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Boosting photoelectrochemical activities of heterostructured photoanodes through interfacial modulation of oxygen vacancies

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ABSTRACT

Oxygen deficiency control has become an on-looming strategy for improving the catalytic ability of semiconductors, while the impact of defect distribution on the separation of charge carriers is still an open question. Herein, $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterostructures are used as a typical model to demonstrate the hypothesis of boosting photoactivity of photoanodes through modulating the spatial distribution of oxygen vacancies. Compared to pristine TiO_2 , significantly improved photoelectrochemical performance is achieved through suppressing intrinsic defects in Bi_2WO_6 and tuning the formation sites of interfacial oxygen vacancies. Both experimental and theoretical investigations demonstrate that the distribution of interfacial oxygen vacancies around interface of Bi_2WO_6 and in the TiO_2 side is beneficial for the efficient extraction of photogenerated electrons toward counter electrodes. This research shed atomic-level insight into the interfacial modulation of defect distribution. Therefore, it provides a new principle to develop efficient heterostructures for photoelectrochemical and photocatalytic applications.

1. Introduction

Photoelectrochemical (PEC) is widely considered as a promising way to mitigate environmental issues caused by the combustion of fossil fuels and to meet increasing worldwide demands for energy. By far, the major limiting factors affecting the performance of photoelectrodes include light absorption, charge separation and surface reactions [1,2]. Substantial efforts have been put into solving these problems, while the construction of heterostructured photoanodes is one of the most effective strategies. Over the past decades, many different types of heterostructures have been designed and extensively studied, such as type-I, type-II (staggered alignment), Z-scheme system and p–n junctions [3–5]. However, it still remains a great challenge to overcome the limitation of charge extraction for potential industrial applications. This is largely caused by the complicated interfacial mechanism, involving the formation of structural defects, strain field, surface states, etc. [6,7]. Especially, it is of both scientific and technical importance to evaluate the effect of interfacial structures on the PEC performance at the atomic-level [8,9].

Due to the significant impact on material properties ranging from ionic conductivity, charge localization to surface reactivity, defect modulation has become one of the most promising emerging strategies for developing high-efficiency photocatalysts [10,11]. Tremendous studies demonstrate that oxygen vacancy (O_v) states can remarkably affect the surface adsorption and reactivity of semiconductors [12–14]. Importantly, our recent study indicates that unpredictable activities of controversial heterojunctions is essentially dependent with the spontaneous formation of interfacial oxygen vacancies [15,16]. From the perspective of interfacial modulation, the comprehensive investigation of creation, migration, aggregation and distribution of oxygen vacancies is prerequisites for establishing the full picture of defective structures of heterostructures. Unfortunately, most prevailing strategies of defect modulation focus on the macroscopic characteristics of oxygen vacancies around heterostructured interfaces [17]. The impact of spatial distribution of oxygen vacancies on the separation of photogenerated charge carriers is still an open question [18]. Nevertheless, the orders-of-magnitude enhanced electrical conduction in non-stoichiometric heterostructures demonstrates the great potential of

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oxygen-deficiency modulation for emergent behavior [19].

Taking these facts into consideration, we unveiled a principle of boosting PEC activities of photoanodes through atomic-level modulation of interfacial oxygen vacancies. $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterostructured interfaces was selected as a prototypical example to demonstrate the fundamental impacts of intrinsic defects and spontaneously formed interfacial oxygen vacancies on the charge separation behaviors. Both experimental observations and theoretical calculations demonstrated that significantly improved photoactivity could be achieved through suppressing the formation of intrinsic defects in W-O-W coordination layer and simultaneously modulating the spatial distribution of interfacial oxygen vacancies. The separation of charge carriers in the heterostructures was greatly facilitated through controlling the spontaneous formation of vacancies around the interface of Bi_2WO_6 and in the TiO_2 side. This simple and effective strategy provides new and unexplored opportunity of defect modulation by controlling oxygen stoichiometry, for high-efficiency photoelectrochemical and photocatalytic applications.

2. Experimental section

2.1. Synthesis of Bi_2WO_6 with controlled oxygen vacancies

A facile glycol-assisted solvothermal method was used to fabricate Bi_2WO_6 photocatalysts with different concentration of oxygen vacancies. In a typical synthesis, 0.4 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 25 mL of ethylene glycol in a Teflon-lined autoclave. The solution was sonicated for 5 min, then 0.2 mmol of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was added. The concentration of oxygen vacancies in Bi_2WO_6 products could be well controlled by changing the mixing conditions of the reaction solution. For lower concentration of oxygen vacancies, the suspension was stirred for 30 min at room temperature and then heated at 160 °C for 15 h. An additional ultrasonic process was adopted to facilitate the formation of oxygen vacancies, as the concentration increased along with the prolonged sonication time. Finally, the products were collected by centrifuging, washed with deionized water thoroughly and dried at 60 °C. For the convenience of descriptions, Bi_2WO_6 with low, medium and high concentration of oxygen vacancies were denoted as $\text{L-O}_v\text{-Bi}_2\text{WO}_6$, $\text{M-O}_v\text{-Bi}_2\text{WO}_6$ and $\text{H-O}_v\text{-Bi}_2\text{WO}_6$, respectively.

2.2. Fabrication of $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterostructures

To construct heterostructured interfaces between TiO_2 and Bi_2WO_6 , rutile TiO_2 (R- TiO_2) and rutile/anatase TiO_2 (R/A- TiO_2) were synthesized using a hydrothermal method described in our previous paper [16]. Then, FTO substrate coated with different types of TiO_2 films were placed at an angle against the wall of the Teflon-liner. During the subsequent solvothermal treatment, similar reaction conditions were used to deposit Bi_2WO_6 with different concentration of oxygen vacancies onto TiO_2 .

2.3. Characterizations

X-Ray diffraction (XRD) was performed using a Rigaku RINT 2100, with a voltage of 40 kV. The morphologies of the products were characterized by field emission scanning electron microscope (FE-SEM, JSM-7600F, JEOL) and high-resolution transmission electron microscope (HR-TEM, JEOL-2010). The elemental composition of films was examined by energy dispersive X-ray spectrometer (EDS). X-ray photoelectron spectroscopy (XPS) was carried out using the XPS spectrometers (ESCALab220I-XL). The diffuse reflectance spectra were characterized by UV–vis–NIR spectrophotometer (Cary 5000). Electron spin resonance (ESR) analysis was operated at a Bruker E500 spectrometer.

2.4. Evaluation of photocatalytic activities

Photoactivity of Bi_2WO_6 with different concentration of oxygen vacancies was evaluated by the photocatalytic degradation of RhB, with a 300 W Xe lamp as light source. Typically, 10 mg of photocatalysts were dispersed in the dye solution (50 mL, 10 ppm) in a cylindrical vessel under magnetic stirring. The suspension was stirred in the dark for 2 h before irradiation to ensure the adsorption–desorption equilibrium. Certain amount of suspension was sampled every 15 min by micropore filtration membranes for the subsequent measurement. The concentrations of filtrates were analyzed using a UV–Vis spectrophotometer (Hitachi UV-3100).

2.5. Photoelectrochemical measurements

Electrochemical and photoelectrochemical measurements were performed using a three-electrode configuration. TiO_2 -based heterostructures were used as working electrode, with Ag/AgCl as reference and Pt plate as counter electrode. For PEC studies, 0.2 M Na_2SO_4 aqueous solution was used as electrolyte. The tests were carried out using a 150 W Xe lamp equipped with AM 1.5 G filter, with light intensity of 100 mW cm^{-2} . Photocurrent was measured by linear-sweep voltammetry (Gamry electrochemical workstation, Interface 1000). The electrical impedance spectroscopic (EIS) and Mott-Schottky plots at a frequency of 1000 Hz were measured in the dark.

2.6. First-principles calculations

The density functional theory (DFT) calculation was performed by applying CP2K/Quickstep package [20]. The PBE exchange correlation functional was used for all calculations. Hubbard U correction was applied to W 5d and Ti 3d orbitals with the corresponding U values set to 5 eV and 4.2 eV, respectively [21,22]. The norm-conserving Goedecker, Teter, and Hutter (GTH) pseudo potentials were used to describe core electrons [23]. The wave function of valence electrons were expanded in terms of Gaussian function with molecularly optimized double-zeta polarized basis sets ($m\text{-DZVP}$) [24]. A 320 Ry cut off energy was used for auxiliary basis set of plane waves.

With a perovskite-like layered structure, Bi_2WO_6 -(010) are usually selected as typical exposed facets for structural simulation. Accordingly, A- $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterostructures were modeled by four layers of anatase-(101) and twelve layers of Bi_2WO_6 -(010). R- $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterostructures were modeled by four layers of rutile-(110) and twelve layers of Bi_2WO_6 -(010).

3. Results and discussion

3.1. Modulation of intrinsic defects of Bi_2WO_6

Photoactivity of heterostructures is highly dependent on the electronic structures of component semiconductors. To demonstrate the strategy of interfacial modulation, TiO_2 and Bi_2WO_6 , typical semiconductors with finely tuned electronic structures, were selected as model photocatalysts. A facile glycol-assisted solvothermal method was used to modulate intrinsic oxygen vacancies in Bi_2WO_6 , by changing mixing conditions of precursor solution (Fig. S1). Fig. 1a and Fig. S2 show the SEM images of Bi_2WO_6 prepared from precursor solutions with or without ultrasonic treatment, respectively. Both samples possess the morphology of flow-like superstructures assembled by 2-D nanoplates. XRD patterns in Fig. S3 reveal that all of the samples are consisted of orthorhombic phase of Bi_2WO_6 (JCPDS No. 79-2381).

The effect of fabrication conditions on the electronic structure of Bi_2WO_6 were studied by XPS. In the high resolution W 4f spectrum of $\text{L-O}_v\text{-Bi}_2\text{WO}_6$ (Fig. 1b), the two bands at 37.4 and 35.3 eV are ascribed to W 4f_{7/2} and W 4f_{5/2} of W^{6+} . Differently, the core-level spectrum of

Fig. 1. (a) SEM image of H-O_v-Bi₂WO₆; (b) W 4f XPS spectrum of L-O_v-Bi₂WO₆; (c) W 4f XPS spectrum of H-O_v-Bi₂WO₆; (d) ESR spectra of Bi₂WO₆ with different concentration of oxygen vacancies.

H-O_v-Bi₂WO₆ can be fitted into spin-orbit doublets (Fig. 1c). The appearance of +5 oxidation state of W at 36.3 and 35.0 eV indicates the change of electronic structures [25]. The formation of oxygen vacancy-related species can be confirmed by the significant change of O 1s spectra in Fig. S4a [26]. ESR spectra can further elucidate the defective structure of Bi₂WO₆ photocatalysts. In Fig. 1d, H-O_v-Bi₂WO₆ with ultrasonic treatment exhibits much stronger ESR signal than that with mild stirring (L-O_v-Bi₂WO₆). The intensity of broad signal in the region of $g=1.9\text{--}2.3$ increases with prolonged treatment time, which can be ascribed to the formation of abundant oxygen-centered surface hole trapping sites generated by oxygen vacancies [27]. These results strongly support that successful modulation of oxygen vacancy defects in Bi₂WO₆ by changing treatment method of reaction precursors.

To better understand the intrinsic nature of defects, the possible formation sites of oxygen vacancies in Bi₂WO₆ were evaluated by first-principles calculations. As one of the simplest member of Aurivillius family, Bi₂WO₆ with a layered structure is composed of perovskite-like slabs of [WO₄]²⁻ sandwiched between (Bi₂O₂)²⁺ units [28]. DFT calculation was utilized to calculate the formation energies of O_v in different coordination sites, using a 3×1×3 supercell. The O_v formation energy is calculated by equation: $E_f = E_{\text{defect}} + u_o - E_{\text{perfect}}$, where the E_f , E_{defect} , u_o and E_{perfect} represent the O_v formation energy, total energy of defect structures, oxygen chemical potential and total energy of perfect structures, respectively. The relatively small O_v formation energies indicate the easy formation of defects in Bi₂WO₆ during solvothermal reactions. The relative energy and O_v formation energy of different defective sites in Bi₂WO₆ are shown in Table 1. Bi–O–Bi and W–O–W are determined to be the most stable sites for O_v formation, with similar calculated values. In contrast, O_v formation energy in Bi–O–W is

Table 1
Relative energy and O_v formation energy of defect structures.

O _v site	Relative energy (eV)	Formation energy (eV)
Bi–O–Bi	0.00	3.00
W–O–W	0.05	3.05
Bi–O–W	1.18	4.23

much higher (4.23 eV), indicating the unfavorable formation of intrinsic defects in this layer (Table 1).

The electronic structure and spin density of the highest occupied molecular orbitals of Bi₂WO₆ with O_v in the W–O–W and Bi–O–Bi coordination layers were calculated. For the former case, the defect states are mainly composed of W, indicating that electrons released by oxygen vacancies are captured by W atoms in the [WO₄]²⁻ layers. The generation of O_v in the Bi–O–Bi layer exhibits different impact on the electronic structure of Bi₂WO₆, as electrons released by oxygen vacancies are mainly distributed on Bi atoms. Note that no obvious change of Bi 4f peaks is seen in Fig. S4b, indicating the preferential formation of oxygen vacancies in W–O–W layers.

The impact of oxygen vacancy formation on the light absorption ability of Bi₂WO₆ was evaluated. In the DRS spectra (Fig. 2a), both L-O_v-Bi₂WO₆ and H-O_v-Bi₂WO₆ exhibit strong absorption in the visible light region, with similar absorption edges around 450 nm. Differently, Bi₂WO₆ with high concentration of oxygen vacancies shows broad absorption tail in the wavelength range of 450–800 nm. The obviously extended absorption towards to near infrared region implies the existence of trap states induced by oxygen vacancies [29]. Accordingly, the color of Bi₂WO₆ powders

Fig. 2. (a) UV-vis diffuse reflection spectra of Bi₂WO₆ with different concentration of oxygen vacancies; (b) Photocatalytic degradation of RhB over different types of Bi₂WO₆ under full-arc irradiation.

changes from white to dark-gray, accompanied with the gradual formation of non-stoichiometric structures.

Rhodamine B (RhB) was used as a model pollutant to evaluate the photocatalytic activity of Bi₂WO₆ with modulated intrinsic defects. As shown in Fig. 2b, photoactivity of Bi₂WO₆ is highly dependent with the concentration of oxygen vacancies, as L-O_v-Bi₂WO₆ presents 4 times higher apparent rate constant than H-O_v-Bi₂WO₆. It indicates that oxygen vacancies in the [WO₄]²⁻ layers is detrimental for the full spectrum activity of photocatalysts, although the intermediate state absorption contributes to the superior charge mobility and near-infrared photoactivities (Fig. S5a) [30]. This effect can be well interpreted by the defect-dependent formation of surface reactive species. It has been reported that oxygen molecular activation can be facilitated by oxygen deficiency, which agrees well with the enhanced oxygen reduction property of H-O_v-Bi₂WO₆ compared to L-O_v-Bi₂WO₆ (Fig. S6). Therefore, formation of superoxide radicals should be favorable for H-O_v-Bi₂WO₆ under illumination, whereas nonradiative relaxation in the defective structures inevitably decreases the oxidation ability of photogenerated holes [31]. Noted that holes are determined to be the dominant reactive species for degrading RhB (Fig. S5b), it is reasonable that deteriorated photoactivity is achieved for Bi₂WO₆ with oxygen vacancies in W-O-W coordination sites. Therefore, the facile modulation of intrinsic defects of component semiconductors is a prerequisite for designing efficient heterostructured photoanodes.

3.2. Modulation of interfacial oxygen vacancies of heterostructures

To reveal the fundamental role of oxygen vacancy distribution for interfacial charge separation, Bi₂WO₆ with modulated intrinsic defects was used to construct TiO₂/Bi₂WO₆ heterostructures. XRD patterns of TiO₂/Bi₂WO₆ are presented in Fig. 3a, distinct peaks at $2\theta=37.1^\circ$, 63.7° and 70.7° can be indexed to tetragonal phase of rutile TiO₂ (R-TiO₂, JCPDS No. 88–1175). The formation of orthorhombic Bi₂WO₆ is confirmed by the appearance of new diffraction peaks around 34.5° and 42.4° . According to SEM observations (Fig. 3b and c), dense and highly aligned TiO₂ nanorod arrays are formed on FTO substrates, with the film thickness of 2 μm (Fig. S7a). Fig. 3c indicates the successful deposition of Bi₂WO₆ nanoparticles onto the surface of TiO₂ nanorods (Fig. S7b). In the HR-TEM image of a typical nanoparticle (Fig. 3d), the lattice space of 0.27 nm is consistent with the (200) facets of Bi₂WO₆.

The band alignment of TiO₂/Bi₂WO₆ heterostructures was firstly studied by valence band (VB) XPS and Mott-Schottky measurements. In Fig. 4a, the valence band maximum (VBM) of TiO₂ and L-O_v-Bi₂WO₆ are determined to be 2.1 and 2.4 eV, respectively. Based on the Mott-Schottky plots in Fig. 4b, the flat band potentials (V_{fb}) of TiO₂ and Bi₂WO₆ are calculated to be -0.65 and -0.41 V vs. Ag/AgCl. Considering the

bandgap of 3.05 and 2.75 eV for TiO₂ and Bi₂WO₆, more positive conduction band minimum (CBM) is achieved for L-O_v-Bi₂WO₆. The formation of inverse Type II band alignment is well confirmed by the first-principles calculation results in Fig. S8 [32].

The impact of heterostructure formation on the interfacial structure of TiO₂/L-O_v-Bi₂WO₆ was comprehensively investigated. The formation of two distinct slopes in the Mott-Schottky plot of R-TiO₂/Bi₂WO₆ indicates the existence of partial ionized surface states under applied potential (Fig. 5a) [33,34]. Furthermore, the interfacial energy states is substantially influenced by the phase structure of TiO₂, as evidenced by the shifted intercept of anatase TiO₂ (A-TiO₂) deposited heterostructures (Fig. S9). ESR results in Fig. 5b clearly verify the spontaneous formation of defective interfaces in the heterostructures. Compared to blank TiO₂ and L-O_v-Bi₂WO₆, R-TiO₂/Bi₂WO₆ exhibits intense paramagnetic signal with g value of 1.996, which can be ascribed to oxygen vacancies in oxides. Due to the formation of defect-induced surface species (such as $\cdot\text{O}_2^-$), (R/A)-TiO₂/Bi₂WO₆ possesses broad ESR signal, indicating the facilitated formation of oxygen vacancies around A-TiO₂/Bi₂WO₆ interfaces [35].

XPS measurements were carried out to investigate the influence of defect formation on the electronic structure of heterostructures. In the Ti 2p spectrum of rutile TiO₂/Bi₂WO₆ heterostructures (Fig. 5c), the rightward shift of Ti 2p_{3/2} peak (458.1 eV) with respect to pristine TiO₂ (458.5 eV) demonstrates the reduction of Ti⁴⁺ into Ti³⁺ caused by oxygen vacancies [36]. Meanwhile, the formation of defective Bi₂WO₆ is supported by the co-existence of W⁶⁺ and W⁵⁺ oxidation states in the core-level W4f spectrum (Fig. 5d) [37]. The simultaneous formation of oxygen vacancies in TiO₂ and Bi₂WO₆ suggests the complicated interfacial interactions in the heterostructures. Different chemical states of component elements are detected in (R/A-TiO₂)/Bi₂WO₆, which is in accordance with the Mott-Schottky and ESR results. The slight shift of Ti 2p_{3/2} peak (Fig. S10a) and the relatively higher content of W⁵⁺ (Fig. S10b) demonstrate that electrons caused by interfacial oxygen vacancies are more prone to distributing on Bi₂WO₆.

The influence of TiO₂ phase structure on the distribution of oxygen vacancies was thereafter simulated by first principles calculations (Fig. S11). For the atomic-level understanding of O_v formation, different sites in A/R-TiO₂/Bi₂WO₆ heterostructures are considered. The formation energies of O_v can be clearly divided into TiO₂ sides, Bi₂WO₆ sides and interface region, respectively (Fig. 6). The formation trends of oxygen vacancies between R-TiO₂/Bi₂WO₆ and A-TiO₂/Bi₂WO₆ interfaces are obviously different, which is in consistent with the experimental observations. Generally, O_v formation energies in A-TiO₂ sides and interface region are quite close for different positions in A-TiO₂/Bi₂WO₆ heterostructures. Meanwhile, the formation of oxygen vacancies in Bi₂WO₆ sides seems to be more stable than interface region. Differently, O_v formation

Fig. 3. XRD patterns of TiO_2 and $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterostructures; (b) Top-view SEM image of R- TiO_2 nanorod arrays; (c) Top-view SEM image of $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterostructures; (d) HR-TEM image of $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterostructures.

energies in R- TiO_2 monotonically increases from 3.24 eV to 5.42 eV, when the position moves from R- TiO_2 sides towards the interface region. Based on the minimum formation energy of 4.1 eV, interface region of Bi_2WO_6 should be the preferential location for defect formation. Note that R- TiO_2 in R- $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterostructures exhibits relatively larger O_v formation energy than Bi_2WO_6 sides, the migration of O_v from the Bi_2WO_6 side to the TiO_2 side is thermodynamically unfavorable. This blocking effect is beneficial for retaining high concentration of O_v around the heterostructured interfaces. As a result, the sufficient exposure of reactive sites in Bi_2WO_6 can promote the transfer of electrons from Bi_2WO_6 to TiO_2 . [38,39] Thus, our theoretical investigation fundamentally demonstrates the specific distribution modulation of oxygen vacancies in depth level through controlling phase structures. This result is also consistent with

the recent reports that adsorption behavior and surface reactivity of semiconductors can be significantly influenced by the distribution of oxygen vacancies. [40,41] Thus, it is expected that our strategy of defect modulating could provide a new paradigm for boosting PEC performance of heterostructured photoelectrodes. [42,43].

3.3. Oxygen vacancy boosted photoelectrochemical activity of heterostructures

PEC water splitting was carried out to evaluate the significant impact of oxygen vacancy modulation on the performance of $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterostructures. Compared to blank TiO_2 , the deposition of Bi_2WO_6 can obviously improve the photoresponse of photoanodes in

Fig. 4. (a) VB XPS of TiO_2 and Bi_2WO_6 photocatalysts; (b) Mott-Schottky plots of rutile TiO_2 and Bi_2WO_6 photocatalysts.

Fig. 5. (a) Mott–Schottky plot of R-TiO₂/L-Ov-Bi₂WO₆ heterostructures; (b) ESR spectra of TiO₂, Bi₂WO₆ and TiO₂/Bi₂WO₆ heterostructures; (c) Ti 2p XPS spectra of TiO₂ and R-TiO₂/Bi₂WO₆; (d) W4f XPS spectrum of R-TiO₂/Bi₂WO₆.

the linear sweep voltammetry (LSV) curves (Fig. 7a). Importantly, the current density of heterostructures is highly dependent on the concentration of intrinsic vacancy defects in Bi₂WO₆. R-TiO₂/L-Ov-Bi₂WO₆ exhibits the highest PEC response at 1.0 V vs. Ag/AgCl, which is about 3 times higher than that of pristine TiO₂. In contrast, only slightly improved photoactivity is achieved for TiO₂/H-Ov-Bi₂WO₆ heterostructures, indicating the negative contribution of intrinsic oxygen vacancies in Bi₂WO₆ to PEC performance.

Besides intrinsic defects in Bi₂WO₆, interfacial oxygen vacancies also present significant influence on the charge separation behaviors. As expected, R-TiO₂/L-Ov-Bi₂WO₆ exhibits obviously superior photoactivity than (R/A-TiO₂)/Bi₂WO₆ heterostructures (Fig. 7b). It further confirms the beneficial role of oxygen vacancies spontaneously formed in the TiO₂ side and around the interface region of Bi₂WO₆. Having revealed the fundamental strategy of defect modulation, facile vacuum treatment process was finally used to facilitate the formation of interfacial oxygen vacancies. When vacuum-treated rutile nanorods (O_v-TiO₂) was used to construct heterostructured photoanodes, unprecedented photocurrent density of 1.58 mA/cm² can be readily achieved. It indicates that PEC performance of photoanodes can be rationally boosted by inhibiting the intrinsic defects and simultaneously promoting the interfacial oxygen vacancies with modulated depth distribution.

Based on the above results, the mechanism of oxygen vacancy modulation in the heterostructured photoanodes is illustrated in Scheme 1. In the PEC water splitting devices, holes migrate to the photoanode surface to drive interfacial oxidation reaction, whilst electrons are transferred to the counter electrode to drive the reduction reaction. In order to achieve efficient charge separation, it is essential to facilitate the electron

transfer to TiO₂ matrix and then electrodes. The neutral or positive nature of oxygen vacancies can significantly influence the charge balance and charge mobility over the heterostructured interfaces. For the requirement of optimizing charge transfer pathways through decreasing interfacial energy barriers, it is reasonable to suppress the formation of intrinsic oxygen vacancies in W-O-W layers of Bi₂WO₆ and simultaneously generate more oxygen vacancies in TiO₂. The distribution of interfacial oxygen vacancies exhibits remarkable impact on the behavior of interfacial charge transfer. The presence of oxygen vacancies in the interface region of Bi₂WO₆ is beneficial for the migration of electrons from Bi₂WO₆ to TiO₂ through interfacial re-equilibrium, while those distributed in the TiO₂ side tend to migrate toward conducting skeleton. Furthermore, recent studies have also demonstrated that diminished interfacial oxygen vacancies in TiO₂ is beneficial for the formation of bridged water molecules, which could efficiently trap photogenerated holes for photooxidation reactions. [44–46] It is reasonably believed that the superior electron transfer and hole trapping abilities undoubtedly result in the significantly improved photoactivity of R-TiO₂/Bi₂WO₆ heterostructures for photoelectrochemical water splitting. In contrast, the competitive capture of extra electrons by adsorbed oxygen molecules is unavoidable when oxygen vacancies are located in the interface region of A-TiO₂, also known as oxygen activation reactions. [47] Due to the favorable formation of oxygen vacancies in the Bi₂WO₆ side, the relatively lower concentration of interfacial defects is ascribed to the poor charge separation in A-TiO₂/Bi₂WO₆ heterostructures. Thus, PEC performance of heterostructures can be definitely boosted through modulating the distribution of intrinsic and interfacial defects in non-stoichiometric semiconductors. The great contribution of oxygen vacancy modulation on the photoactivity is well evidenced by the deteriorated performance of air-calcined heterostructures (Fig. S12), with eliminated oxygen vacancies in

Fig. 6. The relation between O_v formation energy and relative positions of O_v in TiO_2/Bi_2WO_6 heterostructures: (a) A- TiO_2/Bi_2WO_6 and (b) R- TiO_2/Bi_2WO_6 . The corresponding possible positions of oxygen vacancies are shown in (c) A- TiO_2/Bi_2WO_6 and (d) R- TiO_2/Bi_2WO_6 . Here, zero means the interface region. The negative values stand for O_v in different layers of A/R- TiO_2 , and the positive values stand for O_v in different layers of Bi_2WO_6 (010) surface. The relatively large absolute values mean that O_v stays in the layers away from interface region. The interface regions are highlighted in blue. The green solid and dash arrows in (c) and (d) point to the position of O_v in different layers of TiO_2 and Bi_2WO_6 , respectively.

Fig. 7. (a) Effect of intrinsic oxygen vacancies in Bi_2WO_6 on the PEC performance of photoanodes; (b) Effect of interfacial oxygen vacancies on the PEC performance of photoanodes.

semiconductors. It should point out that the significant contribution of depth distribution of O_v to the photocatalytic activities of other heterostructured semiconductors was also observed, which further evidenced the applicability of our defect modulation strategy. The corresponding results will be reported in our following papers.

4. Conclusion

In summary, TiO_2/Bi_2WO_6 heterostructures with facily controlled interfacial electronic structures were used to demonstrate the principle of interfacial oxygen vacancy modulation of heterostructured photo-

Scheme 1. Band diagram and mechanism of oxygen vacancy modulation in $\text{TiO}_2/\text{Bi}_2\text{WO}_6$ heterostructures.

electrodes. Both experimental observations and theoretical calculations indicate that the consecutive transfer of electrons from Bi_2WO_6 to TiO_2 and then electrodes could be facilitated by suppressing intrinsic oxygen vacancies in Bi_2WO_6 and simultaneously increasing those in TiO_2 . A comprehensive study evidenced that the distribution of oxygen vacancies in depth level played a crucial role in determining the pathways of charge collection in heterostructured photoanodes. Oxygen vacancies around the interface region of Bi_2WO_6 and in the TiO_2 side is beneficial for the substantial migration of electrons toward conducting substrates. The strategy of oxygen vacancy modulation resulted in unprecedented photocurrent density of 1.58 mA/cm^2 , which is more than 4 times higher than pristine TiO_2 . Our research can serve as a versatile approach to bridge heterostructure design with defect control by modulating the local distribution of oxygen vacancies.

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Dr. Xiaoliang An and Dr. Le Zhang contributed equally to this work.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2017.04.002.

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