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Abstract

Highly efficient visible-light photocatalysts are strongly in demand because they make it possible to achieve higher efficiency in utilization of solar energy, which is renewable and abundant. A narrow band gap, effective separation of photoexcited charge carriers, and proper band-edge positions, which depend on the band structure of the photocatalyst, are crucial for solar-energy conversion efficiency. In this review, we have summarized reports on the strategy of exploiting highly efficient visible-light photocatalysts by constructing their band structure with anisotropic p and s-p hybridization states. Taking advantage of their dispersive and easily tunable band properties, enhanced efficiency in solar light absorption, efficient separation of photoexcited charge carriers and catalytic reactions are expected to be simultaneously achieved.

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Efficient visible-light photocatalysts by constructing dispersive energy band with anisotropic p and s - p hybridization states

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Abstract

Highly efficient visible-light photocatalysts are strongly in demand because they make it possible to achieve higher efficiency in utilization of solar energy, which is renewable and abundant. A narrow band gap, effective separation of photoexcited charge carriers, and proper band-edge positions, which depend on the band structure of the photocatalyst, are crucial for solar-energy conversion efficiency. In this review, we have summarized reports on the strategy of exploiting highly efficient visible-light photocatalysts by constructing their band structure with anisotropic p and s - p hybridization states. Taking advantage of their dispersive and easily tunable band properties, enhanced efficiency in solar light absorption, efficient separation of photoexcited charge carriers and catalytic reactions are expected to be simultaneously achieved.

Keywords: p state, s - p hybridization, anisotropic orbitals, visible-light photocatalysts, solar energy.

Main text

1. Introduction

In recent decades, the excessive use of fossil fuels has resulted in a serious global crisis involving energy shortages and environmental pollution. There is a great demand to develop green and sustainable technologies for clean energy production and environmental remediation. Photocatalysis, through which one can convert solar energy into chemical energy, has been regarded as one of the most promising strategies. It has been demonstrated to exhibit great potential in several applications, including photocatalytic water splitting, photosynthesis, and the treatment of pollutants in aqueous or gas phase [1-4]. Unfortunately, reliable photocatalysts are scarce, although the appeal of the direct conversion of solar into chemical energy via semiconductor compounds has been recognized for a long time. This is mainly due to their low solar-energy conversion efficiency, especially in the visible-light spectrum.

Generally, a typical photocatalytic process involves three steps: (i) absorption of solar light (with the efficiency denoted as η_A), (ii) separation of photoexcited charge carriers (with the efficiency denoted as η_S), and (iii) reduction or oxidation reactions at the surface to complete the solar energy conversion (with the efficiency denoted as η_C). The overall efficiency (η) is therefore determined by multiplying the efficiencies of the individual steps: $\eta = \eta_A \times \eta_S \times \eta_C$. Thus, several criteria are essential for the design and development of novel photocatalysts that possess high solar-energy conversion efficiency.

First of all, the band gaps of the photocatalysts should be narrow enough ($E_g < 3.0$ eV), which allow absorption of both ultraviolet (UV) and visible light in the solar spectrum. This is because UV and visible light account for 5% and 43% of the solar spectrum, respectively. Secondly, a high separation rate and high mobility of the photoexcited charge carriers (electrons and holes) are essential for high-efficiency photocatalysts. The former can lead to high quantum conversion efficiency, while the latter increases the effective charge-carrier diffusion length and thus enhances the photocatalytic activity. For semiconductors, the mobility of electrons and holes is determined by their effective mass (m^*). As shown in Eq. (1), the m^* is estimated to the second order derivative of energy (E) with respect to the wave vector (k), which is reflected by the curvature of the band edges.

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \times \frac{d^2E}{dk^2} \quad (1)$$

As illustrated in Figure 1a, a larger curvature of the band leads to a small m^* (light effective mass) of the charge carriers. This means the dispersion of the electronic band determines m^* , that is, the more dispersive the band the smaller m^* will be, and consequently, the higher the mobility it will have. In contrast, a dispersion-less band leads to large m^* (heavy effective mass) of charge carriers with low mobility. Thirdly, the positions of the valence and conduction bands (VB and CB) are of importance to determine the chemical potential of photoexcited electrons and holes, which have significant impact on the efficiency of different photocatalytic reactions (Figure 1b). The overall

solar-energy conversion during the photocatalysis process is, therefore, determined by the electronic structures of photocatalysts.

Recently, semiconductor photocatalysts mainly or partially constructed by *p*-block elements have been reported to exhibit high visible-light photocatalytic activity and considerable efficiency [5-11]. Their alluring visible-light photocatalytic performances could be ascribed to their unique electronic structures, which involve *p* orbitals or *s-p* hybridized orbitals in constructing their band edges. Through *p* or *s-p* hybridizations, *p* electrons from *p*-block elements lift the top of the VB and/or lower the bottom of the CB in photocatalysts, hence reducing the band gap [12-15]. In addition, spatially anisotropic *p* and *s-p* hybridization states create highly dispersive band structures, which promote separation and mobility of photoexcited electron-hole pairs by reducing their effective mass. All these features significantly contribute to high energy conversion efficiency under solar light. Thus, through selecting suitable elements, which have valence electrons residing in *s* or *p* orbitals, it is expected that we could design and develop visible-light photocatalysts with the desired band structure. This strategy is essentially in accordance with the fact that almost all the superior electronic devices in the semiconductor industry are based on *p*-block elemental semiconductors or compounds with *s-p* hybridizations, such as Si, Ge, and GaAs. One of their major advantages over other semiconductors is the high mobility of their charge carriers, which originates from their dispersive *p* or *s-p* hybridized bands. Based on the above

principles, compounds constructed from the elements in three regions (IA and IIA, IB and IIB, and the *p*-block) in the periodic table have aroused our interest as shown in Figure 1c. This is because their configurations of *d* orbitals are either d^0 or d^{10} in these compounds, which has the result that their band edges are constructed from anisotropic *p* or *s-p* hybridization states. Therefore, taking advantage of the easily tunable band gap and anisotropic orbitals, exploiting semiconductors built from these elements has great potential to create visible-light photocatalysts with high overall efficiency. This review will exclusively focus on the recent advances in visible-light photocatalysts with electronic structures constructed from anisotropic *p* or *s-p* hybridization states.

2. Visible light photocatalysts composed of only *p* elements

A typical example of the visible-light photocatalysts that are only constructed from *p*-block elements, is the bismuth oxyhalides family, $\text{Bi}_x\text{O}_y\text{X}_z$ ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$). As a heavy metal, bismuth atoms tend to form very weak bonds with non-metal elements, which generally tend to have small molecular orbital overlap and favours the establishment of narrow band gaps. Along with a narrow band gap, a small effective mass may to be acquired for semiconductors with similar crystal and band structures, according to the $\mathbf{k}\cdot\mathbf{p}$ perturbation theory. Various $\text{Bi}_x\text{O}_y\text{X}_z$ compounds exhibit high visible-light activity towards photocatalytic degradation of organic and inorganic toxic substances, water splitting, and N_2 fixation [5,6,16-25]. Their VB maximum (VBM) is mainly composed of O 2*p* and X *np* states ($n = 3, 4, \text{and } 5$ for Cl, Br, and I,

respectively). Their CB minimum (CBM) in most cases is constructed from Bi $6p$ states [26-28]. Thus, the band structures of $\text{Bi}_x\text{O}_y\text{X}_z$ are expected to be tunable via the halogen species and the ratios of Bi: O: X. Meanwhile, due to the dispersive properties of the p and s - p hybridization states, high-mobility charge carriers can be obtained in many $\text{Bi}_x\text{O}_y\text{X}_z$ compounds. As shown in Figure 2a and b, both experimental and theoretical works have suggested that the band gap of BiOX can be gradually narrowed from 3.4 eV for BiOCl to 2.8 eV for BiOBr and 1.9 eV for BiOI, due to the increasing participation of the X np states [29,30]. As a result, Zhang et al. proved that BiOI shows a wider visible-light absorption range than BiOCl and BiOBr, and higher visible-light photocatalytic activity towards degradation of methyl orange (MO) [31]. On the other hand, due to the appropriate VB edge, BiOBr and BiOCl exhibited much higher oxygen evolution efficiency and better photocatalytic degradation of Rhodamine B (RhB) and phenol under visible light or simulated sunlight irradiation than BiOI [29, 32]. As shown in Figure 2 d and e, Bhachu et al. demonstrated that BiOBr also had much superior water oxidation activity compared to BiOI and BiOCl under simulated sunlight irradiation, due to its more positive VB edge [33].

Adjusting the ratio of Bi: O: X in $\text{Bi}_x\text{O}_y\text{X}_z$ has also been demonstrated to be an effective approach to obtain visible-light photocatalysts with the desired electronic structure [6,34-36]. Shang et al. reported that $\text{Bi}_{24}\text{O}_{31}\text{Br}_{10}$ ($E_g \approx 2.8$ eV, similar to BiOBr) exhibited considerable photocatalytic activity towards Cr(VI)

ion reduction and H₂ evolution through water splitting (Figure 3b and c) [6]. BiOBr cannot split water to release H₂ through photocatalytic reactions, however, because its CBM is more positive than the electrode potential of H⁺/H₂. While in the case of Bi₂₄O₃₁Br₁₀, as illustrated in Figure 3a, the CBM, mainly consisting of hybridized Bi 6*p* and Br 4*s* orbitals, is uplifted to be more negative than the electrode potential of H⁺/H₂, which enables Bi₂₄O₃₁Br₁₀ to reduce water into H₂ under visible-light irradiation. In addition, the hybridization *s-p* orbitals lead to a dispersive band, which is expected to increase its efficiency through promoting the separation of the photoexcited electrons and holes.

It should be noted that for Bi_{*x*}O_{*y*}X_{*z*} photocatalysts, the nature of their internal electric field contributes to the efficiency of separating photoexcited charge carriers, which is induced by their layered structure, consisting of interleaving positive [Bi-O] layers and negative X⁻ layers [18,33,37,38]. In a recent work, Li et al. demonstrated that substituting C atoms on Cl sites in Bi₃O₄Cl is an efficient way to enhance the internal electric field, which dramatically increases its bulk-charge separation efficiency to as high as 80%. The enhanced separation efficiency of photoexcited electrons and holes led to a higher capability for photocatalytic water oxidation under visible light without any noble metals and electron scavengers [39].

Besides Bi_{*x*}O_{*y*}X_{*z*}, some new *p*-block compounds have emerged as highly active visible-light photocatalysts due to their appropriate band structures. Huang et al. reported a ternary boron carbon nitride (B-C-N) alloy, which

showed great potential in visible-light photocatalytic water splitting and CO₂ reduction due to its adjustable band gap and two-dimensional (2D) electron system [40]. *p*-block elemental photocatalysts, such as Si [41], S [42], and P [43] have also been reported to show visible-light photocatalytic activity because their electronic structures are tunable towards crystalline structures and phases. With the special advantages of 2D materials, several monolayer or few-layer materials in composites with *p*-block elements are expected to exhibit high visible-light photocatalytic activity due to their narrow band gaps and special electronic structures. For examples, black phosphorus (BP) is a narrow bandgap semiconductor with a flexible and adjustable band-gap value. In addition, its CBM is highly asymmetric, and there is anisotropic charge mobility between the electrons and the holes. BP is thus predicted to be an excellent candidate for photocatalysis [44]. Monolayer red phosphorus (RP) is also predicted to be a semiconductor with a direct band gap of 2.4 eV, and to possess a very dispersive conduction band, which will be beneficial to the separation of photoexcited charge carriers [45].

3. Visible light photocatalysts integrating *p*-block elements with other elements with d^0 or d^{10} electron configurations

Integrating *p*-block electron configuration states with other elements with d^0 or d^{10} electron configurations in photocatalysts is another effective way to obtain charge carriers with small effective mass and high mobility, because dispersive *s-p* hybridization states are easily formed without the participation of

d orbitals. $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$, one of the silver silicates, is reported to be an excellent visible-light photocatalyst towards the degradation of organic compounds, owing to its unique band structure and ferroelectric polarization [46-50]. As shown in Figure 4a, the hybridized CBMs are very dispersive, whereas the VBMs are quite flat. The photoexcited electrons, consequently, have a small effective mass, which enables photoexcited electrons to easily move to surface active sites due to their high mobility. In contrast, heavy holes will be generated in the photoexcitation process. This special electron configuration is beneficial to the separation of photoexcited charge carriers and promotes solar-energy conversion efficiency in photocatalysis. Lou et al. found that the visible light absorption and band structures of amorphous silver silicates are tunable (Figure 4b and c) by the Ag/Si ratio. With an Ag/Si ratio of 3.2, silver silicate exhibits optimal photocatalytic activity due to its suitable band gap and high redox activity of carriers [51].

$\text{M}(\text{BiO}_3)_n$, where M are alkali metals, including Na, Li, K, Ca, and Mg [52-54], is another family of visible-light photocatalysts with high photocatalytic oxidation activity towards the decomposition of organic pollutants. With the empty 6*s* orbital of Bi^{5+} , the *s* states of Bi and the alkali metals have the opportunity to participate in both the CBM and the VBM, forming the *s-p* hybridization states with strong dispersion. For example, the VBM of NaBiO_3 is constructed mainly from O 2*p* orbitals, while the CBM is constructed from the hybridization of Na 3*s* and O 2*p* orbitals, which produces light electrons, and

thus contributes to the high activity of this material.

4. Conclusion

In this review, recent developments are reviewed in exploiting highly efficient visible-light photocatalysts through constructing their electronic structure with p and s - p hybridization states. Some photocatalysts have already been demonstrated to exhibit excellent visible-light photocatalytic activity, especially towards photocatalytic oxidation, by taking advantage of their tunable band structure and dispersive band features. It should be noted that substantial increases in the efficiency of visible-light photocatalysts are still urgently needed to realize wide industrial applications of photocatalysis. To achieve this goal, an in-deep understanding of each step of the photocatalytic processes is essential to acquire a high overall solar-energy conversion efficiency. Considering that there is an appreciable number of semiconductors that have not been exploited through quantitatively integrating the elements in the regions that we marked in Figure 1c, visible-light photocatalysts with a substantially increased efficiency have a high probability of being captured by this strategy.

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Figures and figure captions

Fig. 1 (a) Diagram of the relationship between the band shape and the effective mass of electrons and holes. (b) Diagram of the band structure of direct-gap semiconductors, illustrating its role in determining the catalytic properties of photocatalysts. (c) The periodic table of the elements with the IA and IIA, IB and IIB, and p -block regions marked using red ovals.

Fig. 2 (a) Ultraviolet-visible (UV-Vis) diffuse reflectance spectra of BiOX (X = Cl, Br, and I) [29]. (b) Calculated band gap and the band alignment of the BiOX (X = Cl, Br, I and F) compounds by density functional theory (DFT) [30]. (c) Oxygen evolution of BiOX under simulated sunlight irradiation [29]. (d) Photoanodic activity measurement of BiOBr film under simulated sunlight irradiation. (e) Stability of the BiOBr film at an applied voltage of 1.0 V vs. Ag/AgCl [33].

Fig. 3 (a) Schematic diagram of the uplifting of the CBM of Bi₂₄O₃₁Br₁₀. (b) Experiments on photocatalytic reduction of Cr(IV) under visible-light irradiation by Bi₂₄O₃₁Br₁₀, BiOBr and Bi₂O₃. (c) H₂ evolution by water splitting using Bi₂₄O₃₁Br₁₀ as photocatalyst under visible-light irradiation [6]. (d) Internal electric field (IEF)-mediated bulk-charge separation in carbon-doped Bi₃O₄Cl [39].

Fig. 4 (a) DFT calculated electronic structure of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$, in which a dispersive CB and flat VB can be observed. (b) Photodegradation rate of organic dyes over $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ under visible light; the inset shows the kinetics of the photocatalytic degradation process of organic dyes under visible light over $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$, indicating its high visible-light photocatalytic oxidation activity [47]. (c) UV-Vis diffuse reflectance spectra of Ag_2O and silver silicates prepared with different Ag/Si atomic ratios. (d) Estimated band gap (E_g) of amorphous silver silicates with different Ag/Si atomic ratios x ; the inset shows an enlargement of the indicated range [51].