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The nature of photogenerated charge separation among different crystal facets of BiVO₄ studied by a density functional theory

Taifeng Liu^{1,2,‡}, Xin Zhou^{1,‡}, Michel Dupuis³, and Can Li^{1,*}

¹ State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, 457 Zhongshan Road, Dalian 116023, PR China.

² Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China.

³ Department of Chemical and biological engineering and Computation and Data-enabled Science and Engineering Program University at Buffalo, State University of New York Buffalo, NY 14260.

‡ These authors contributed equally to this work

*canli@dicp.ac.cn

Abstract:

Charge separation among different crystal facets of a semiconductor has been observed experimentally, but the underlying reasons behind this phenomenon are unknown. In this work, the activation energies of carrier hopping and the mobility of electron/hole transport along seven low-index crystal orientations of bulk BiVO₄ have been calculated using a small polaron model. The calculated mobility and our previous experimental results reveal that there is a parallel relationship between the carrier mobility along the crystal axis and the carrier preferred accumulation on the corresponding crystal facets. It is proposed that the mobility of electrons (or holes) along the crystal axis [hkl] might be essentially related to the charge separation among the indices corresponding facets (hkl); namely, the mobility of electrons (or holes) along the crystal axis [hkl] is the largest among all possible crystal axes, and the photogenerated electrons (or holes) tend to be accumulated on the indices corresponding facet (hkl) when the factors of surface like surface band bending, surface energetic differences etc are not considered.

1. Introduction

Solar driven water splitting with semiconductor-based photocatalysts is one of the most ideal routes to convert solar energy into chemical fuel.¹⁻³ However, most semiconductor-based photocatalysts provide a quite low overall energy conversion efficiency that is far from practical for application. One of the key issues related to this problem is the limited charge separation efficiency upon photo-excitation, which largely depends on the intrinsic electronic and structural properties of semiconductors.^{4, 5} To improve the photocatalytic activity, various strategies have been used to promote charge separation in semiconductor-based photocatalysts⁶. For example, proper junctions formed between two kinds of semiconductors, or two phases of the same semiconductor, could lead to enhanced activity in hydrogen and/or oxygen evolution reaction.^{7, 8}

Recent investigations⁹⁻¹¹ demonstrated that crystal facet engineering of semiconductors has become an important strategy employed to promote the separation of photoexcited electrons and holes. For instance, efficient charge separation can be achieved on different crystal facets of BiVO₄, evidenced by the observed phenomenon that the reduction and oxidation reactions take place separately on the (010) and (110) facets under photo-irradiation.⁹ Recent reports showed that for single crystals of anatase TiO₂, the noble metals (Au, Ag, and Pt) were selectively photodeposited on the exposed (010) facet, and metal oxides (PbO₂ and MnO_x) were selectively photodeposited on the exposed (110) facet. These results suggest that photogenerated electrons and holes are mainly accumulated on the (010) and (110) facets, respectively.¹⁰ Wang and co-workers reported that the BiOCl@Au/MnO_x hierarchical structure obtained by selectively depositing the Au and MnO_x on the (001) and (110) crystal facets of BiOCl results in a significant enhancement of photocatalytic activity in a water splitting reaction.¹¹ Several reasons for the selective photodeposition have been proposed. According to the theory advocated by Ohno et al., photoillumination on a semiconductor could result in the preferred migration of holes and electrons to specific crystal facets.¹² Miseki et al. ascribed the structure-directed deposition of Au,

Ni, and PbO_2 on BaLaTiO_4 to preferred sorption phenomena.¹³ Wang et al. suggested that the different energy levels of the conduction band and valence bands for different facets and the internal electronic field along a particular axis in a crystal are possible reasons for these experimental observations.¹¹ However, the nature of photogenerated charge separation among different facets of a single crystal of semiconductor remains unclear.

When semiconductors are excited by photons with energy equal to or higher than their energy band gaps, electrons are excited from the valence band (VB) to the conduction band (CB). The photo-generated electrons and holes could recombine in bulk or on the surface of the semiconductor within a very short time, releasing energy in the form of heat or photons. The surviving photogenerated electrons and holes, without recombination, migrate to the surface of the semiconductor and participate in reduction and oxidation reactions, respectively. Commonly the semiconductor possesses anisotropic properties, so the transport of the charge carrier will be diverse along the different crystal orientations.

In this work, we presumed that the intrinsic electron and hole transport properties in the anisotropic semiconductor might essentially be associated with charge separation between different facets. We used monoclinic scheelite (ms-) BiVO_4 as a model to investigate charge separation among different facets. We investigated the transport of the charge carrier in the bulk material by the DFT+ U approach combined with Marcus/Holstein theory.^{14, 15} Our calculations show that 1) the mobility of electrons is predicted to be much larger than that of holes in the same crystal orientation; 2) surprisingly, we found that in the exposed facets of the crystal, the mobility of electrons (or holes) along the crystal axis $[\text{hkl}]$ is the largest, and the photogenerated electrons (or holes) tend to be accumulated on the indices corresponding facet (hkl) . ($[\text{hkl}]$ is indices of crystal direction and (hkl) is the indices of corresponding crystal plane)

2. Computational Methods and Details

Theoretical calculations based on density functional theory (DFT) have been

proven to be very useful and powerful for elucidating the structural, electronic, and physical chemical properties of semiconductor materials.¹⁶⁻¹⁸ To understand the intrinsic mechanism concerning photoexcited electron and hole transport through the crystal, a small polaron model has been used to investigate metal-oxide semiconductors^{19,20} and proven to be valid both experimentally and theoretically.^{21,22} A polaron commonly results from charge localization accompanied by lattice distortions: a small polaron localized at atomic scale,^{23,24} and a large polaron spreads over many lattice sites. As for BiVO₄, it was demonstrated that a small polaron hopping conduction mechanism dominates at temperatures from 250 to 400K.^{25,26} In this work, we studied the transport of electrons and holes in BiVO₄ at room temperatures using a small polaron model.

We performed spin-polarized DFT calculations using the Vienna *ab-initio* Simulation Package (VASP).^{27,28} The exchange correlation potential was described by the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation.²⁹ The projector-augmented wave method was applied to describing electron-ion interactions.^{30,31} We used a 2×2×2 supercell with 192 atoms as our model and 2×1×2 K-point mesh was used to calculate electronic structures. The structures were relaxed until all forces on atoms were less than 0.01 eV/Å, and a plane-wave cutoff energy of 400 eV was employed.

To overcome the self-interaction error of standard DFT methods, we employed a DFT+*U* approach to study the polaron structures involved in adding an extra electron to, or removing an electron from, bulk supercells.³² Within this framework, the on-site Coulomb interaction *U* and exchange parameter *J* are the determining factors for the magnitude of the correction. Here, we used a fixed *J* value of 1.0 eV and varied the *U* value to find an appropriate parameter $U_{\text{eff}}=U-J$ for both electron and hole localization in BiVO₄. Previous calculations and experimental results found that the valence band maximum (VBM) of bulk BiVO₄ mainly consists of O 2p orbitals, and the conduction band minimum (CBM) is primarily composed of V 3d orbitals.^{33,34,35} We attempted to localize the electron or hole by varying the U_{eff} values from 1.0 to 11.0 eV for both O 2p and V 3d orbitals. We try our efforts to find an optimal U_{eff} in

the section 3.

Small polaron mobility in metal-oxide solids is typically modeled within the framework of Marcus/Holstein theory, with the parameters derived from DFT calculations.^{19, 20} Within the framework of Marcus/Holstein theory, a basic polaron transfer process involves three relevant states: the initial, final, and transition states. In the initial state, the polaron is localized on one particular atom (such as O) site. When the polaron moves to an adjacent site (another O atom with the same coordinative environment), the final state is formed. In a period crystal, the initial and final states are identical. With the electron and hole localized on equivalent initial and final sites, we can use a linear interpolation scheme to calculate the polaron transfer pathway. $\mathbf{R}_1$ and $\mathbf{R}_2$ are defined as vectors of the three-dimensional coordinates of all atoms in the initial and final polaron states, respectively. Then, the coordinates of all atoms along the hopping path can be approximated as $\mathbf{R}_x = x\mathbf{R}_1 + (1-x)\mathbf{R}_2$, where x varies in the range from 0.0 to 1.0. Where $x=0.5$ corresponds to the midpoint that happens to be the transition state due to the translation or symmetry equivalence of the final and initial states. The energy barrier ΔG is calculated as $\Delta G = E_{R_{0.5}} - E_{R_1}$. Using Einstein's formula, the electron/hole mobility can be estimated approximately by

$$\mu = \frac{eD}{k_B T} = \frac{e(1-c)a^2\nu_0 \exp(-\frac{\Delta G}{k_B T})}{k_B T} \quad (1)$$

where $(1-c)$ is the probability that a neighboring site is available for hopping, ΔG is the energy barrier, ν_0 is the longitudinal optical phonon frequency, k_B is Boltzmann's constant, T is temperature, and a is the transfer distance. In this calculation, $(1-c) \approx 1$, $T=300$ K, $\nu_0 = 10^{13}$ Hz.³⁶ All low-index crystal orientations of [100], [010], [001], [110], [101], [011], and [111] were selected as possible polaron transfer pathways.

3. Results and Discussions

Determination of an appropriate U_{eff} parameter is necessary for DFT+U calculations in order to correct the electron self-interaction in DFT. There is no universal U value that works equally well for all materials or for all properties of

interest. We selected the U_{eff} value as follows. Firstly, we chose to examine how the band gap was affected by the choice of U_{eff} values. The band gap versus the U_{eff} values is shown in Fig. 1. Experimentally, the band gap has been found to be 2.4 eV for BiVO_4 . From the Fig. 1, we found that although the U_{eff} value reaches to 12 eV, the band gap is still far away from the experimental value. The change of band gap with the increase of U_{eff} value is within 0.1 eV. So for BiVO_4 , it is hard to find a suitable U_{eff} which results in the band gap in satisfactory accord with experiment. But we can find something useful to determine the U_{eff} values in the Fig. 1. There are three convergent trends sections in it. The first section is the U_{eff} value from 3 eV to 5 eV, the second section is the U_{eff} value from 6 eV to 8 eV, and the third section is the U_{eff} value from 9 eV to 12 eV. The band gap doesn't change when $U_{\text{eff}}=4$ and 5 eV in the first section and the band gap is almost the same when $U_{\text{eff}}=6, 7$, and 8 eV in the second section. When increasing the U_{eff} value, the band gap has no a little bit of change. This is probably because these U_{eff} values will not reflect the properties of this material. In the third section, the band gap increases slowly to a convergent value from $U_{\text{eff}}=9$ eV. These U_{eff} values could reflect the properties of this material correctly and we decided preliminary the U_{eff} value should begin from 9 eV.

Secondly, we attempted to localize the electron or hole by varying the U_{eff} values from 1 to 11 eV. We found when U_{eff} is less than 5 eV, electron is delocalized. When U_{eff} value is less than 6 eV, hole is delocalized. Similar phenomena were also observed for bulk TiO_2 cases¹⁹. As shown in Fig. 2 and Fig. 3, we gave the position of trap state in the band gap by varying U_{eff} values for electron from 5 to 11 eV and for hole from 6 to 11 eV.

For electron, the trap state is supposed to be closer to the CBM because electron is localized in the V atom. The position of the localized state to the CBM is 0.71, 0.9, 1.16, 1.38, 1.68, and 0.3 eV for $U_{\text{eff}}=5, 6, 7, 8, 9$ and 10 eV. For $U_{\text{eff}}=11$ eV, no localized state appear in the band gap. So we can find only $U_{\text{eff}}=5$ and 10 eV are suitable. But when U_{eff} value is 5 eV, the density of charge localized on one V atom is only less than 50%. Therefore, we choose U_{eff} value for electron to be 10 eV.

For hole, the trap state should be closer to the VBM because hole is localized in the

O atom. The localized state is located above the VBM by 0.80, 1.11, 1.35, and 0.90 eV for $U_{\text{eff}}=6, 7, 8,$ and 9 eV, respectively. For $U=10$ eV, the localized state appears in the CB band and for $U=11$ eV, the localized states appears in the VB band. So we can find only $U_{\text{eff}}=6$ eV and 9 eV is suitable. But when U_{eff} value is 6 eV, the localized density of charge on one O atom is only less than 40%. Therefore, we choose U_{eff} value for hole to be 9 eV.

BiVO_4 mainly exists three different crystal phases, tetragonal zircon (tz-), tetragonal scheelite (ts-), and monoclinic scheelite (ms-)³⁷. Among them, ms- BiVO_4 has been found to exhibit the highest photocatalytic activity under visible-light irradiation.³⁸ The tz- BiVO_4 has large band gap of 2.9 eV which is the reason for its lower photocatalytic activity³⁸. Ms- BiVO_4 and ts- BiVO_4 have similar band gaps (2.4 eV and 2.3 eV³⁸) and lattice parameters (ms- BiVO_4 : $a=5.195$ Å, $b=11.701$ Å, $c=5.094$ Å; $\alpha=\gamma=90.00^\circ$, $\beta=90.38^\circ$;³⁹ ts- BiVO_4 : $a=c=5.147$ Å; $b=11.722$ Å, $\alpha=\gamma=\beta=90^\circ$)⁴⁰, but the monoclinic lattice distortion can induce modifications of the valence-band (VB) electronic structure of ms- BiVO_4 ⁴¹. In addition, it has been suggested that the increased overlap between the Bi $6s$ and the O $2p$ orbitals would lead to enhanced migration of photogenerated charges in ms- BiVO_4 ³⁸.

BiVO_4 has been found to exist in the monoclinic scheelite phase at ambient temperature and pressure, and undergoes monoclinic-to-tetragonal phase transition under compression (around 1.5 GPa or 255°C)⁴². The scheelite-type BiVO_4 structure consists of isolated VO_4 tetrahedra that are corner connected by BiO_8 dodecahedra. In ts- BiVO_4 , Bi^{3+} cations are located at the centrosymmetric sites of BiO_8 polyhedra, whereas, the ms- BiVO_4 structure exhibits a distorted BiO_8 dodecahedron due to the Bi^{3+} off-centering.

The ball and stick model of monoclinic BiVO_4 is shown in Fig. 4a. The experimental lattice parameters are maintained in our calculations. As illustrated in Fig. 4b, it is the polyhedron model of ms- BiVO_4 with VO_4 tetrahedra (in gray) and distorted BiO_8 dodecahedra (in purple). In the VO_4 tetrahedra, the length of V-O bond are 1.7849 Å and 1.7829 Å; in the BiO_8 dodecahedra, the length of Bi-O bond are 2.4875 Å, 2.4683 Å, 2.3995 Å, and 2.3991 Å. The different length of the Bi-O bonds

can reflect the distortion of the BiO_8 dodecahedra, which is consistent with the experimental results³⁹.

The orbital-decomposed electron density of states (DOS) are presented in Fig. 5. It reveals that the top of the VB is mainly composed of O 2p states, whereas there is an additional contribution of Bi 6s states. The Bi 6s and O 2p states caused bonding states below the Fermi level, which may make the monoclinic phase BiVO_4 energetically more favorable. The CB is principally V 3d states in character with minor contributions from the O 2p states. Cooper and co-workers used a comprehensive approach to understand the electronic structure of monoclinic scheelite bismuth vanadate (ms- BiVO_4), including both valence band (VB) and conduction band (CB) orbital character. They confirmed the VB maximum and CB minimum are comprised primarily of O 2p and V 3d orbitals by DFT calculations and experimental data³⁵. Our calculated band structure is consistent with their results. In the following small polaron model calculation, we consider the electron polaron is the V 3d states and the hole polaron is only in O 2p state.

We considered the addition of an extra electron and hole separately in a supercell of bulk BiVO_4 in this study. A compensating uniform background of charge was introduced to re-establish the neutrality of the supercell. For the initial structure, we took the geometry of the neutral BiVO_4 ground state, created some small distortions around V or O sites in the periodic cell, and then allowed it to fully relax, keeping the cell size fixed.

As shown in Fig. 6a, adding an electron to the BiVO_4 creates a localized state within the band gap. After structural relaxation, the excess electron becomes self-trapped at a V^{5+} lattice site, which then becomes formally V^{4+} . Most of the excess charge tends to reside on a V atom, and only a small fraction is on the surrounding four O atoms. The fraction of the localized electron density at the V^{4+} site is approximately 98%. Fig. 6b shows the total and projected density of states of BiVO_4 after adding one extra electron. The electron polaron state of the excited electron at the V^{4+} site is V 3d states and it locates 0.30 eV below the CBM. The electron self-trapping is accompanied by significant local distortions around the reduced V^{4+}

site, forming a small polaron. Combining Fig. 7a with Table 1, one observes that around the V^{4+} site, the V-O bonds elongate by 0.073 Å and 0.142 Å, respectively. The Bi-O bonds in the second shell region are shortened by approximately 0.100 Å. Distortions seldom occur in other parts of supercell. Based on the calculations and previous results,³³ we ascribe the increased V-O bond lengths to the partial electron-density filling of the antibonding orbitals formed by the mixing of V 3d and O 2p atomic orbitals. A possible reason for the decreased Bi-O bond lengths is that stronger hybridization between Bi 6s and O 2p states and unoccupied Bi 6p states reduces the antibonding interaction.

Because the VBM of BiVO_4 shows O 2p dominant character with a non-negligible contribution of Bi 6s states,^{33, 34} it is more difficult to localize a hole than an electron. The spin density contours in Fig. 8a clearly demonstrates hole localized on the selected O atom. About 70% of the charge density of hole is predicted to reside on the O site, and the rest of the charge spreads on the surrounding O atoms. After the hole localized, the O^{2-} becomes formally O^- and the hole state turns out lie about 0.9 eV above the top of the VB as shown in Fig. 8b. The hole self-trapping is accompanied by local lattice distortions to yield a highly distorted BiO_8 polyhedron, indicating the formation of small polaron. The polaronic distortion involving all of the V-O and Bi-O bonds close to the hole are shown in Fig. 7b and Table 2. The V-O bond elongates by 0.080 Å and the Bi-O bonds elongates by 0.204 Å and 0.144 Å. In the second shell region, the changes in Bi-O bond lengths vary between -0.163 Å and 0.151 Å, and the V-O bond lengths are shortened by approximately 0.081 Å. The bond length changes very little beyond the second shell region. After adding a hole (namely removing an electron from) at an O site, the V-O and Bi-O bonding orbitals will become weakened and as a result the V-O bonds and Bi-O bonds become longer.

A small polaron may undergo thermally-activated hopping from site to site⁴³. The activation energy for polaron hopping can be estimated by calculating the variation of potential energy as the polaronic lattice configuration is displaced from the initial to the final geometry; if the initial and the final states are identical, the transition state may occur midway between the two local minima. Using a 192-atom $2 \times 2 \times 2$ supercell,

we computed activation energies employing the methodology described in the previous section. To identify saddle-point geometries for polaron hopping, we generated configurations with atomic positions at the midpoint between those corresponding to the initial and final polaron sites along a particular crystal orientation. The calculated activation energies of electron/hole transfer, denoted as $\Delta G_e/\Delta G_h$, for all the low-index crystal orientations are listed in Table 3. The energy barriers for electron transfer are range from 0.194 to 0.576 eV for different direction, which reflect the anisotropy properties of the BiVO₄ crystal. In the ref. 26, the authors demonstrated the electrons transport in BiVO₄ is described by a thermally activated small plaron hopping mechanism from 250 to 400 K. The electron transport taking place between V⁴⁺ and V⁵⁺, they got the activation energy is about 0.29 eV. In our calculation, the activation energy of [100] is about 0.3 eV, which is consistent with the experimental values. So, the methods we used are appropriate for dealing with charge transport in the BiVO₄.

The energy barriers for hole transfer are in the range from 0.433 to 0.848 eV. There are no direction experimental activation values of BiVO₄ for comparison. In the case of TiO₂, the activation energy for hole transfer is about 0.6 eV²⁰. Our calculated values have the same magnitude as that in TiO₂. In addition, the activation energy for hole transport is larger than the activation energy of electron transfer, which is consistent with the experimental result that electron is transfer faster than the hole.

We assumed that electron/hole transport in BiVO₄ follows an adiabatic small polaron hopping mechanism.²⁶ The processes of electron and hole migration can be described by gradual changes in the distorted lattice configurations between two adjacent polaron configurations along the selected crystal orientation. Based on Einstein's formula, the electron and hole mobilities were calculated. As shown in Table 3, the mobilities of electrons are much larger than those of hole in the same crystal orientations, and the mobility of an electron is the largest along the [010] direction, and the mobility of a hole is the largest along the [100] direction. The mobility of electron along [010] is the largest one which has the value of 8.53×10^{-4} cm²/Vs. The mobility of hole along [100] is the largest one which has the value of

$5.64 \times 10^{-8} \text{ cm}^2/\text{Vs}$. We realized that the value of our calculated mobility is much smaller than the values reported so far for this material system. There are several reasons for this difference. Firstly, it is an intrinsic poor carrier transport properties in BiVO_4 . Time-resolved microwave conductivity (TRMC) measurements reveals the carrier mobility of $\sim 4 \times 10^{-2} \text{ cm}^2/\text{Vs}$ for undoped BiVO_4 under ~ 1 sun illumination conditions, which is at least 1-2 orders of magnitude lower than in typical semiconductor for water splitting⁴⁴. Secondly, despite the low mobility, high quantum efficiencies can nevertheless be achieved in BiVO_4 due to the long lifetime of the photogenerated charge carriers ($\sim 40\text{ns}$), which leads to relatively long carrier diffusion lengths ($\sim 70 \text{ nm}$). The long lifetime implies that there are few intrinsic recombination centers, which indicated that BiVO_4 is a highly “defect-tolerant” material⁴⁴. Thirdly, doping can improve the photocurrent and increase the quantum efficiencies remarkably. Berglund. *et al.* synthesized films with a $\text{Bi}:\text{V}:\text{M}_0:\text{W}$ atomic ratio of 46:46:6:2 (6% M_0 , 2%W), which demonstrate the best PEC performance with photocurrent densities 10 times higher than that for pure BiVO_4 and is greater than previously reported for M_0 and W containing BiVO_4 . They also demonstrated backside illumination utilizes light scattering off the irregular surface structure resulting in 30-45% higher photocurrent densities than frontside illumination⁴⁵. This may be explained by the long lifetime photogenerated charge carriers, the long carrier diffusion lengths and the increased charge density caused by doping.

We must emphasize that what we calculated are intrinsic diffusional mobilities for BiVO_4 along different low-index crystal orientations. In contrast, experimentally measured mobility is typically drift or Hall mobility.²⁶ Thus, the calculated quantities are not directly comparable to experimental values, a more complete model would have to include other factors, such as structural defects and disorder, applied voltage, and so on. But a comparison of the relative order of mobilities along different directions is reasonable. With the correct carrier conductor mechanism, the main goal of our work is the comparison of the relative order of the mobility along different crystal directions.

To estimate which are the highly exposed facets, slabs with six stoichiometric

repeated layers were constructed for each low-index surface. The computed total energies of the slabs, together with their corresponding numbers of BiVO_4 units, were then fitted into the following equation used to calculate the surface formation energy γ , $\gamma = (E_{\text{slab}} - nE_{\text{BiVO}_4})/2A$, where E_{slab} and E_{BiVO_4} is the total energy of the slab and bulk, n is the number of BiVO_4 units in the slab, and $2A$ is the total exposed area of the two identical sides of the slab. The computed surface energies are collected in Table 3. The smaller the surface energy, the more stable the corresponding facet. Based on the calculated results, the relative stability trend of low-index surfaces is predicted to be $(010) = (011) \approx (110) > (111) > (001) > (100)$. Our results are in good agreement with the observed morphology of BiVO_4 , in which (010) and (110) are highly exposed.⁹

We are able to obtain the following results from our calculations. Firstly, the mobility of electron is much larger than those of hole in the same crystal orientations. Secondly, the facets of (010) and (110) of BiVO_4 are highly exposed. Finally, in the highly exposed facets, the mobility of an electron is the largest along the $[010]$ direction, and the mobility of a hole is the largest along the $[110]$ direction.

Our recent experiments on BiVO_4 found that photo-deposition of metals/metal oxides have facet-selective property⁹. The photo-depositions of metals on the surface of BiVO_4 were carried out using HAuCl_4 (H_2PtCl_6 and AgNO_3) as precursors and water as a hole scavenger. SEM images clearly show that the particles of Ag, Au, and Pt are solely deposited on the (010) facets. Namely, the photogenerated electrons are readily available for the reduction reaction on the (010) facets. Photo-oxidation depositions of Mn^{2+} or Pb^{2+} ions on BiVO_4 were performed with IO_3^- as electron acceptors. The formation of PbO_2 and MnO_x oxides is an indication that the photo-oxidation selectively takes place on the (110) facets, that is, the photogenerated holes tend to migrate to the (110) facets for selective metal oxidation. The photo-deposition of dual precursors with simultaneous reduction and oxidation were also investigated. It is interesting to note that the Au, Pt, and Ag particles are still selectively photo-deposited on the (010) facets, while the MnO_x and PbO_2 particles are loaded only on the (110) facets of BiVO_4 . All of these results unambiguously reveal that the photogenerated electrons and holes tend to accumulated on the (010)

and (110) facets, respectively, which results in the reduction and oxidation reactions taking place on the corresponding (010) and (110) facets.

In the process of photocatalytic reactions, some of photogenerated electrons and holes migrate to the surface of the semiconductor and then participate in reduction and oxidation reactions. The semiconductor can be divided into bulk region and surface region. Here, we only investigated the transfer of photogenerated electrons/holes in the bulk region. This means that the conditions of the surface, such as surface band bending, surface energetic difference, are neglected in this work.

According to the calculated results and our previous experimental results, we can see that there is a parallel relationship between the carrier's mobility along the crystal axis and the carrier's preferred accumulation on the corresponding crystal facets. The mobility of electrons (or holes) along the crystal axis $[hkl]$ might be essentially related to the charge separation among the corresponding facets (hkl) . So it could be proposed that, as shown in Fig. 9, for the exposed facets of a crystal, the mobility of electrons (or holes) along the crystal axis $[hkl]$ is the largest among all possible crystal axes, the photogenerated electrons (or holes) tend to be accumulated on the corresponding facet (hkl) , when the factors of surface, such as surface band bending, surface energetic differences, are not considered.

4. Conclusions

In summary, we have studied the charge migration in BiVO_4 employing the formalism of DFT with Hubbard U corrections and Marcus/Holstein theory using a small polaron model. We calculated the activation energy and the mobility of carriers in seven low-index crystal orientations. The surface energies of these seven low-index surfaces were also calculated. The results show that 1) the mobility of electrons is much larger than that of holes along the same crystal axis orientations, 2) the facets of (010) and (110) are highly exposed, and 3) for the exposed facets of (010) and (110), the mobility of electrons along $[010]$ is five orders of magnitude larger than that of the $[110]$ direction and the mobility of holes along $[110]$ is two orders of magnitude larger than that of the $[010]$ direction. Our calculated mobilities and the

experimental results reveal that there is a parallel relationship between the carrier mobility along the crystal axis and the carrier preferred accumulation on the corresponding crystal facets. The mobility of electrons (or holes) along the crystal axis $[hkl]$ might be essentially related to the charge separation among the corresponding facets (hkl) . Namely, for exposed facets of the crystal, it could be proposed that the mobility of electrons (or holes) along the crystal axis $[hkl]$ is the largest among all possible crystal axes, and the photogenerated electrons (or holes) tend to accumulate on the corresponding facet (hkl) , when the factors of surface like surface band bending, surface energetic differences etc are not considered. Our theoretical understanding of spatial charge separation between different crystal facets of BiVO_4 may give greater understanding of charge separation in semiconductor based photocatalysts.

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Table 1. Geometry with an excess electron before and after relaxed. The structure shown is in Figure 7a.

Structure with electron	Before relaxed (Å)	After relaxed (Å)	Change (Å)
V-O1	1.785	1.858	+0.073
V-O2	1.785	1.858	+0.073
V-O3	1.783	1.925	+0.142
V-O4	1.783	1.925	+0.142
Bi1-O1	2.399	2.278	-0.121
Bi2-O1	2.468	2.323	-0.145
Bi3-O2	2.487	2.366	-0.121
Bi4-O2	2.399	2.253	-0.146
Bi5-O3	2.487	2.366	-0.121
Bi6-O3	2.399	2.253	-0.146
Bi7-O4	2.468	2.323	-0.145
Bi8-O4	2.399	2.278	-0.121

Table 2. Geometry with an excess hole before and after relaxed. The structure shown is in Figure 7b.

Structure with hole	Before relaxed (Å)	After relaxed (Å)	Change (Å)
Bi1-O1	2.487	2.631	+0.144
Bi2-O1	2.399	2.603	+0.204
V-O1	1.785	1.865	+0.08
Bi1-O2	2.487	2.599	+0.112
Bi1-O3	2.399	2.346	-0.053
Bi1-O4	2.399	2.513	+0.114
Bi1-O5	2.468	2.345	-0.123
Bi1-O6	2.468	2.371	-0.097
Bi1-O7	2.399	2.401	+0.002
Bi1-O8	2.399	2.530	+0.131
Bi2-O8	2.487	2.638	+0.151
Bi2-O9	2.399	2.366	-0.033
Bi2-O10	2.468	2.305	-0.163
Bi2-O11	2.399	2.360	-0.039
Bi2-O12	2.468	2.464	-0.004
Bi2-O13	2.399	2.427	+0.028
Bi2-O14	2.487	2.597	+0.11
V-O15	1.785	1.719	-0.066
V-O16	1.783	1.705	-0.078
V-O17	1.783	1.684	-0.099

Table 3. Electrons and holes transfer paths and the corresponding facets. ΔG_e and ΔG_h are the activation energy of electrons and holes, μ_e and μ_h are the mobility of electrons and holes, γ is the surface energy.

Crystal Axis	Crystal Surface	ΔG_e (eV)	ΔG_h (eV)	μ_e (cm ² /Vs)	μ_h (cm ² /Vs)	γ (J/m ²)
[010]	(010)	0.226	0.848	8.53×10^{-4}	3.10×10^{-14}	0.20
[110]	(110)	0.576	0.707	1.36×10^{-9}	8.63×10^{-12}	0.21
[100]	(100)	0.301	0.433	9.26×10^{-6}	5.64×10^{-8}	0.50
[001]	(001)	0.194	0.734	5.56×10^{-4}	4.81×10^{-13}	0.48
[101]	(101)	0.345	0.799	3.29×10^{-6}	7.90×10^{-14}	0.42
[011]	(011)	0.231	0.844	8.36×10^{-4}	4.30×10^{-14}	0.20
[111]	(111)	0.549	0.831	1.12×10^{-9}	2.07×10^{-14}	0.35

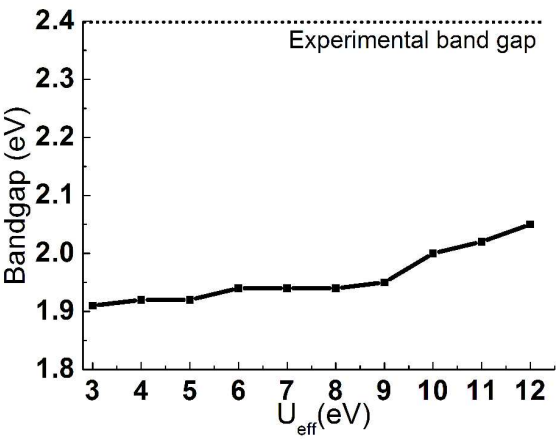


Fig. 1. Band gap versus U_{eff} .

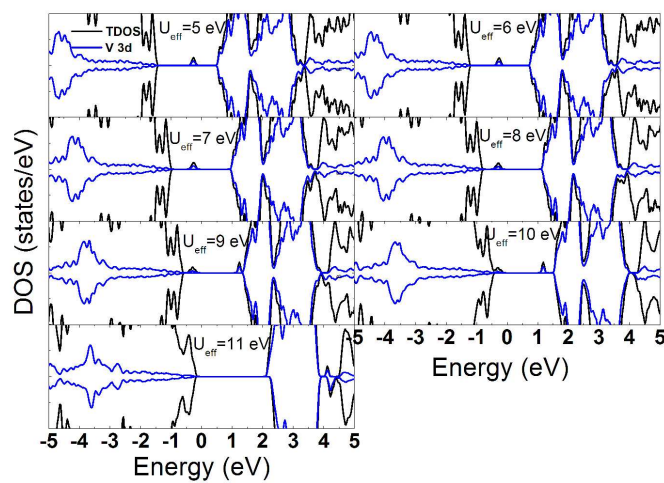


Fig. 2. Total and projected density of states of one extra electron for different U_{eff} , Fermi level is set at 0 eV.

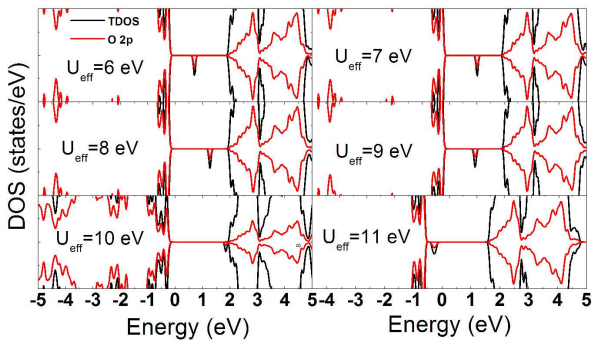


Fig. 3. Total and projected density of states of one extra hole for different U_{eff} , Fermi level is set at 0 eV.

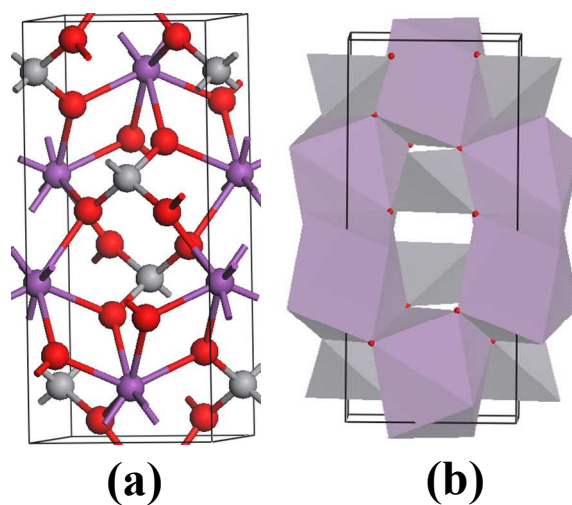


Fig. 4. BiVO_4 unit cell (a) ball and stick model, purple, silver and red balls represent Bi, V and O atoms (b) polyhedron model with distorted BiO_8 dodecahedron (in purple) and VO_4 tetrahedra (in gray).

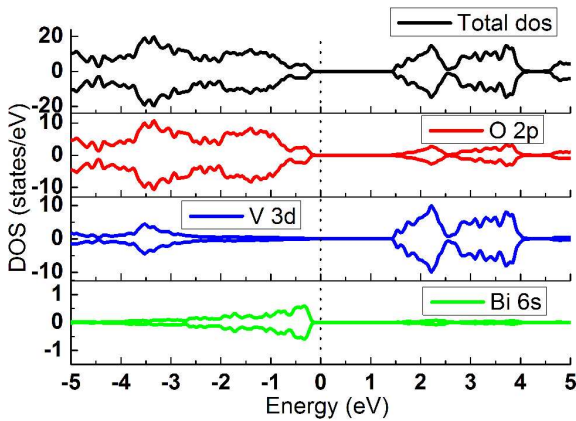


Fig. 5. Total and projected density of states (DOS) of BiVO₄, Vertical dashed line indicates the Fermi level.

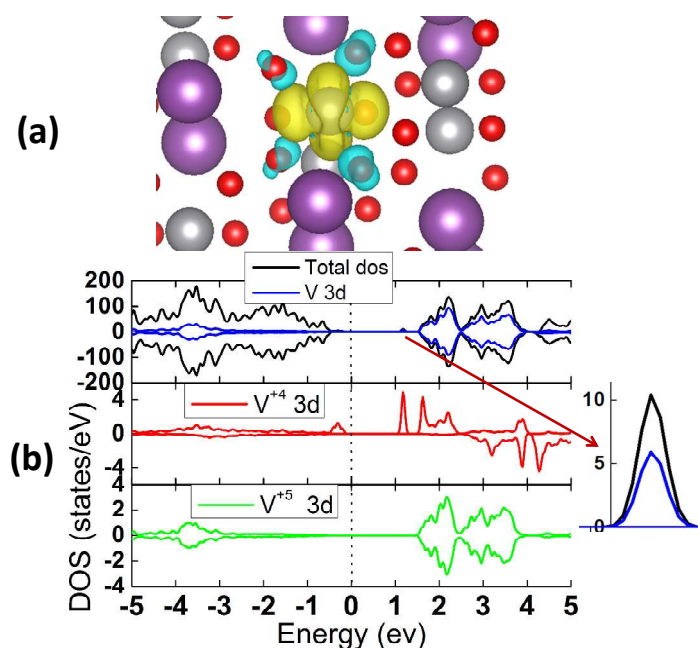


Fig. 6. Spin density contours and total and projected density of states : (a) spin density contours of one extra electron, (b) total and projected density of states of one extra electron, vertical dashed line indicates the Fermi level.

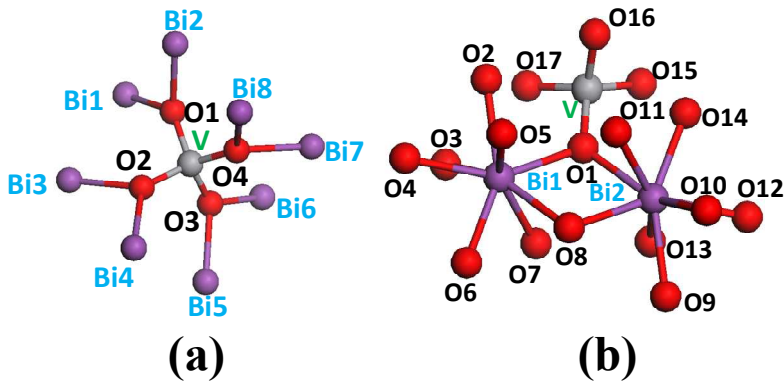


Fig. 7. Geometry with an extra (a) electron and (b) hole, electron is localized on V site in (a) and hole is localized on O1 site in (b).

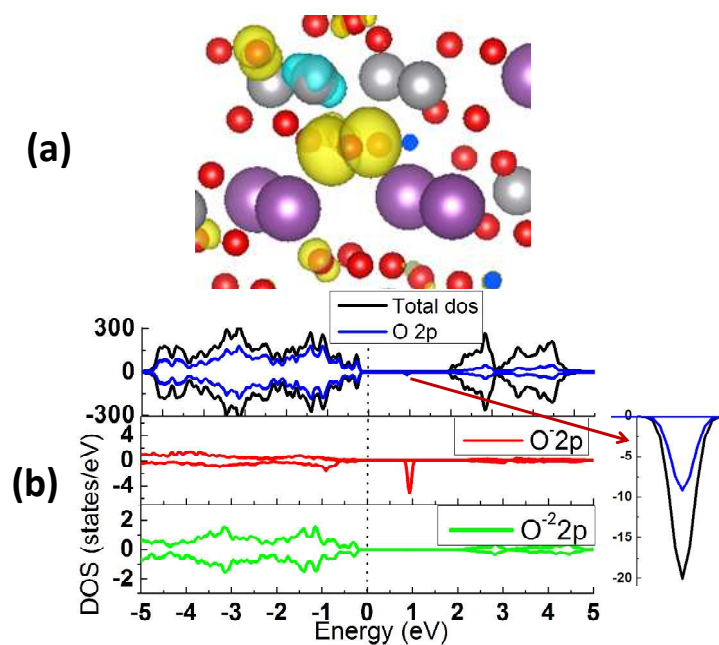


Fig. 8. Spin density contours and total and projected density of states : (a) spin density contours of one extra hole, and (b) total and projected density of states of one extra hole, vertical dashed line indicates the Fermi level.

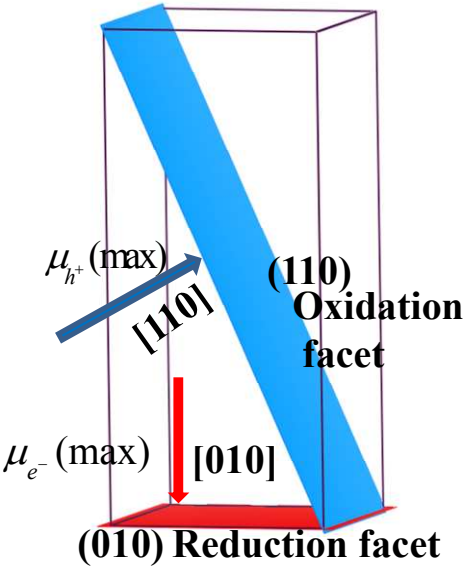
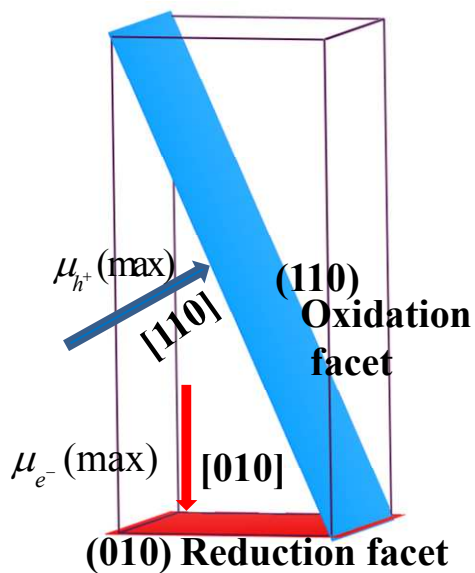


Fig. 9. Electrons (or holes) transfer path along the crystal axis [hkl] and corresponding facet (hkl).

TOC



Electrons and holes transfer path along the crystal axis $[hkl]$ and corresponding facet (hkl) .