (UV) light.¹ Over the past four decades, an important number of investigations have been devoted to such photoelectrochemical (PEC) reactions. Namely, TiO₂ is well-suited for photocatalytic applications because of its low cost, its high stability in aqueous solutions, and the right positioning of its valence band maximum (VBM) and conduction band minimum (CBM). Unfortunately, because of its overly large band gap (>3 eV), it operates only in the UV range and thus considerably decreases the efficiency of the conversion of solar energy to hydrogen. To have efficiencies of >15%, a band gap of <2.2 eV is required.² One strategy for reaching this band gap requirement is to consider multinary oxides combining nd⁰ (e.g., Ti⁴⁺, V⁵⁺, and Nb⁵⁺) and ns² cations (e.g., Bi³⁺ or Sn²⁺). Then, energy levels can be interspaced between the former valence and conduction bands and thus favor the absorption in the visible range. In that context, bismuth vanadate (BiVO₄), initially known for its ferroelastic and ionic conductivity properties,³ is now considered as one of the most promising candidates for solar energy-to-hydrogen conversion processes operating in the visible light range.⁴⁻⁶ However, its properties strongly depend on the allotropic form of BiVO₄. Three main polymorphs are known, namely, the zircon structure with tetragonal symmetry (Zₜ-BiVO₄) and two (almost identical) scheelite structures with monoclinic (Sₘ-BiVO₄) and tetragonal (Sₜ-BiVO₄) symmetries, the former being ferroelastic and the latter paraelastic.⁷⁻⁹ Sₘ-BiVO₄ and Sₜ-BiVO₄ were selectively prepared by many groups, showing that Sₘ-BiVO₄ exhibits high photoelectrochemical (PEC) properties, whereas the photoactivity of Zₜ-BiVO₄ is negligible.⁵⁻⁷,⁹ It has also been demonstrated that both Sₘ-BiVO₄ and Sₜ-BiVO₄ structures are photocatalytically active for the degradation of rhodamine B in solution under visible light, but not Zₜ-BiVO₄.¹⁰

Recently, Fan et al.¹¹ shed light on the higher PEC activity of Sₘ-BiVO₄ compared to that of Zₜ-BiVO₄. On the basis of surface photovoltage and transient photovoltage measurements under visible light irradiation, the authors clearly evidenced that photoinduced electrons (holes) flow from the surface (bulk) to the bulk (surface) for Zₜ-BiVO₄ while the opposite is observed for Sₘ-BiVO₄. This explains why Sₘ-BiVO₄ is more active than Zₜ-BiVO₄ for oxidation reactions. In addition, Li et al.¹² have shown that, under photorradiation, efficient charge separation is achieved in Sₘ-BiVO₄ leading to a reduction reaction with photogenerated electrons and an oxidation reaction with photogenerated holes on the {010} and {110} crystal facets, respectively.

Received: June 5, 2016
Revised: March 28, 2017
Published: March 28, 2017

DOI: 10.1021/acs.chemmater.6b02261
To address the differences among $S_{M}^{-}$, $S_{T}$, and $Z_{T}$-BiVO$_{4}$ their optical properties have been investigated. To date, only the optical band gaps of $S_{M}^{-}$, $S_{T}$, and $Z_{T}$-BiVO$_{4}$ have been estimated on the basis of diffuse reflectance spectra of powder samples, and no experimental investigation of their frequency-dependent dielectric function (DF) has been reported. From the theoretical side, a significant number of studies have been performed using density functional theory (DFT) with the generalized gradient approximation (GGA) and hybrid functionals. However, contradictory results have been published. For instance, the band gap nature of $S_{M}$-BiVO$_{4}$ was reported as both direct$^{2,1}$ and indirect$^{4,15}$. Moreover, two different groups have reported simulations of the frequency-dependent dielectric function$^{14,15}$ suggesting that the optical anisotropy is strong in $S_{M}$-BiVO$_{4}$ and negligible in $Z_{T}$-BiVO$_{4}$.\(^{14}\)

Clearly, all these previous studies of the optical properties of BiVO$_{4}$ suffer from being purely experimental or theoretical. An investigation of the optical and excitonic properties of BiVO$_{4}$ combining experiments and theory to improve our understanding of the photocatalytic activity of this material is still missing. This is, indeed, the main purpose of this work, which reports, for the first time, on the local-field, optical anisotropy, and excitonic effects in $S_{M}^{-}$ and $Z_{T}$-BiVO$_{4}$ based on electron energy-loss spectroscopy (EELS) measurements, ground-state DFT calculations, including crystal local-field effects\(^1\) (LFE), and many-body corrections using the Bethe–Salpeter equation\(^\dagger\) (BSE). Excellent agreement is obtained between EELS experiments and DFT calculations, which fully validates such \textit{ab initio} calculations as a starting point for more sophisticated calculations devoted to the excitonic properties. In particular, solving the BSE allows one to study the spatial distribution of the photoinduced electron–hole pairs, i.e., the excitons, in $S_{M}^{-}$ and $Z_{T}$-BiVO$_{4}$ phases, and evidences the impact of the long-range crystalline structure on it. From this work, a unified picture of the optical and excitonic properties of $S_{M}^{-}$ and $Z_{T}$-BiVO$_{4}$ that emphasizes the link among the nature of the band gap, the photocatalytic activity, and the excitonic properties is proposed. Finally, this result is supported by a comparison of two materials, namely, TiO$_{2}$ anatase and rutile, which are well-known for the differences in their photocatalytic properties, being important and negligible, respectively.

\section*{RESULTS AND DISCUSSION}

In structural terms, $S_{M}^{-}$ and $S_{T}$-BiVO$_{4}$ are very similar,\(^{18}\) except for a small distortion, which reduces the symmetry from tetragonal (space group $I4_{1}/a$ for $S_{T}$, with $a = b = 5.147$ Å and $c = 11.7216$ Å) to monoclinic (space group $I2/b$ for $S_{M}$, with $a = 5.1935$ Å, $b = 5.0898$ Å, and $c = 11.6972$ Å). In contrast, the zircon phase$^{20}$ ($Z_{T}$-BiVO$_{4}$, space group $I4_{1}/amd$, with $a = b = 7.303$ Å and $c = 6.584$ Å) is significantly different from the two scheelite phases, leading to a large volume expansion to 87.8 Å$^3$/formula unit compared to those of the $S_{M}$ and $S_{T}$ phases, with volumes of 77.6 and 77.3 Å$^3$/formula unit, respectively.

Using the following setting, i.e., $I4_{1}/amd$, $I4_{1}/a$, and $I2/b$ space groups for $Z_{T}$, $S_{T}$, and $S_{M}$-BiVO$_{4}$, respectively, it is possible to compare these three allotropes, with a common definition of the $c$-axis and the $a$–$b$ plane. Such a setting will be used hereafter, allowing us to discuss optical anisotropy and excitonic spatial distribution using a common setting for the crystallographic directions for the BiVO$_{4}$ phases. Both scheelite ($S_{T}$ and $S_{M}$) and zircon ($Z_{T}$) structures consist of isolated [VO$_{4}$]$^{5-}$ tetrahedra connected by [BiO$_{4}$]$^{5-}$ antiprisms but differ in the way these polyhedra are connected to each other. The structural phase transition between zircon and scheelite has been evidenced on the basis of a first-order reconstruction involving a “bond-switching” mechanism.\(^{20}\) Panels a and b of Figure 1 show the consequences of such a structural filiation between the $S_{M}$-BiVO$_{4}$ (or $S_{T}$) and $Z_{T}$-BiVO$_{4$ phases. With the $S_{M}$ phase as a starting point, three changes are observed to reach the $Z_{T}$ phase: (1) a rotation of the [VO$_{4}$]$^{5-}$ tetrahedral units, (2) an expansion along the $a$- and $b$-axes of the monoclinic cell, and (3) a strong compression along the $c$-axis.

The main impact of these structural modifications concerns the interconnection between the [VO$_{4}$]$^{5-}$ and [BiO$_{4}$]$^{5-}$ units as shown in panels c and d of Figure 1. The $Bi$–$V$ bond lengths and $Bi$–$O$–$V$ bond angles of $S_{M}$ and $Z_{T}$-BiVO$_{4}$ are summarized in Table S1 and will be discussed in more detail below, in the section devoted to optical anisotropy. Before discussing our optical anisotropy results for these compounds, the properties of their excitons, and their potential impact on the related photocatalytic properties, we first validated our theoretical approach. To do so, we have compared the calculated energy-loss functions with the measured low-loss EELS spectra obtained from $S_{M}$- and $Z_{T}$-BiVO$_{4}$ samples. The DFT calculations have been performed by using two different codes, the Vienna Ab initio Simulation Package (VASP)\(^{21}\) for the energy-loss functions, including LFE and the WIEN2k program package,\(^{22}\) as a starting point for BSE evaluations of the excitonic properties. Most DFT calculations were performed with the Perdew, Burke, and Ernzerhof parametrization of the GGA (PBE-GGA) of the exchange-correlation potential.\(^{23}\) BSE calculations were performed using a strategy similar to the one we used for the CuAlO$_{2}$ compound.\(^{24}\)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Schematic representation of the atomic structures of (a) $S_{M}$- BiVO$_{4}$ and (b) $Z_{T}$-BiVO$_{4}$. The structure transition from $S_{M}^{-}$ to $Z_{T}$-BiVO$_{4}$ is highlighted with the green arrows (cell expansion along $a$ and $b$, cell contraction along $c$) and the red arrows (rotation of VO$_{4}$tetrahedra). The resulting local environments of bismuth atoms are different from the two compounds, the properties of their excitons, and their potential impact on the related photocatalytic properties, we first validated our theoretical approach. To do so, we have compared the calculated energy-loss functions with the measured low-loss EELS spectra obtained from $S_{M}$- and $Z_{T}$-BiVO$_{4}$ samples. The DFT calculations have been performed by using two different codes, the Vienna Ab initio Simulation Package (VASP)\(^{21}\) for the energy-loss functions, including LFE and the WIEN2k program package,\(^{22}\) as a starting point for BSE evaluations of the excitonic properties. Most DFT calculations were performed with the Perdew, Burke, and Ernzerhof parametrization of the GGA (PBE-GGA) of the exchange-correlation potential.\(^{23}\) BSE calculations were performed using a strategy similar to the one we used for the CuAlO$_{2}$ compound.\(^{24}\) Energy-Loss Function of $S_{M}$ and $Z_{T}$-BiVO$_{4}$. Electron energy-loss spectroscopy (EELS) measurements are directly related to the energy-loss function (ELF) defined by $Im[-1/\epsilon(\nu)] = \epsilon_1(\nu)/[\epsilon_1(\nu)^2 + \epsilon_2(\nu)^2]$, where $\epsilon_1(\nu)$ and $\epsilon_2(\nu)$ are the...}
real and imaginary parts of the dielectric function, respectively, where \( \nu \) is the frequency.\(^{25}\) Properly combined with first-principles calculations, it is an unrivalled tool for probing the frequency-dependent dielectric function over a high energy range.\(^{26}\) The optical diffusion and absorption processes are directly related to \( \varepsilon_1(\nu) \) and \( \varepsilon_2(\nu) \), respectively. Figure 2 shows the energy-loss function, \( \text{Im}(-1/\varepsilon) \), of \( S_{\Delta}\)-BiVO\(_4\) and \( Z_{\Gamma}\)-BiVO\(_4\). The experimental measurements have been performed with a small collection angle, allowing a direct comparison between the recorded and calculated loss functions at zero momentum transfer (\( q \rightarrow 0 \)). Excellent agreement is obtained between these DFT calculations and orientation-dependent EELS measurements, as soon as the local-field effects (LFE) are taken into account in our simulations (more details on LFE are provided in the Supporting Information). In particular, the energy position and respective intensity of each spectral feature are well-reproduced. Such an agreement between PBE-GGA calculations and EELS measurements is not expected at first sight. Indeed, we expect an underestimation of the band gap value using PBE-GGA and thus a shift of all the simulated peaks with respect to the experimental spectrum. However, as previously reported,\(^{26}\) PBE-GGA simulations give correct peak positions for the high-energy part of the spectrum (\( E > 5 \text{ eV} \)), while the band gap underestimation has a significant impact on the low-energy part of the spectrum (\( E < 5 \text{ eV} \)). We are in a similar situation except that no significant spectral feature can be detected at low energy, explaining such an overall agreement. In addition, it should be noted that PBE-GGA underestimates the band gap of BiVO\(_4\) compounds by only 0.4 eV (see below).

We should mention that the loss functions are nearly the same along the three crystallographic directions for \( S_{\Delta}\)-BiVO\(_4\) in contrast to the case for \( Z_{\Gamma}\)-BiVO\(_4\). This observation is important and allows us to consider an average loss function for \( S_{\Delta}\)-BiVO\(_4\) which makes the results independent of the orientation chosen during the experiments. In contrast, the comparison for \( Z_{\Gamma}\)-BiVO\(_4\) requires a careful definition of the orientation axis (the origin of the different features is explained in Figure S2). It also should be noted that the tail of the zero-loss peak hinders the proper extraction of information below \( \sim 5 \text{ eV} \) [the energy resolution of the microscope is around 0.8 eV (see the Supporting Information)]. As a consequence, the band gap offset and excitons cannot be probed with this experimental setup.

### Optical Anisotropy in BiVO\(_4\) and TiO\(_2\).

Using a standard DFT functional appears to be adequate for the description of the high-energy range of the dielectric function (from 5 to 60 eV). However, because band gaps are strongly underestimated in conventional DFT, a more advanced method is needed for an accurate description of the low-energy range (from 0 to 5 eV for instance). Consequently, we have used the Tran–Blaha modified Becke–Johnson (TB–mBJ) potential,\(^{27}\) which is known for its ability to describe band gaps with an accuracy comparable to that of sophisticated GW calculations. In our DFT calculations, we have also taken into account relativistic effects on the valence electrons by including the spin–orbit (SO) coupling in our DFT calculations, to properly describe the Bi p\(^{3/2}\) and Bi p\(^{1/2}\) states, which are involved in the bands close to the Fermi level. Indeed, a band gap reduction of \( \sim 0.1 \text{ eV} \) is observed when the SO coupling is switched on, for both \( S_{\Delta}\)- and \( Z_{\Gamma}\)-BiVO\(_4\).

Because in optical excitations the excited electron may interact with the hole it left behind, we had to go beyond standard DFT. By solving the two-particle BSE, one can properly describe the interaction between the electron and the hole of a photogenerated pair, i.e., the bound exciton state. Here, the starting point of the BSE calculations was not based on GW eigenvalues but on our GGA results with a band gap correction, which was defined in such a way to reproduce the TB–mBJ and GW band gaps of BiVO\(_4\) and TiO\(_2\), respectively. Such an approximation of the BSE spectra leads to results for TiO\(_2\) similar to those starting from GW eigenvalues.\(^{31}\)

From our DFT calculations (including SO coupling), we obtain an indirect and direct fundamental band gap for \( S_{\Delta}\)- and \( Z_{\Gamma}\)-BiVO\(_4\) which changes from 2.06 to 2.46 eV and from 2.47 to 2.84 eV for the two phases, respectively, when the TB potential mBJ is taken into account. This leads to a band gap correction of \( \sim 0.4 \text{ eV} \) for the BiVO\(_4\) compounds.

It should be noted that the indirect nature of the band gap of \( S_{\Delta}\)-BiVO\(_4\) has been recently experimentally confirmed,\(^{28}\) with an energy difference between the indirect (2.56 eV) and direct (2.68 eV) band gaps of 0.12 eV, which agrees quite well with our prediction of 0.12 eV (2.47 and 2.59 eV for indirect and direct band gaps, respectively, for \( S_{\Delta}\)-BiVO\(_4\)). In contrast, our calculations show a difference of 0.02 eV between the indirect (2.85 eV) and direct (2.87 eV) band gaps for \( Z_{\Gamma}\)-BiVO\(_4\), which is not significant.

In panels a and b of Figure 3, the \( \varepsilon_2 \) function (in the low-energy range), deduced from BSE calculations, is plotted for \( S_{\Delta}\)- and \( Z_{\Gamma}\)-BiVO\(_4\) respectively. For comparison, we also show (in panels c and d of Figure 3) the \( \varepsilon_2 \) functions (based on BSE calculations) for anatase- and rutile-TiO\(_2\), respectively. TiO\(_2\) is the reference material in terms of photocatalytic performance in the UV range, while of the two phases of BiVO\(_4\) one is a very promising candidate for photocatalysis in the visible range. In both cases, one phase (i.e., \( S_{\Delta}\)-BiVO\(_4\) and anatase-TiO\(_2\)) is known to have photocatalytic properties better than those of the other. Our idea is to compare these four systems and extract the main parameters that determine why only two of them is promising candidate for photocatalysis in the visible range. In particular, we will focus on the optical absorption and exciton formation.

The in-plane (along the x-axis and/or y-axis) and out-of-plane (along the z-axis) contributions to the complex DF have been analyzed for the four aforementioned materials. The in-plane and out-of-plane notation refers to the 4-fold axis in \( Z_{\Gamma}\)-BiVO\(_4\), anatase, and rutile, and the 2-fold axis in \( S_{\Delta}\)-BiVO\(_4\). Before discussing our predictions for BiVO\(_4\), we consider the
different at low energy, leading to an intense optical excitation in the visible range for a polarization perpendicular and parallel to the c-axis for $S_{3\alpha}$ and $Z_T$-BiVO$_4$, respectively. In other words, $S_{3\alpha}$-BiVO$_4$ and $Z_T$-BiVO$_4$ differ in their photoexcitations, which use two polarizations (x and y) in the former but one (z) in the later compound, respectively.

We cannot conclude at this stage that such a correlation between the anisotropy of the dielectric function and the photocatalytic performances does exist, but it is interesting to note that, in both TiO$_2$ and BiVO$_4$, the better photocatalytic phase is the one that shows an in-plane polarization. Additional aspects must be considered to explain the nearly zero photocatalytic activity of $Z_T$-BiVO$_4$ under visible light excitation, compared to $S_{3\alpha}$-BiVO$_4$. This difference could stem from the significantly larger band gap in the $Z_T$ phase, which is in our TB-mBJ calculations is $\sim 2.9$ eV and thus on the very edge of energies that can be reached by visible light.

**Excitonic Effects in BiVO$_4$ and TiO$_2$.** An exciton is by definition a correlated electron–hole, bound by a Coulombic interaction. Figure 4 shows the first thousand excitons of the four systems and their energy distribution. Their binding energies ($E_b$) characterize their stability. A common feature is observed in the two photocatalytically active compounds, anatase-TiO$_2$ and $S_{3\alpha}$-BiVO$_4$. In both of these phases, the first exciton is bright and polarized perpendicularly with respect to the c-axis. This is in contrast to the inactive compounds rutile-TiO$_2$ and $Z_T$-BiVO$_4$, for which the first exciton is dark. In addition, the first bright exciton for rutile-TiO$_2$ is the 24th at 3.82 eV, with a polarization parallel to the c-axis and a strong binding energy of 605 meV.

From the BSE calculations presented here, we can estimate the hole–electron weighted mean distance, hereafter $d_{he}$, which combined with $E_b$, the binding energy of the exciton, will be a measure of the probability of a hole–electron recombination,
i.e., the exciton lifetime. $d_{he}$ has been estimated using the expression

$$
\langle d_{he} \rangle = \frac{\sum_{h=1}^{N} \sum_{e=0}^{M} \sum_{c=1}^{N} (d_{h,e} \cdot P_{h,e}^c)}{\sum_{h=1}^{N} \sum_{e=0}^{M} \sum_{c=1}^{N} P_{h,e}^c}
$$

where $P_{h,e}^c$ is the probability of an hole–electron pair characterized by distance $d_{h,e}$ given by

$$
P_{h,e}^c = \int_{r_h} d^3r_h \int_{r_e} d^3r_e W(r_h, r_e)
$$

where $W(r_h, r_e)$ is the conditional probability of having an electron at $r_e$ and a hole at $r_h$ by

$$
W(r_h, r_e) = \phi(r_h, r_e) \phi^*(r_h, r_e)
$$

$\phi(r_h, r_e)$ and $\phi^*(r_h, r_e)$ are the BSE excitonic envelope function.

The three indices $(h, e, c)$ refer as to the position of the electron ($e$) and the hole ($h$) over the $N$ atomic sites in the cell defined by the index $c$, where $c$ ranges between 0 (origin cell) to $M$. $M$ is taken such that the maximal $h$–$e$ distance is $\sim 30$ Å. The calculated probabilities for larger distances are negligible. In the calculations presented here, the hole is systematically in the cell at the origin ($c = 0$) and the bound electron in the cell $c$. A similar approach was used by Sharifzadeh et al. to estimate the average $h$–$e$ distance in organic solids.

Figure 5a shows a schematic representation of the way $\langle d_{he} \rangle$ is estimated. For the sake of simplicity, the unit cell contains only two atoms. The cell at the origin is highlighted in yellow; the orange lines represent the $h$–$e$ contacts. Here the hole is defined on the oxygen site inside the cell at the origin and the promoted electron on a metal site. The $h$–$e$ probabilities are proportional to the width of the lines; i.e., the thicker the lines, the larger the probabilities of creating an exciton between the two connected sites. By averaging all these weight distances, we can thus define $\langle d_{he} \rangle$ based on the previous formula.

Panels b and c of Figure 5 show the distribution of the $e$–$h$ probabilities for the first bright excitons of rutile-TiO$_2$, anatase-TiO$_2$, SM-BiVO$_4$, and ZT-BiVO$_4$. It clearly shows that in both rutile- and anatase-TiO$_2$, $\sim 95\%$ of the excitons occur between oxygen and titanium atoms (the second largest $P_{h,e}$ is very small and corresponds to transitions between oxygen atoms due to hybridization effects). In BiVO$_4$, the main contribution to the exciton spectra originates from optical transitions between oxygen and vanadium (O $\rightarrow$ V, i.e., hole on O and electron on V) (66 and 63% of the transitions for SM- and ZT-BiVO$_4$, respectively), much more than the bismuth to vanadium transitions (with 12 and 13% relative weights for SM- and ZT-BiVO$_4$, respectively). Finally, O $\rightarrow$ Bi and O $\rightarrow$ O contributions are also observed but can be neglected. Moreover, while in TiO$_2$ the photohole was located nearly exclusively on oxygen, in BiVO$_4$ it is mainly positioned on oxygen but partly also on bismuth (>10%). Similarly, in TiO$_2$, the photoelectron is nearly exclusively located on the metal center (titanium). In contrast, in the vanadate ternary compounds, it is distributed on vanadium (slightly less than 80% with two transitions, O $\rightarrow$ V and Bi $\rightarrow$ V), bismuth (due to the O $\rightarrow$ Bi transition, with 7% and 10% in SM- and ZT-BiVO$_4$, respectively), and oxygen (due to the O $\rightarrow$ O transition, with 10% and 6% in SM- and ZT-BiVO$_4$, respectively). Such an excitonic distribution is a direct consequence of the orbital overlap in these compounds as illustrated in Figure S3 for ZT-BiVO$_4$.

The optimal situation for avoiding electron–hole recombination is to have a small $E_b$ and a large $d_{he}$. On the basis of the examination of average $d_{he}$ and $E_b$ values, we plot in Figure 6 the probability that an electronic transition occurs versus its associated $d_{he}$ distance. Only the first bright excitons of the four compounds are taken into account. Among all the photo-excitation (represented with gray circles), some specific ones are highlighted. The ones corresponding to excitons localized in the unit cell are represented by yellow squares. The ones corresponding to an exciton that propagates in [uvw], [00w], and [uuw] directions are depicted by blue triangles, orange pentagons, and green circles, respectively. Finally, a green bar highlights the previously calculated average $d_{he}$ distance in each
material for the given exciton. Note the similarities between $S_{\alpha}$ and $Z_T$-$BiVO_4$ in terms of both the $d_{eh}$ distance and the shape of the $h$–$e$ distribution. In $S_{\alpha}$-$BiVO_4$, $Z_T$-$BiVO_4$ and anatase-$TiO_2$, the excitons that propagate along $\langle wuu \rangle$ directions have high probabilities. In contrast, the highest probability in rutile-$TiO_2$ is found for excitons propagating along the $\langle 001 \rangle$ direction. Figure 7 gives a very simple interpretation by showing the projection of the four structures along specific directions. Indeed, it appears that the exciton will propagate mainly in the direction of the highest packing of Bi in both $BiVO_4$ phases, which is along the $\langle wuu \rangle$ directions, and along the direction where the $TiO_6$ octahedra are sharing their edges, which is along $\langle uuu \rangle$ and $\langle 00w \rangle$ directions for anatase- and rutile-$TiO_2$, respectively.

Another way to analyze our BSE data is to consider Tables S1–S4, which give the excitation energies, the oscillator strengths, and the binding energies of the principal bright excitons in the four systems. For instance, considering the first 50 excitons, 13 are bright in $S_{\alpha}$-$BiVO_4$ but only 5 are bright in $Z_T$-$BiVO_4$. Similarly, among the first 50 excitons, 10 are bright in anatase-$TiO_2$ while only 1 is bright in rutile-$TiO_2$. In summary, under visible light excitation, more electron–hole pairs are formed in $S_{\alpha}$-$BiVO_4$ than in $Z_T$-$BiVO_4$, and these excitons have the propensity to recombine more frequently in $Z_T$-$BiVO_4$ than in $S_{\alpha}$-$BiVO_4$. A similar analysis could be done for anatase- and rutile-$TiO_2$.

**CONCLUSION**

In conclusion, this investigation reveals many common features between the reference UV light photocatalytic compound anatase-$TiO_2$ and the promising candidate for visible light photocatalytic properties $S_{\alpha}$-$BiVO_4$. Indeed, both exhibit an indirect band gap, and their first exciton is bright and shows a polarization perpendicular to the c-axis. The fact that the band gap of the two photocatalytic active materials is indirect is essential in the sense that it prevents a direct recombination of the hole–electron pair, leading to a lifetime of photoexcited electrons and holes longer than that of direct band gap rutile-$TiO_2$ and $Z_T$-$BiVO_4$. In addition, the first excitons of these two last compounds are dark and show a polarization parallel to the c-axis. These inter-related properties appear to be essential and should be considered with care in the quest for an optimal photocatalytic material.

**ASSOCIATED CONTENT**

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b02261.

Details on the structural (Table S1), EELS (Figures S1–S2), densities of states (Figure S3) and BSE data (Tables S2–S5) are provided. Table S6 summarizes the main results in terms of optical and excitonic properties of $S_{\alpha}$, $Z_T$-$BiVO_4$, Anatase & Rutile $TiO_2$ (PDF).

**AUTHOR INFORMATION**

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X.R. thanks T. Saison for the synthesis of $S_{\alpha}$-$BiVO_4$ and $Z_T$-$BiVO_4$ and the CCIPL (Nantes) computing centre for the financial support received from the European Union Seventh Framework Program under Grant 312483 ESTEME2 (Integrated Infrastructure Initiative, I3) and from the European Union H2020 program under Grant 696656 Graphene Flagship.

**ACKNOWLEDGMENTS**

X.R. thanks T. Saison for the synthesis of $S_{\alpha}$-$BiVO_4$ and $Z_T$-$BiVO_4$ and the CCIPL (Nantes) computing centre for computational facilities. P.B. was supported by the Austrian Science Foundation FWF (SFB F41 “Vicom”). L.L. acknowledges the support received from the European Union Seventh Framework Program under Grant Agreement 696656 Graphene Flagship.

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