ABSTRACT: The impact of the four predominant (010), (110), (001), and (121) exposed facets obtained experimentally for monoclinic BiVO₄ on its photocatalytic performance for water splitting reactions is investigated on the basis of the hybrid density functional theory including the spin–orbit coupling. Although their electronic structure is similar, their transport and redox properties reveal anisotropic characters based on the crystal orientation and termination. The particular role of each facet in proton reduction was correlated with the surface Bi coordination number and their geometrical distribution. Our work predicts the (001) facet as the only good candidate for both HER and OER, while the (010) facet is a fitting candidate for OER only. The (110) and (121) surfaces are acceptable candidates only for OER but less potential than (001) and (010). These outcomes will efficiently conduct experimentalists for an attentive design of facet-oriented BiVO₄ samples toward improving water oxidation and proton reduction.

Upon the report of Fujishima and Honda on TiO₂ water photolysis, photoelectrochemical (PEC) water splitting has been considered as one of the most attractive ways to generate hydrogen using solar energy by maintaining sustainable green environment. In order to reduce cost and achieve high conversion order, considerable attempts have been focused on developing an ideal and active semiconductor photocatalyst for O₂ evolution reaction (OER) and H₂ evolution reaction (HER) simultaneously by controlling its fundamental physicochemical properties. In water splitting reactions, the photogenerated charge carriers are situated at the valence band maximum (VBM) and conduction band minimum (CBM) of the photocatalyst. Hence, the well-pronounced delocalized nature of the orbitals associated with the VBM and CBM electronic states inside the bulk is required to ensure good mobility likelihood throughout the crystal structure of the material to the surface. Moreover, suitable VBM/CBM positions lying energetically lower than O₂/H₂O and higher than H⁺/H₂ potentials, respectively, are necessary for the driving force of released holes and excited electrons needed to oxidize water and reduce proton. Several ways have been put in to enhance the photocatalytic properties, either by addressing the problem of sluggish transfer kinetics of holes and electrons through the addition of a cocatalyst on top of the electrode surface or by forming a heterojunction. Lately, facet engineering has become an effective way to tune the semiconductor photoanode characteristics and thus improving its photocatalytic activity. A recent study on facet-engineered WO₃ electrode for photoelectrochemical hydrogen generation from natural seawater has given an average rate of 38.18 μmol h⁻¹. Among numerous visible-light driven semiconductor photocatalysts, BiVO₄ is the frontier in a wide range of applications. The monoclinic crystalline phase was particularly given the highest activity for photocatalytic OER. This result motivated several researchers to focus on the BiVO₄ monoclinic phase in order to determine its photocatalytic behavior. As reported, it has an appropriate VBM position for OER oxidizing water with an onset potential around 0.9 V vs the reversible O₂/H₂O potential. Its CBM position and flat band potential are impartially negative or just positioned at the H₂/H₂O level. As invoked in the literature, this material has poor carrier transport and slow kinetics transfer at the material–electrolyte interface, which restrict its PEC performance.

Since bismuth vanadate is a common photoanode utilized for water splitting, it is required to determine the role of each exposed facet in photoredox reactions because different facets of BiVO₄ show different thermodynamic and photocatalytic behaviors. Among the low-Miller-index surfaces, (001) tends to be the preferred growth orientation and has also been shown to be the most important facet for photocatalytic oxidation of water for O₂ generation. It has 16 times higher photocurrent density as reported experimentally than the randomly oriented BiVO₄ photoanode. Another dominant
surface is (010), which possesses the lowest surface energy and showed good visible photocatalytic degradation activities. Li and co-workers showed in their experiment that the photogenerated charges could be separated between the (010) and (110) facets, where the (110) facet was used for water oxidation and (010) for proton reduction. Cao and co-workers recently reported a first-principle study on the (101) Bi₂O₄/(010) BiVO₄ heterojunction, revealing that the (010) BiVO₄ can form a coherent stable interface with the (101) Bi₂O₄ to improve BiVO₄ utilization of visible light for water splitting with better charge separation. This method of selective photocatalyst deposition yields higher photocatalytic and photoelectrocatalytic OER activities. Li and co-workers also reported a higher PEC activity of (010) than (121) and correlated that with the higher electron mobility of the former one. In summary, selective facets of BiVO₄ yields better charge separation and efficient photochemical water splitting.

Computationally, very few reports have studied the low Miller indexes of BiVO₄ surfaces using PBE. Therefore, an accurate investigation of these surfaces is needed to understand the difference in photocatalytic behavior. In our previous works, we examined principle bulk properties of several photocatalytic bismuth-based materials including BiVO₄. We adopted a computational framework based on the density functional theory (DFT) together with the hybrid Hyd–Scuseria–Ernzerhof (HSE06) exchange–correlation functional. This method has also proven good accuracy by matching the experimental band gap and band energy positions relative to the water redox potential of a wide number of photocatalytic materials. Recently, ideal exposed facets for OER and HER of the widely utilized UV light- and visible light-driven photocatalysts, TiO₂ and Ta₂N₅, were predicted on the basis of an optoelectronic and redox characteristics combination using this computational scheme and relevant information was proposed for improving materials performance.

The impact of the four predominant (010), (110), (001), and (121) exposed facets obtained experimentally for monoclinic BiVO₄ on the material performance for photocatalytic water splitting reactions still remained unclear and are addressed in this letter. The objective of this work is to provide this knowledge by performing an accurate and comprehensive DFT-based computational study based on the hybrid HSE06 functional including the spin–orbit coupling (SOC) to take into account the relativistic effects on Bi. Their electronic structure, transport features, and relative band alignment to water splitting limits are investigated. The role of each exposed facet in photooxidoreduction process and the most appropriate candidates for HER and OER are given. All details on the computational models and methods used in this work are given in the Supporting Information.

Bulk monoclinic BiVO₄ (C₂h point group and C2/c space group) has a layered structure made by Bi³⁺ and V⁵⁺ cations in coordination with O²⁻ and linked to each other by distorted BiO₆ dodecahedra and VO₄ tetrahedra, leading to four and two different oxygen neighbors in each subunit. Our PBE computed lattice constants of 7.23, 11.56, and 5.10 Å reproduced very well the experimental values (7.25, 11.7, and 5.09 Å). Four predominant (010), (110), (001), and (121) exposed facets are obtained experimentally in the prepared BiVO₄ samples. The (010) and (110) facets are made by 6- and 5-coordinated Bi with 4-coordinated V and 2-coordinated O, respectively. The (001) and (121) facets are characterized 4-coordinated Bi together with 4-coordinated V and 2-coordinated O (Figure 1).

For bulk monoclinic BiVO₄ our HSE06+SOC computed band gap energy of 2.8 eV is in agreement with the experimental value (2.5 eV) and much more accurate than the PBE+SOC computed one of 1.7 eV. The same effect of SOC on the band gap energy revealing 0.2 eV reduction was obtained at both levels of functional. The CBM is mainly made by V⁵⁺ (3d⁰) orbitals. The VBM consists of O²⁻ (2p⁶) orbitals together with weak Bi³⁺ (6s²) orbitals contribution, in agreement with photoemission data. The hybridization effect of Bi³⁺ (6s²)/O²⁻ (2p⁶) lone pair states at VBM is attributed to the distortions in BiO₆ dodecahedra, in accordance with the experimental photoemission with X-ray diffraction results. Similar contribution of orbital types at the VBM/CBM states are also obtained for (010), (110), (001), and (121)-oriented BiVO₄ slabs (Figure 2). Comparing to the bulk material, their corresponding band gap energy is slightly broader by 0.1 or 0.2 eV. The (001) slab gives 2.9 eV, while the (010), (110), and (121) slabs give 3.0 eV. A minimal effect of SOC on the band gap energy was revealed only for (010) and (001) slabs with a reduction of 0.1 eV, as shown in Figure S2 in the Supporting Information.

The computed partial charge density maps using HSE06+SOC associated with the VBM and CBM electronic states of the (010)-, (110)-, (001)-, and (121)-oriented BiVO₄ slabs are displayed in Figures 3 and 4. For the (010)- and (001)-oriented BiVO₄ slabs, the partial charge densities associated with VBM/CBM electronic states are delocalized over O 2p, Bi 6s, and V 3d orbitals throughout the crystal lattice, leading to good mobility of holes/electrons from bulk to (010) and (001) surfaces (Figure 3). The partial charge densities corresponding to the CBM electronic state of the (010) slab reveal better orientations of V 3d orbitals than those obtained for (001). This result is expected to lead to easier migration or better mobility of electrons toward (010) than (001). In both cases, the partial charge densities are in line with the projected density of states results shown in Figure 2. For the (121)-oriented BiVO₄ slab, the partial charge density associated with
the VBM electronic state is mainly distributed over O 2p orbitals located on the surface with very minor contribution from the bulk O species, while the partial electron density corresponding to the CBM electronic state is localized on some V 3d orbitals over sublayers of the slab located in planes parallel to the surface (Figure 4). This result tends to lower the mobility of electrons and holes from bulk to (110) surface. For the (121)-oriented BiVO$_4$ slab, the partial charge density corresponding to the VBM electronic state is partially distributed over some O 2p orbitals and very few Bi 6s orbitals, forming a disconnected tube-like shape from the bulk to the surface, while the CBM partial electron density is delocalized on V 3d orbitals located in sublayers, forming a tube-like shape parallel to the surface (Figure 4). As a consequence, this result is expected to lead to lower hole mobility to this surface than to the (010) and (001) surfaces and poor electron mobility to the (121) surface. These predicted results highlight the fundamental origin behind the...
higher PEC activity of (010) than (121) as reported experimentally and correlated with the higher electron mobility of (010) with respect to (121).30

The absolute VBM/CBM energies obtained using HSE06+SOC of BiVO4 slabs are $-2.6/0.4$ eV for (010), $-3.0/0.0$ eV for (110), $-1.6/1.3$ eV for (001), and $-3.05/0.05$ eV for (121), as shown in Figure 2. Their computed electrostatic potential profile using HSE06+SOC gives an absolute vacuum energy of 5.0, 5.0, 5.5, and 4.2 eV for (010), (110), (001), and (121), respectively (Figure 5). As described in the methodology and computational details (see the Supporting Information for more details), the VBM and CBM energy levels of (010), (110), (001), and (121) BiVO4 slabs were defined with respect to a common energy scale, which is the vacuum. An anisotropic behavior is obtained on the basis of the characteristics of the facet. Our predicted CBM band energy position versus vacuum of the (010) slab ($-4.6$ eV) is in excellent agreement with the available experimental data obtained from photoemission spectroscopy, where the CBM energy level is found between $-4.5$ and $-4.7$ eV.35 For the (010) and (110) BiVO4 slabs, the respective VBM energy levels are 1.87 and 1.52 eV lower than the O$_2$/H$_2$O level, while their respective CBM energy level is 0.3 and 0.25 eV higher than the H$^+$/H$_2$ level (Figure 4). Due to the incorrect CBM levels of (010) and (110) BiVO4 slabs with respect to H$^+$/H$_2$ potential, the excited electrons toward these surfaces after absorption of photons will suffer from absent driving force to reduced proton. On the basis of the correct VBM levels with respect to O$_2$/H$_2$O potential, these two facets...
are predicted to be good candidates for OER only. Contrarily, the upward shift by 0.4–0.8 eV of the CBM positions using the (001)- and (121)-oriented slabs will significantly enhance the low capability of the excited electrons to reduce H⁺. Consequently, these two surfaces become suitable candidates for both HER and OER in terms of appropriate predicted CBM and VBM energy levels relative to H⁺/H₂ and O₂/H₂O potentials. The minimal SOC effect on the band alignment was revealed only for the (010)- and (001)-oriented slabs. A downward shift by 0.1 eV of the CBM energy level for (010) and a downward shift by 0.1 eV/0.2 eV of the VBM/CBM energy levels for (001) was obtained (Figures S3 and S4 in the Supporting Information).

The similar phenomenon observed in the redox characteristics between the (001) and (121) slabs can be justified by the appearance of four-coordinated Bi with four-coordinated V and two-coordinated O on both facets. The small downward shift in the energy levels of (110) slab with respect to those of the (010) slab can be justified by the appearance of some five-coordinated surface Bi. These predicted results highlight the fundamental origin behind the spatial carrier separation between (010) and (110) facets of BiVO₄ as invoked in experiment.²⁸ The significant modification in the redox characteristics of (001) and (121) slabs leading to the drastic upward shift in the band energy levels with respect to those obtained for the (010) and (110) slabs, can also be justified by the difference in the surface Bi species coordination number going from six for (010) or six and five for (110) to four for both (001) and (121).

If we merge the redox and carrier transport characteristics together for each surface, our work highlights the (001) facet as the only appropriate candidate for both OER and HER, though the (010) facet is a good candidate for OER only. The two (110) and (121) surfaces are acceptable candidates only for OER but have less potential than (001) and (010). These predicted results explain the fundamental origin behind the reported experimental data showing (001) as the most important and stable facet for photocatalytic oxidation of water for O₂ generation and (010) for good visible light splitting reactions.²⁹ In water splitting reactions, the two cocatalysts for OER and HER should be anchored on the best facets to boost the holes and electrons transfer kinetics to water. Obtaining appropriate flat band potentials of powder samples with respect to water splitting levels cannot guarantee an active photocatalyst for water splitting reactions due to the anisotropic character of its transport and redox characteristics and their correlation with the type/nature of exposed facet. The obtained results from this work could successfully explain the fundamental reasons why powder BiVO₄ samples have good activity for photocatalytic OER, while relatively poor PEC performance for hydrogen evolution was obtained.¹⁹,²⁰,²³–²⁷ Overcoming the H₂ evolution performance limitation in an effective way requires a selective depositions of the HER cocatalyst on the (001) surface. The OER cocatalyst is required to be selectively deposited on the (010) facet for water oxidation to minimize the electron–hole recombination on the photocatalyst surface. The 2-coordinated O species would be the active site of water oxidation toward OER on the (001) surface. The 4-coordinated V together with 4-coordinated Bi species would be the active sites for proton reduction toward HER on the (001) surface.

In summary, we have investigated the impact of the four predominant (010), (110), (001), and (121) exposed facets obtained experimentally for monoclinic BiVO₄ photocatalyst on its performance for water splitting reactions. Although the electronic structure is similar for these four surfaces, their redox and transport properties revealed an anisotropic nature based on the crystal orientation and termination. The particular role of each facet in proton reduction was correlated with the surface Bi coordination number and their geometrical distribution. After having combined the charge carrier transport and redox characteristics for each surface, our study predicted the (001) facet as the only appropriate candidate for both HER and OER, while the (010) facet is a good candidate only for OER. The (110) and (121) facets were classified as acceptable candidates only for OER but less potential than (001) and (010). These outcomes open up proper direction toward a careful design of facet-oriented BiVO₄ samples for improved photocatalytic overall water-splitting reactions.

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