Remarkable Influence of α -SnWO₄ Exposed Facets on its
Photocatalytic Performance for H₂ and O₂ Evolution Reactions

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ABSTRACT

A significant effect of the five major (121), (210), (111), (200), and (040) exposed facets obtained experimentally for orthorhombic α -SnWO₄ material on its performance for photocatalytic water splitting is highlighted from a hybrid DFT-based comprehensive study. Their electronic, redox, and transport characteristics reveal significant anisotropic characters. The specific function of each surface in water oxidation and proton reduction is in direct relationship with the exposed W coordination number. Our study predicts the (210) facet as being the only possible good candidate for OER and HER upon surface modification, whereas the (200) facet is found a good candidate only for HER. The (121) facet is an acceptable candidate for both OER and HER and the (111) facet for HER only but less potentials than (210) and (200). The (040) facet is an unsuitable candidate neither for OER nor for HER. Interestingly, the proposed (001) facet is predicted to be the best candidate for HER. These results indicate the right direction to be followed for enhanced photocatalytic water splitting reactions based on a rational design of facet-oriented α -SnWO₄ samples.

Introduction

Direct photoelectrochemical solar water splitting for hydrogen generation is expected to be a promising technology for a sustainable green environment and future clean energy framework.¹⁻⁴ For reducing cost and achieving high conversion efficiency, great efforts have been devoted to the development of a perfect and operating semiconductor photocatalyst. The objective is to obtain both H₂ and O₂ evolution reactions (HER and OER) at the same time by monitoring its original characteristics. In water splitting, the photogenerated electrons and holes are placed at the conduction band minimum (CBM) and valence band maximum (VBM) of the photocatalyst. Thus, suitable CBM/VBM positions are lying, respectively, higher than H⁺/H₂ and lower than O₂/H₂O potentials. They are needed for driving the electrons and holes to reduce proton and oxidize water.⁵ Furthermore, in order to ensure good mobility of electrons and holes all over the crystalline lattice of the material toward the surface, delocalized character of the orbitals related to the CBM and VBM states is required.⁶⁻¹⁰ Different strategies have been adopted to improve the photocatalytic features, either by adding co-catalysts on the photoelectrode surfaces to enhance the kinetics of electrons and holes to electrolyte or by making heterojunctions.¹¹⁻¹⁴ Lastly, engineering facet has been considered as a successful method to modulate the photoanode features and enhance its photocatalytic activity.¹⁵⁻¹⁸

Numerous visible-light-responsive oxide- and (oxy)nitride-based materials have been previously outlined as suitable candidate photocatalysts for water splitting,¹⁹⁻²⁵ Recently, α -SnWO₄ has been considered as a new promising candidate based on its indirect narrow band gap between 1.6 and 2.1 eV (theoretical maximal photocurrent density of 24.4 mA.cm⁻²) and its onset potential between -0.14 and 0.05 V vs RHE.²⁶⁻³² Until now, the various reported α -SnWO₄ photoelectrodes revealed poor photoelectrochemical performance, which has been assumed to be

caused by poor carrier transport preventing the released holes from arriving to the material surface.²⁸⁻³⁰ As the photoelectrochemical performance is strongly influenced by the optoelectronic and redox properties, there is indeed a crucial demand for a robust determination of the corresponding properties for α -SnWO₄.

Since α -SnWO₄ has gained particular attention as a potential photoanode for solar water splitting, determining the function of each of its exposed facets in photoredox reactions is indeed extremely important. Different preparation methods of α -SnWO₄ samples have given different morphologies and led to different photocatalytic behaviors.²⁶⁻³² Therefore, controllable preparation methods of α -SnWO₄ samples with selective facets are highly required to enable for better charge carrier separation and higher efficiency.

Theoretically, a few works have been reported on the bulk properties of α -SnWO₄,^{29,32-34} while no study was achieved so far on the properties of its corresponding surfaces. The principal factor limiting the performance still remains unclear and needs to be deeply investigated. Understanding the discrepancy in photocatalytic behavior thus requires an accurate examination of these surfaces. Previously, we investigated essential bulk characteristics of diverse photocatalytic compounds including α -SnWO₄^{6-10,30,35-40} using the density functional theory (DFT) with the hybrid Hyeed-Scuseria-Ernzerhof (HSE06) exchange-correlation functional.^{41,42} This approach proved, with various photocatalytic materials, to give a good reliability by reproducing the measured band gap and band positions relative to water redox potential.^{6-10,30,35-40} Recently, we identified the best possible facets for HER and OER of the extensively employed UV and visible light-driven photocatalysts, like TiO₂ and Ta₃N₅.^{43,44} Very recently, we have shown a significant impact of the predominant exposed facets obtained experimentally for the common visible-light-driven photoanode, BiVO₄, on its photocatalytic performance for water

splitting reactions.⁴⁵ These predictions were obtained from optoelectronic and redox features connection using this theoretical procedure and pertinent information for enhancing performance of the materials was proposed.⁴³⁻⁴⁵

In this paper, we address the impact, on the photocatalytic water splitting performance, of the five predominant (121), (210), (111), (200), and (040) exposed facets experimentally obtained for the orthorhombic α -SnWO₄ synthesized samples. This was achieved by performing a comprehensive study based on DFT with HSE06. For each exposed facet, we determined the electronic structure, the relative band alignment to water redox potential, and the generated electron/hole transport characteristics. The function of each facet in photoredox reactions and relevant candidates for OER and HER are thus defined. An ideal exposed facet on α -SnWO₄ for HER is predicted to be the (001) low Miller index surface. The methodology and computational details adopted in this work are reported in the Supporting Information (SI).

Results and Discussion

Bulk Properties: Atomic and Electronic Structures

The crystal structure of α -SnWO₄ is orthorhombic (*Pnna* space group). Its corners share distorted layers of WO₆ octahedra in the *ac* plane. These layers are connected between each other by layers of Sn²⁺ ions located in an edge sharing tetrahedral O environment (Figure 1). The WO₆ octahedra are characterized by W–O bond lengths between 1.80 and 2.06 Å. The SnO₄ tetrahedra are characterized by Sn–O bond lengths between 2.18 and 2.82 Å. Our PBE computed lattice constants ($a = 5.59$ Å, $b = 11.63$ Å, $c = 4.98$ Å, and $\alpha = \beta = \gamma = 90^\circ$) reproduced well the measured ones ($a = 5.62$ Å, $b = 11.69$ Å, c

= 4.99 Å, and $\alpha = \beta = \gamma = 90^\circ$).^{28-30,32,33} For bulk orthorhombic α -SnWO₄, our HSE06 computed band gap of 1.5 eV is close to the reported experimental values (in the 1.6-1.9 eV range) and is much more precised than the PBE calculated one of 0.8 eV.²⁶⁻³² No spin-orbit coupling effect on the band gap energy of this material was observed. The conduction band edge electronic states are mainly composed of unoccupied W⁶⁺ (5d⁰) orbitals. The valence band edge electronic states consist of a mixture of filled Sn²⁺ (6s²) and O²⁻ (2p⁶) orbitals, in accordance with X-ray absorption spectroscopy data.³³ The hybridization effect of Sn²⁺ (5s²) and O²⁻ (2p⁶) states at the valence band edge is assigned to the deformation in SnO₄ tetrahedra, in line with the X-ray absorption spectroscopy results.³³

Figure 1. Bulk crystal structure view depictions of α -SnWO₄ in the ab and ac planes using the $2 \times 1 \times 2$ supercell. Color legend: W in green, Sn in blue, and O in red.

Surface Properties: Atomic and Electronic Structures

Five predominant (121), (210), (111), (200), and (040) facets are experimentally acquired in α -SnWO₄ samples.²⁶⁻³² The two (121) and (210) facets are characterized by 3-coordinated Sn with both 4- and 5-coordinated W. The two (111) and (200) facets are composed of 2-

coordinated Sn and 4-coordinated W. The (040) facet consists of 3-coordinated Sn and 2-coordinated O without exposed W species that are presented in sub-layers (Figure 2).

Figure 2. DFT-based most stable slab atomic structures (top views) of the (121), (210), (111), (200), and (040) α -SnWO₄ surfaces. W in green, Sn in blue, and O in red. For the elements on each surface, the coordination numbers are indicated.

Similar orbitals contributions at the band edge electronic states are also obtained for (121)-, (210)-, (111)-, (200)-, and (040)-oriented α -SnWO₄ slabs. Compared to the bulk, their band gap is larger by 0.4 to 0.9 eV or smaller by 0.4 eV. The two (121) and (210) slabs give 2.2 and 2.4 eV band gaps, whereas the two (111) and (200) slabs give 1.9 and 2.1 eV band gaps. The (040) slab gives 1.1 eV band gap (Figure 3). The averaged band gap value for the various exposed

facets obtained from the prepared samples reproduced very well the reported experimental values with much better agreement than the bulk calculated one. For instance, the averaged band gap value (1.9 eV) for (121), (200), (040), and (210) slabs is in excellent agreement with the experimental value of Kölbach and co-workers (1.9 eV).²⁸ Again, the averaged band gap value (1.66 eV) for (121), (040), and (111) slabs reproduced very well the experimental value of Ziani and co-workers³⁰ and of Cho and co-workers (1.64 eV).³² Moreover, the averaged band gap value (2.0 eV) for (121) and (111) slabs is in excellent agreement with the experimental one obtained by Zhu and co-workers and by Pyper and co-workers (2.1 eV).^{29,31} These outcomes highlight a remarkable effect of the facets on the band gap of the prepared α -SnWO₄ samples.

Surface Properties: Relative Band Alignment to Water Redox Potential

As reported in the methodology and computational details (SI), the VBM and CBM energy levels for the (121), (210), (111), (200), and (040) SnWO₄ slabs were elucidated with regard to vacuum. Anisotropic trend is acquired on the basis of the facet identity (Figure 3). The predicted results highlight the remarkable effect of the facets on the redox characteristics of the prepared α -SnWO₄ samples. For the two (121) and (210) SnWO₄ slabs, the VBM levels are 0.5 and 0.3 eV below the O₂/H₂O one. Their CBM level is 0.3 and 0.9 eV above the H⁺/H₂ one (Figure 3). As their VBM and CBM levels are correctly positioned *versus* water redox potential, the two surfaces are appropriate candidates for OER and HER. However, the CBM energy levels for the (111) and (200) slabs are 0.7 and 0.9 eV above the H⁺/H₂ one, whereas their VBM level is located just at the O₂/H₂O level (see Figure 3). Owing to the wrong VBM levels for the (111) and (200) slabs relative to O₂/H₂O level, the released holes

cannot oxidize water. Thanks to the correct CBM levels with regard to the H^+/H_2 one, these two facets are predicted as suitable candidates only for HER. Nevertheless, the VBM energy level for the (040) slab is 0.4 eV lower than the $\text{O}_2/\text{H}_2\text{O}$ potential. Its CBM level is 0.5 eV below the H^+/H_2 level (see Figure 3). As a result of the incorrect CBM level of the (040) $\alpha\text{-SnWO}_4$ slab relative to H^+/H_2 level, the excited electrons cannot reduce proton. Consequently, this surface is considered as an appropriate candidate only for OER.

Figure 3. VBM and CBM energy levels for the optimized (121)-, (210)-, (111)-, (200)-, and (040)-oriented $\alpha\text{-SnWO}_4$ slabs *versus* vacuum obtained using HSE06. The correspondence *versus* normal hydrogen electrode (NHE) is also indicated.

The similarity noticed in the redox features between (121) and (210) slabs could be understood by the existence of 3-coordinated Sn with 4- and 5-coordinated W on the two facets. The little downward shift in the levels of (121) slab relative to those of (210) slab could be explained by the existence of some 5-coordinated sublayer W resulting from some broken W-O bonds in the bulk counterpart. These predicted results highlight the possible spatial separation of carriers between (121) and (210) facets of $\alpha\text{-SnWO}_4$. The similar situation also noticed in the redox features between the two (111) and (200) facets can be explained by the 3-coordinated Sn with 4-

coordinated W present on the two surfaces. The little upward shift in the levels of (111) and (200) slabs relative to those of (121) slab could be explained by the absence of some 5-coordinated surface W. The notable variation in the redox characteristics of (040) slab promoting the radical downward shift particularly in the CBM band level relative to those acquired for the (121), (210), (111), and (200) slabs, can also be explained by the existence of only 3-coordinated Sn and 2-coordinated O without exposed W species that are presented in sub-layers (Figure 2).

Surface Properties: Generated Electron/Hole Transport Characteristics

In Figures 4 and 5, we display the partial charge density maps for VBM and CBM states of (121)-, (210)-, (111)-, (200)-, and (040)-oriented α -SnWO₄ slabs obtained using HSE06. For the (121) and (210) surfaces, the partial densities of VBM/CBM states are somehow distributed over O 2p, Sn 5s, and W 5d orbitals in the lattice, giving such holes/electron mobility from bulk to (121) and (210) surfaces (see Figure 4). However, the densities for the VBM/CBM states of the (210) slab exhibit more pronounced delocalization of Sn 6s orbitals throughout all Sn species in the slab and of W 5d orbitals delocalization towards the 5-coordinated surface W (Figure 4). This result would predict easier migration or better mobility of holes and electrons from the bulk to the (210) surface rather than to the (121) one. However, the surface Sn species in the case of (210) needs to be modified with other neighboring hetero elements to enhance the hybridization with the sublayer Sn 6s orbitals and increase the hole mobility to the (210) surface. In the case of (111) slab, the CBM partial electron density map is similar to that obtained for (121), and therefore the electron mobility towards the (111) surface is expected to be similar as (121) but lower than (210) (Figure 5). For the (200)-oriented α -SnWO₄ slab, the density map for the CBM state is similar to that obtained for (210), and therefore the electron mobility towards the (200) surface is expected to be similar to that of (210) but higher than that of (121) (Figure 5). With

respect to the (040)-oriented α -SnWO₄ surface, the partial density for the VBM state is strongly localized on Sn 6s orbitals located deeply inside the bulk counterpart with very minor contribution from the first sub-layer Sn species (Figure 5). This result strongly limits the holes mobility from bulk to the (040) surface. These outcomes also highlight the significant impact of the exposed facets on the charge carrier transport characteristics of the prepared α -SnWO₄ samples.

Figure 4. Charge density contour plots for VBM (in light blue) and CBM (in light green) electronic states of (121)- and (210)-oriented α -SnWO₄ slabs (side views) obtained using HSE06.

Figure 5. Charge density contour plots for CBM (in light green) electronic states of (111)- and (200)-oriented α -SnWO₄ slabs and for VBM (in light blue) electronic state of (040)-oriented SnWO₄ slab (side views) obtained using HSE06.

If we combine the redox and optoelectronic characteristics for each surface, our study points up the (210) facet to be the only possible good candidate for HER and OER upon surface modification, followed by the (121) facet as an acceptable candidate. The two (200) and (111) facets are good or acceptable candidates for HER only, respectively. The (040) facet is an unsuitable candidate neither for OER nor for HER. The obtained results explain the fundamental reason behinds the poor photoelectrochemical performance of α -SnWO₄ prepared samples as reported experimentally.²⁸⁻³⁰ We correlate this phenomenon with the very limited choice of suitable candidate surfaces for OER to (121) and (210) together with the low mobility of photogenerated holes to reach these two surfaces.

Comparison with the Fundamental Features of the Predicted (001) α -SnWO₄ Surface

Following this methodology, we have also investigated the fundamental features of the remaining low Miller index (001) surface of α -SnWO₄, which was not observed so

far in experiments. Note that the two (200) and (040) exposed facets obtained experimentally for α -SnWO₄ are identical to the low Miller index (100) and (010) ones. In Figure 6, we show the most stable slab atomic structure, VBM and CBM energy levels *versus* NHE, and electron density map for the CBM state of the predicted (001) α -SnWO₄ surface. The (001) surface is made of 4-coordinated Sn and 4-coordinated W, differently from all the previous investigated ones. Comparing to bulk, its band gap is broader by 0.2 eV. Its CBM energy level is 0.5 eV above the H⁺/H₂ level, while the VBM level is located just at the O₂/H₂O one, similarly as obtained in the cases of (111) and (200) surfaces. Due to its incorrect VBM level relative to the O₂/H₂O one, the released holes cannot be driven for oxidizing water, and therefore, this facet is predicted as an appropriate candidate for HER only. The density associated to the CBM electronic state of (001) facet is well distributed over all W 5d orbitals in the slab. The W 5d delocalization orbitals throughout all W species in the slab is much more pronounced here than in the two previous (210) and (200) cases. This result leads to smoother migration or better electrons mobility from bulk to the (001) surface as compared to (210) and (200). In the case of (001), the active sites for HER would be the 4-coordinated W species covering the entire surface. The 5-coordinated W species partially covering the two (210) and (200) surfaces were found to be the active sites for HER. This means that the number of active sites in the case of (001) is higher than in the two (210) and (200) cases. Therefore, the predicted (001) facet would be the best candidate for HER.

The surface energy of the six explored facets was computed, and values of 0.51, 0.48, 0.55, 0.31, 0.85, and 1.06 J/m² are obtained for the (121), (210), (111), (200), (040) and (001) facets, respectively. The surface energy of (001) is 0.5-0.7 J/m² higher than those obtained for (121), (210), (111), (200), and (040). This makes the (001) surface thermodynamically less stable than the five others. The sensitivity of this surface comes from the presence of four-coordinated Sn. This result might explain the reason why (001) was not reported experimentally. However, the kinetic effect present in controllable preparation methods can stabilize this surface. The interesting fundamental results obtained for the (001) facet will certainly motivate the experimentalists to target, stabilize, and test this surface for HER.

Figure 6. DFT-based most stable slab atomic structure (top view, left), VBM and CBM energy levels *versus* NHE (middle), and electron density map (in light green) for CBM state (side view, right) of the predicted (001) α -SnWO₄ surface obtained using HSE06.

Rational Way to Overcome the Photocatalytic Performance Limitation of α -SnWO₄

In principle, the co-catalysts for HER and OER must be deposited on the greatest exposed facets to raise the electrons and holes transfer kinetics to the electrolyte. Getting fitting flat band potentials to water redox reactions of a powder sample cannot confirm an operating material for photocatalytic water splitting because of the anisotropy in the redox and optoelectronic features

as well as their direct relationship with the identity of the facet. In this work, the obtained results could give the fundamental explanations why α -SnWO₄ photocatalyst powder samples possess low activity for OER, whereas better performance for HER was acquired. Overcoming this limitation in a rational way entails a selective deposition of the co-catalyst for HER on the (001) before the (200) surface. The co-catalyst for OER must be deposited on the (210) facet. This is expected to enhance the stability of this material from self-oxidation. The 4-coordinated W situated on the two (001) and (200) surfaces would be the active site for HER. The 3-coordinated Sn situated on the (210) surface is the active site for OER.

One should be reminded here that this work mainly calculated the conduction and valence band positions as well as the corresponding partial charge density for these α -SnWO₄ facets, which could provide the thermodynamic feasibility prediction for their H₂ and O₂ evolution reactions. However, the kinetics-related simulations of H₂ and O₂ evolution on these α -SnWO₄ facets have not been taken into account in this work. Specifically, the adsorption of water molecules and related intermediates, the desorption of H₂ or O₂ molecule on the α -SnWO₄ facets surface are all closely related to their photocatalytic activity. This is indeed an important aspect to be also explored for the prediction of their water splitting performance. DFT computations considering these different elements are currently ongoing and will be reported in the near future.

Conclusions

To summarize, we have highlighted a significant effect of the five major (121), (210), (111), (200), and (040) exposed facets obtained experimentally for orthorhombic α -SnWO₄ material on the performance for photocatalytic water splitting. Their electronic, redox, and transport characteristics revealed significant anisotropic characters. The specific function of each surface in water oxidation and proton reduction was in direct relationship with the exposed W

coordination number together with and their structural configuration. By combining the redox and optoelectronic characteristics of each surface, we predicted the (210) facet to be the only possible good candidate for OER and HER after surface modification, whereas the (200) facet is a good candidate only for HER. The (121) facet was classified as an acceptable candidate for both OER and HER and the (111) facet for HER only but less potentials than (210) and (200). The (040) facet was predicted as an unsuitable candidate neither for OER nor for HER. Interestingly, the proposed (001) facet was predicted to be the best candidate for HER. By adopting a rational design of facet-oriented α -SnWO₄ samples, these results will serve as guideline for enhancing photocatalytically water splitting reactions using this material.

Associated Content

Supporting Information

Methodology and computational details used in this work.

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Notes

The authors declare no competing financial interest.

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TOC Graphic

Predicting the most appropriate surface candidates of orthorhombic α -SnWO₄ photocatalyst for H₂ and O₂ evolution reactions