Enhanced Photocatalytic and Photoelectrochemical Activities of Reduced TiO_{2-x}/BiOCl

Heterojunctions

Rongrong Fu ^a, Xiaoqiao Zeng ^b, Lu Ma ^b, Shanmin Gao ^{a,c,*}, Qingyao Wang ^a, Zeyan Wang ^c, Baibiao

Huang ^c, Ying Dai ^c, Jun Lu ^{b,*}

^a College of Chemistry and Materials Science, Ludong University, Yantai, 264025, P R China

^b Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, USA

^c State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, P R China

*corresponding authors:

Shanmin Gao, E-mail: gaosm@ustc.edu; Jun Lu, E-mail: junlu@anl.gov

Abstract:

A key issue to design highly efficient photoelectrodes for hydrogen production is how to prohibit the rapid carrier recombination. In order to use the visible light and reduce the recombination of electrons and holes, reduced TiO_{2-x}/BiOCl heterojunctions are successfully synthesized and the photoelectrodes are assembled in this work. The effects of various Bi/Ti molar ratios on the structural, morphological, optical, photoelectrochemical and photocatalytic activities of the resultant samples are investigated systematically. The TiO_{2-x} nanoparticles contain Ti³⁺, Ti²⁺, and oxygen vacancies (Ov), while the BiOCl nanosheets exposed {001} facet. Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) results indicate that the existence of Ti³⁺, Ti²⁺ and Ov expand the light-response range. Linear scan voltammetry and electrochemical impedance spectroscopy results indicate that more efficient **electron transportation** is presented in the heterojunctions **with the appropriate Bi/Ti molar ratio**. Consequently, the reduced TiO_{2-x}/BiOCl heterojunction **with the most appropriate Bi/Ti molar ratio** exhibits a high

photocurrent density of 0.755 mA cm^{-2} with photoconversion efficiency up to 0.634%, 10.5 and 22.6 times larger than that of pure TiO_2 and BiOCl . Furthermore, this heterojunction exhibit 48.38 and 12.54 times enhancement for the visible-light decomposition of rhodamine B compared with pure TiO_2 and BiOCl .

Keywords: reduced TiO_{2-x} ; BiOCl ; heterojunctions; hydrothermal treatment; photoelectrochemical water-splitting; visible-light photocatalyst

1. Introduction

Semiconductor photocatalytic (PC) degradation of organic pollutants and photoelectrochemical (PEC) splitting of water into hydrogen by sunlight is a promising and cleaner scheme for environmental remediation and renewable production of clean hydrogen [1,2]. However, in the PC process, the random diffusion of photo-generated electrons and holes results in high recombination rate and therefore, low PC efficiency. An efficient way for promoting the separation rate of electron-hole pairs is the combination of PC and electrochemical technologies via PEC technique [3]. In the PEC process, an electrical bias potential applied between the anode and cathode, which can increase charge separation and restrict their recombination [3,4]. In addition, the formation of heterojunction can efficiently reduce the recombination of carrier, thus, increased the PC and PEC efficiency [4,5].

Among the PC and PEC catalysts available so far, Titania (TiO_2) is one of the most well-known material because of its high photochemical stability and nontoxicity [6]. However, the wide band gap of TiO_2 (anatase TiO_2 , $\sim 3.2 \text{ eV}$; rutile TiO_2 , $\sim 3.0 \text{ eV}$) limits its absorption in the ultraviolet (UV) region, which only contributes $\sim 4\%$ of the solar spectrum. Meanwhile, the photon-generated electron-hole

pairs recombine on or near the TiO_2 surface within 10^{-9} s. These deficiencies impede the practical applications of pristine TiO_2 . Therefore, the key role to produce highly active TiO_2 photocatalyst is to find a way to both narrow the wide band gap and restrain the photoinduced electron–hole pair recombination.

Doping with metal or nonmetal ions has been performed to alter the electronic structures and physical properties of TiO_2 [7]. However, this process could lead to thermal instability and inducing the impurity to the host materials. The impurities would likely become defects and eventually form recombination centers of photoinduced electron-hole pairs. To solve this issue, forming local states at the bottom of the TiO_2 conduction band (CB) by introducing low-oxidation-state Ti ions or Ov is an attractive approach [4,8]. Compared with conventional metal or nonmetal doping, Ov is a type of self-doping that does not introduce impurity into TiO_2 , which is favorable for preserving the intrinsic crystal structures and high stability during the visible light PC progress [9]. In addition, the introduced Ti^{3+} , Ti^{2+} and Ov can increase the electrical conductivity and accelerate the transfer of electrons [10,11]. Therefore, the reduced TiO_2 (TiO_{2-x}) not only increases visible-light absorption performance, but also prohibits the formation of recombination centers from the conventional doped.

Another effective way to control the recombination of photoinduced electrons and holes is to recombine two different semiconductors with appropriate energy bands into one composite with heterojunction structures. The heterojunctions can accelerate the separation of electron-hole pairs and help to significantly increase the PC and PEC efficiency [5,12]. A number of semiconductors can form heterojunctions with TiO_2 and improve the PC and PEC performances. For instance, layered BiOCl has been highlighted because of its unique electron structure and outstanding catalytic performance [13,14].

The unique layered structure consisting of [Cl-Bi-O-Bi-Cl] sheets reducing the recombination probability of electrons and holes. Also, the oxygen-terminated {001} facets can naturally enhance the adsorption of cationic dye and significantly improve the efficiency of photosensitized degradation [15]. Unfortunately, similar to TiO_2 , BiOCl is a wide band gap (~ 3.4 eV) semiconductor that cannot be activated by visible light [13].

So far, pure $\text{TiO}_2/\text{BiOCl}$ composites have been reported with enhanced UV-light PC activity [16-22]. For example, Wang and Fan et al. have prepared pure rutile $\text{TiO}_2/\text{BiOCl}$ composites by a one-step hydrolysis method and studied their PC activities under artificial solar light irradiation by using 500 W Xe lamp without UV cutoff filter [17]. Zhang et al. assembled hierarchical heterostructure based on BiOCl nanosheets and bicrystalline TiO_2 nanofiber frameworks by combining the electrospinning technique and solvothermal method [18]. However, it should be noted that these composites can only be irradiated by UV light. Therefore, their applications in PC and PEC devices are greatly restricted.

Taking advantage of reduced TiO_{2-x} and layered BiOCl , the combination of these two semiconductors could significantly improve the PC and PEC efficiency due to the high visible-light response of the former and low electron-hole pair recombination of the latter. In this paper, we employ a surfactant-free method for preparation of reduced $\text{TiO}_{2-x}/\text{BiOCl}$ heterojunctions that have high visible light PC and PEC activity. The structure, morphology, chemical state, and PEC properties of the materials were investigated. These heterojunctions with the appropriate Bi/Ti molar ratio exhibit a wider visible-light absorption ability and higher PC and PEC activities than those of pure TiO_2 or BiOCl under visible-light irradiation ($\lambda > 400$ nm). The PC and PEC mechanisms were determined.

This novel system shows the potential advantages of enhanced or tunable sunlight absorption, improved photogenerated electron–hole separation, and increased photoconversion efficiency.

2. Experimental details

2.1. Samples preparation

All chemicals were reagent-grade and from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) without further purification. Double distilled water was used throughout the experiments. In a typical procedure, 0.83 g BiCl₃ was dissolved in 30 mL of hydrochloric acid (HCl) solution (1 mol·L⁻¹). Then, 1.35 g TiCl₃ was added into the BiCl₃-HCl aqueous solution. Under vigorous stirring, hydrazine hydrate (N₂H₄·H₂O, 80%) was introduced to the resultant solution until the pH value reached 8, which was accompanied by a bluish violet precipitate. This suspension mixture was stirred in a water bath at 50 °C for 1 h followed by filtration. The precipitate was washed several times with deionized water. The obtained solid with 40 mL deionized water was transferred into a 50 mL Teflon-lined stainless steel autoclave and maintained at 160 °C for 24 h in an electric oven. After being cooled down to room temperature, the precipitates were collected and washed with deionized water, followed by washing with absolute ethanol several times to remove residual impurities. The precipitates were then oven dried at 80 °C for 4 h.

To investigate the effect of BiOCl content on the PC and PEC activity, a series of reduced TiO_{2-x}/BiOCl heterojunctions with different amounts of BiOCl were prepared under identical conditions. The final products were named “TB-x,” where x refers to the molar ratio of BiOCl to TiO₂. For comparison, pure BiOCl nanosheets and TiO₂ nanoparticles were prepared by the same method. In

addition, pure Ti^{3+} self-doped TiO_2 nanoparticles (named as Ti^{3+} - TiO_2) were prepared according to the reference [23].

2.2. Characterization

The crystalline phases of the products were identified with an X-ray diffractometer (Rigaku D/max-2500VPC) with Ni-filtered, $\text{Cu-K}\alpha$ radiation from 10° to 80° at a scanning rate of $0.02^\circ \text{ s}^{-1}$. The TEM and HRTEM were carried out on a JEOL-2100 microscope. The FESEM images were taken with a Hitachi S-4800 field emission scanning electron microscope. XPS measurements were performed with an X-ray photoelectron spectrometer (VG Micro Tech ESCA 3000) using monochromatic $\text{Al-K}\alpha$ with a photon energy of 1486.6 eV at a pressure of $>1 \times 10^{-9}$ torr, a pass energy of 40 eV, and an overall resolution of 0.05 eV. Electron spin resonance (ESR) measurements were carried out at 120 K using a FA-200 spectrometer/X-bond. The photoluminescence (PL) spectra were measured at room temperature with a Perkin Elmer LS 55 Fluorescence Spectrometer. UV-Vis DRS were recorded on a Shimadzu UV-2550 UV-vis spectrophotometer at room temperature from 250 nm to 800 nm, in which fine BaSO_4 was used as the reflectance standard.

2.3. Photoelectrodes preparation and PEC measurements

$\text{TiO}_{2-x}/\text{BiOCl}$ heterojunctions, pure TiO_2 , BiOCl and Ti^{3+} - TiO_2 photoelectrodes were prepared by spreading aqueous slurry of the samples over 1.0 cm^2 of FTO (F-doped SnO_2) glass substrates. A suspension of $3.0 \text{ g}\cdot\text{L}^{-1}$ samples was prepared in ethanol by ultrasonication for more than 30 min. A 50 μL suspension was then printed onto a FTO conductive glass substrate to form a transparent film. All samples were dried in an oven at 120°C for 30 min.

The PEC performances were measured on a standard three-electrode cell using a CHI 660C

electrochemical station (Shanghai Chenhua Instrumental Co., Ltd., China). The as prepared photoelectrodes were used as working electrodes. Ag/AgCl and platinum wire were used as reference and counter electrode, respectively. A 0.5 M Na₂SO₄ aqueous solution was used as the electrolyte. A 300 W Xe lamp (PLS-SXE300, Beijing Trusttech Co., Ltd., China) coupled with an AM 1.5 global filter was utilized as a light source. The scan rate for the linear scan voltammetry (LSV) was 5 mV s⁻¹ over the potential range of -0.8 to 1.0 V. The electrochemical impedance spectroscopy (EIS) of the samples were performed under illumination (100 mW cm⁻²) at open circuit voltage over a frequency range of 10⁴ to 1 Hz with potential amplitude of 5 mV. All experiments were carried out under ambient conditions.

2.4. PC activities test

The PC performance of the as-prepared reduced TiO_{2-x}/BiOCl heterojunctions was evaluated by the degradation of rhodamine B (RhB) dyes as model organic pollutants. A 300 W Xe lamp equipped with a UV cutoff filter was used as a light source ($\lambda > 400$ nm). The illumination intensity is 100 mW·cm⁻² and the distance between the light and the center of the customized quartz reactor was 30 cm. During the degradation process, 40 mg sample was added to 80 mL RhB aqueous solution (5.0×10^{-4} M) in a customized quartz reactor. Each suspension was magnetically stirred in the dark for 30 min until reaching an adsorption–desorption equilibrium. The dispersed suspensions were then irradiated by visible light at 10 min intervals. After illumination, about 3 mL aliquots were centrifuged to remove the trace particles. The absorbance of the centrifuged solution was measured from 400 to 800 nm using a UV–vis spectrophotometer (Shimadzu UV-2550). During the photoreactions, no oxygen was bubbled into the suspension. Parallel measurements were performed on the pure TiO₂, BiOCl and Ti³⁺-TiO₂ for

comparative purposes. The decoloration efficiency (DE) was determined base on equation (1):

$$DE = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where C_0 and C_t are the absorbance of the original solution and the photodegraded solution after time t , respectively.

3. Results and discussion

3.1. Samples characterization

The crystalline structure of the as-prepared reduced $\text{TiO}_{2-x}/\text{BiOCl}$ heterojunctions was analyzed by XRD. Fig. 1 shows the XRD patterns of the samples obtained at 160 °C for 24 h with different amounts of BiOCl. With low BiOCl content, the products were poorly crystallized TiO_2 . Also, there was almost no BiOCl diffraction peaks observed (Fig. 1a, for sample TB-0.05). The peaks at $2\theta = 25.3^\circ$, 37.8° , 48.0° , 53.9° , 62.7° , and 75.0° are indexed as the (101), (004), (200), (105), (204), and (215) crystal planes of anatase TiO_2 (JCPDS No. 21–1272), respectively. As the Bi/Ti molar ratio increases from 0.1 to 0.8 (patterns b-e), the BiOCl diffraction peaks appear gradually with increasing intensity. These XRD patterns of BiOCl agree with the standard diffraction for tetragonal BiOCl (JCPDS No. 06–0249). Moreover, from curves (d) and (e), the obviously stronger intensity of the BiOCl (001) plane leads to (001) crystallization and exposed {001} facets with excellent photoactivity [24]. When the molar ratio of Bi/Ti reach to 0.3, in curves (c-e), the diffraction peaks for TiO_2 become invisible either because of its poor crystallinity at low hydrothermal treatment temperature or because of its signal overlaps with the stronger BiOCl signal [25]. Hence, we believe that TiO_2 nanoparticles had formed and were well-dispersed on the BiOCl surface, and this speculation was confirmed by the TEM, HRTEM and

FESEM observation shown later.

Interestingly, weak signals of titanium monoxide (TiO) with monoclinic phase are observed in curve b, c and d, with diffraction peaks located at 26.9° , 30.2° , and 37.6° (JCPDS No. 23-1078). This result demonstrated that a small amount of Ti^{3+} ions is reduced to Ti^{2+} by the $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and forms TiO. As a high-performance semiconductor, TiO is capable of bringing additional high conductivity to this heterojunction system [10,26].

The morphologies and crystal structures of the reduced $\text{TiO}_{2-x}/\text{BiOCl}$ heterojunctions with different amounts of BiOCl were characterized by TEM, FESEM, and HRTEM (Fig. 2). At the Bi:Ti molar ratios of 0.05, 0.1, and 0.3, the samples exhibit different morphologies as nanoparticles (TB-0.05, Fig. 2a), nanoparticles with nanorods (TB-0.1, Fig. 2b), and nanoparticles with nanosheets (TB-0.3, Fig. 2c), respectively. The HRTEM image in Fig. 2d shows the detailed lattice fringes of nanosheets and nanoparticles in the TB-0.3 sample clearly. The periodic fringe spacing of the nanosheets (0.27 nm) is consistent with the $\{110\}$ and $\{1\bar{1}0\}$ facets of BiOCl. The intersection angle between the $\{110\}$ and $\{1\bar{1}0\}$ facets is 90° , confirming that the BiOCl nanosheets expose $\{001\}$ facets. The lattice fringe spacing of 0.35 nm agrees with the (101) lattice planes of anatase TiO_2 . Obviously, the formation of BiOCl nanosheets follows a gradual self-assembly process of growing from nanorods to lamellar structure, as the amount of Bi increases. During this process, the reduced TiO_2 nanoparticles are attached to or dispersed on the surface of BiOCl nanosheets to form heterojunctions.

Fig. 2 also indicates that the size of BiOCl nanosheets increases with increasing of Bi:Ti molar ratio. With molar ratio of 0.6, the size of the nanosheets reaches 50~100 nm (Fig. 2e). From the FESEM image (inset of Fig. 2e), these aggregated nanosheets are mixed with isolated nanoparticles on

the surface. Two different lattice fringes of such nanoparticle/sheet composites were observed, as shown in the HRTEM image (Fig. 2f). One with 0.27 nm fringes corresponds to BiOCl {110} planes, the other with 0.24 nm fringes corresponds to the anatase TiO₂ {004} planes. At a ratio of 0.8 (sample TB-0.8), aggregated nanosheets with fewer nanoparticles are found in Figs. 2g and 2h due to the higher concentration of Bi. For samples TB-0.3 and TB-0.6, the nanoparticles heavily loaded on the surface of BiOCl nanosheets, leading to a very rough surface (Fig. 2c, e). For pure BiOCl nanosheet, the surface is very smooth (Supporting Information, Fig. S1). These results suggest that the TiO_{2-x}/BiOCl heterojunctions were successfully constructed **at the appropriate Bi/Ti molar ratio**. The preferential exposure of the {001} facets with high catalytic properties of the BiOCl nanosheets is also confirmed in Fig. 2f [24]. The HRTEM characterizations of the lattice fringes and exposed facets are consistent with XRD results.

The composition, chemical state and bonding environment of the reduced TiO_{2-x}/BiOCl heterojunctions were studied by XPS and EDX. The binding energy of the C 1s spectrum at 284.6 eV was used as an internal reference. The XPS survey spectra of the samples indicated the presence of Ti, Bi, Cl, O, and C (Fig. S2). Since XPS is a surface sensitive analysis technique, the chemical content of the samples were also analyzed by EDX (Fig. S3). The EDX results show that Bi, Ti, O and Cl present in the samples and the atomic ratio of the Bi, Ti and Cl are changed with different Bi/Ti molar ratio.

Fig. 3a, 3c, 3d, and 3e show the high-resolution XPS spectra of Ti 2p, Bi 4f, Cl 2p, and O 1s, respectively, for samples TB-0.3 and TB-0.6. The fitting results of Ti 2p and O 1s in sample TB-0.6 are plotted in Fig. 3b and 3f, respectively. The binding energy of Ti 2p_{3/2} at 458.3 eV (Fig. 3a) is lower than that of pure TiO₂ (459.1 eV). Such shift is attributed to the existence of Ov around low-oxidation-state

Ti ions in order to reach charge equilibrium [27]. Binding energies of 458.3, 457.4, and 455.8 eV determined from fitting of the Ti 2p_{3/2} main peak are assigned to the core levels of different Ti oxidation states. The peaks at 458.3 were assigned to the 2p_{3/2} core levels of Ti⁴⁺, and those at 457.4 and 455.8 eV were ascribed to the 2p_{3/2} core levels of Ti³⁺ and Ti²⁺, respectively (Fig. 3b) [28,29]. Therefore, the presence of Ti⁴⁺, Ti³⁺, and low-concentration Ti²⁺ is proved and consistent with the XRD results.

The formation of BiOCl and Ov is further confirmed in Figs. 3c-f. Figure 3c reveals that the band difference of 5.3 eV between Bi 4f_{7/2} and 4f_{5/2} refers to the normal Bi³⁺ state [30]. The two peaks at 199.84 and 198.31 eV in Fig. 3d correspond to Cl 2p_{1/2} and Cl 2p_{3/2} of Cl⁻, respectively [31]. The O 1s spectra (Fig. 3e) show different oxygen states evident by two peaks at 529.31 and 530.43 eV. The fitting of O 1s results in three main peaks at 529.28, 530.55, and 531.86 eV (Fig. 3f). The peak at 529.28 eV can be ascribed to two types of oxygen: the lattice oxygen in the [Bi₂O₂] slabs of BiOCl and the Ov defects within the TiO₂ matrix [32,33]. The Ov will lead to faster accelerate charge transfer and lower recombination of electron-hole pairs [8,10,33]. The peak at 530.55 eV is attributed to the Ti-O bond of TiO₂, whereas the peak at 531.86 eV is from the oxygen of surface hydroxyl groups [34]. The content of hydroxyl groups on the surface influenced the recombination rates of electron-hole pairs [34]. The XPS results are consistent with XRD results, further confirming the coexistence of reduced TiO_{2-x} and BiOCl in the composites. All these results demonstrate that the reduced TiO_{2-x} nanoparticle/BiOCl nanosheet heterojunctions were successfully constructed at the appropriate Bi/Ti molar ratio.

ESR was used to study the uncoupled electrons and their interactions with the surrounding atoms in

the material. The presence of Ti^{3+} and Ov in the samples is further confirmed by ESR. Fig. 4 shows the ESR results of samples TB-0.3, TB-0.6, pure TiO_2 , BiOCl and $\text{Ti}^{3+}\text{-TiO}_2$. No signal emerged from the pure TiO_2 and BiOCl . A signal peak at about $g = 1.95$ appeared for the heterojunction samples and $\text{Ti}^{3+}\text{-TiO}_2$ nanoparticles, corresponding to the Ti^{3+} signal peak [23, 35]. The intensity of this signal peak decreased with increasing Bi/Ti molar ratio for the heterojunction samples, indicating that the Ti^{3+} concentration in the heterojunction samples decreased, which is consistent with the XPS results. An electron trapped on O_v would produce signal at $g = 2.015$; this signal peak indicates the presence of surface Ti^{3+} [36]. The ESR results show that Ti^{3+} not only existed in the lattice, but also on the surface of the reduced TiO_{2-x} nanoparticles. The signal located at $g = 2.015$ is weaker than that of the signal of $g = 1.95$, which confirms that most of the Ti^{3+} exist in the bulk rather than on the surface.

3.2. Formation mechanism of reduced $\text{TiO}_{2-x}/\text{BiOCl}$ heterojunctions

Based on the aforementioned experimental observations, we developed a tentative formation process of reduced $\text{TiO}_{2-x}/\text{BiOCl}$ heterojunctions, as shown schematically in Fig. S4. As indicated, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ plays various important roles in the process: complexing agent, precipitant, and reductant. When $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ is added dropwise to the solution, Bi^{3+} initially forms complexes due to the strong chelation effect between metal cations and ligands. With increasing the pH value, the complexes subsequently participate to form BiOCl precursor, as represented in reaction (1).

Simultaneously, the precursor of reduced TiO_{2-x} is formed as a consequence of oxidation, hydrolysis, and nucleation, as described in reaction (2).

Notably, the BiOCl precipitations should be formed first because of their low K_{sp} (1×10^{-31}) and high Cl^- concentration. The extra N_2H_4 is released to reduce some Ti^{4+} and Ti^{3+} to Ti^{2+} . Hence, the obtained TiO_{2-x} precursor already contains some low-oxidation-state of Ti ions.

During the hydrothermal treatment process, the amorphous precursors become crystallized. To decrease the surface free energy, the BiOCl nanoparticles intend to attach one by one along the low planar density of atoms of BiOCl {001} facets. As a result, BiOCl grows from nanoparticles to nanorods and, eventually, nanosheets, as supported by the TEM images. The reduced TiO_{2-x} nanoparticles and BiOCl nanosheets form heterojunction structures that are attached by reduced TiO_{2-x} nanoparticles on the surface of BiOCl nanosheets.

3.3. Optical and PEC properties

Fig. 5 shows the UV-Vis DRS of pure TiO_2 , BiOCl, Ti^{3+} - TiO_2 and reduced TiO_{2-x} /BiOCl heterojunctions with different BiOCl content. Clearly, pure TiO_2 and BiOCl only exhibit a clean adsorption edge at wavelengths of 387 and 365 nm, demonstrating the fundamental adsorption in the UV region. In contrast to pure TiO_2 and BiOCl, the Ti^{3+} - TiO_2 and TiO_{2-x} /BiOCl heterojunction samples present red shifts and broad absorption bands between 400 and 800 nm, this can be attributed to the Ti^{3+} , Ti^{2+} , and Ov species. These species in reduced TiO_{2-x} introduce a localized state below the CB edge of TiO_2 , expanding the absorption range to the visible-light region [8-11,35-37]. The degree of red-shifting and absorption intensity in the visible-light range differed among the samples obtained under different Bi/Ti molar ratios. The Ti^{3+} - TiO_2 nanoparticle has more red-shifting and absorption intensity in visible-light range than the TB-0.3, TB-0.6 and TB-0.8 heterojunction samples (Fig. 5, the inset figure). In addition, with the increased of Bi/Ti molar ratio, the absorption intensity in the

visible-light range was decreased, which indicates that the Ti^{3+} , Ti^{2+} , Ov content and proportion of reduced TiO_{2-x} to BiOCl are different in the samples. This is consistent with the XRD, TEM and ESR results. Because of this enhanced ability to absorb visible light, Ti^{3+} - TiO_2 and reduced TiO_{2-x} /BiOCl heterojunctions are promising potential visible light PC and PEC catalyst for solar energy-related applications.

Generally, the PC and PEC activity depends on the effective separation of electron-hole pairs. Photocurrent provides a direct demonstration to determine the separation efficiency of the photoinduced electrons and holes in the photoelectrodes [38]. The high photocurrent indicates that the samples have a strong ability to generate and transfer the photoexcited electron-hole pairs [39,40]. LSV technique and transient photocurrent responses against the time were used to study the PEC properties of the different photoelectrodes. For comparison, the PEC response of pure TiO_2 , BiOCl and Ti^{3+} - TiO_2 was also determined. Fig. 6a shows that under visible-light illumination, the pure TiO_2 and BiOCl photoelectrodes yielded relatively low photocurrent density, which can be explained by their poor optical light absorption properties. On the contrary, the Ti^{3+} - TiO_2 and TiO_{2-x} /BiOCl heterojunctions photoelectrodes show increased photocurrent density with increasing the bias potential. The photocurrent density of the pure TiO_2 and BiOCl photoelectrodes are 0.069 and 0.034 mA cm^{-2} , whereas the photoelectrode assembled by TB-0.3 sample is 0.755 mA cm^{-2} , which represents a 10.9 and 22.21-fold increase from the pure TiO_2 and BiOCl, respectively. In addition, under dark condition, the photoelectrodes composed by the TB-0.1, TB-0.3 and TB-0.6 heterojunctions show a relatively stronger dark current than pure TiO_2 , BiOCl and Ti^{3+} - TiO_2 photoelectrodes (Fig. S5). It further indicates that the electron transportation in these heterojunction samples is more efficient than pure

TiO₂, BiOCl and Ti³⁺-TiO₂ [21,41].

The transient photocurrent response against the time of different photoelectrodes was measured under a visible light pulse of 50 s and the results were shown in Fig. 6b. Similar to the LSV results, the pure TiO₂ and BiOCl photoelectrodes only generates a negligible photocurrent under visible light illumination. For the Ti³⁺-TiO₂ and TiO_{2-x}/BiOCl heterojunctions photoelectrodes, larger photocurrent were generated under visible light illumination. When the light was turned off, the current rapidly decayed to a lower level, indicating that the current was completely due to the activity of the photoelectrode and that charge transport was very fast [42,43]. The photocurrent of the TB-0.3 photoelectrode was significantly enhanced comparing with those of the other photoelectrodes, indicating that the separation and transport efficiencies of photogenerated electron-hole pairs were much higher than other photoelectrodes.

To gain more insight into the charge separation and transport of the heterojunction, EIS was used to investigate the charge separation and transport of the samples under visible light illumination [39,43]. The size of the arc radius on the EIS Nyquist spectra reflects the charge-transfer resistance at the photoelectrode/electrolyte interface [43]. The smaller arc radius indicates higher charge transfer efficiency [39,43,44]. As shown in Fig. 6c, it is obvious observed that the radii of the arch for the TiO_{2-x}/BiOCl heterojunctions with the appropriate Bi/Ti molar and Ti³⁺-TiO₂ photoelectrode were smaller than that of pure TiO₂ and BiOCl. Moreover, the arc radius of the Ti³⁺-TiO₂ nanoparticles were smaller than that of pure TiO₂. This demonstrated the importance of Ti³⁺ and Ov behaving in facilitating the photogenerated electrons and holes separation and transfer efficiency [4,8,39].

From the UV-vis DRS results (Fig. 5), the Ti³⁺-TiO₂ nanoparticles have more red-shifting and

stronger absorption intensity in visible-light range than TB-0.3, TB-0.6 and TB-0.8 heterojunction samples, but the current density and photocurrent of $\text{Ti}^{3+}\text{-TiO}_2$ was lower. These results indicated that only the heterojunctions with the appropriate Bi/Ti molar ratio can enhance the separation of photoinduced electrons and holes, suppressed their recombination [42, 45]. When the molar ratio of Bi/Ti was low, the effective heterojunctions cannot be formed. However, the excess of BiOCl may prevent the photoabsorption, and leads to low crystallinity of reduced TiO_{2-x} . Consequently, the heterojunction structures cannot be effectively formed, too. Therefore, there is an optimal BiOCl loading at which the generated photocurrent was maximized.

In general, a higher photocurrent corresponds to a higher efficiency of the PEC device of hydrogen evolution [46,47]. The photoconversion efficiencies (η) of the different photoelectrodes were calculated by using the Eq. (2) [48]:

$$\eta\% = j_p [(E_{rev} - |E_{meas} - E_{aoc}|) / I_0] \times 100 \quad (2)$$

where j_p is the photocurrent density at the measure bias, E_{rev} is the standard reversible potential (1.23 V/NHE), E_{meas} is the potential of working electrode in the case of photocurrent, E_{aoc} is the open circuit potential of the working electrode, I_0 is the irradiation intensity, respectively. The calculated photoconversion efficiency plotted as a function of the applied bias was shown in Fig. 6d. The photoelectrodes assembled by the TiO_{2-x} /BiOCl heterojunctions with the appropriate Bi/Ti molar ratio show higher conversion efficiencies than the pure TiO_2 , BiOCl and $\text{Ti}^{3+}\text{-TiO}_2$. The pure TiO_2 and BiOCl exhibit an optimal conversion efficiency of ~0.06% and 0.028% at about -0.14 V vs Ag/AgCl. However, the TB-0.3 photoelectrode yields a maximum conversion efficiency of ~0.634% at a very low bias of -0.26 V vs Ag/AgCl. This conversion efficiency is about 10.5 and 22.6 times higher than

that of pure TiO_2 and BiOCl , respectively.

The above PEC results indicated that the pure TiO_2 and BiOCl have very low PEC performance while the Ti^{3+} - TiO_2 has relatively high PEC activity than pure TiO_2 , BiOCl and TB-0.05 samples. These results suggest that the introduction of Ti^{3+} , Ti^{2+} , Ov and the formation of effective heterojunctions are obviously contributing to the improvement of the PEC performances, due to the ability of light harvesting and carrier transporting of the photoelectrode [4,5,12,16-18,20].

3.4. PC activities

As a common xanthene dye, RhB is often used as a test model pollutant in semiconductor photocatalysis. Fig. 7a shows the adsorption and photodegradation abilities of the $\text{TiO}_{2-x}/\text{BiOCl}$ heterojunctions in RhB solutions, as well as pure TiO_2 , BiOCl and Ti^{3+} - TiO_2 . A blank experiment was also carried out. Pure RhB solution without catalyst shows no decomposition throughout the entire irradiation time. However, under visible-light irradiation, the reduced $\text{TiO}_{2-x}/\text{BiOCl}$ heterojunctions and Ti^{3+} - TiO_2 nanoparticles show higher PC activities than pure TiO_2 or BiOCl due to the heterojunction structures or the exist of low-oxidation-state Ti ions and Ov. Among all samples, TB-0.3 exhibits the highest visible-light PC activity, with 98.1% degradation efficiency (Eq. 1) after irradiation for 30 min. But the degradation efficiencies were only 17.7% and 23.6% for pure TiO_2 and BiOCl , respectively. The dynamic UV–Vis absorption spectra of RhB solutions in the presence of the sample TB-0.3 was measured (Fig. S6). The corresponding changes in color of RhB solutions with the increasing reaction time were also shown in the insets in Fig. S6. The intensities of the characteristic absorption peaks of RhB (~554 nm) rapidly diminished with increased duration of visible-light irradiation.

The reaction kinetics of RhB PC degradation is described in Eq. (3) by assuming a

pseudo-first-order reaction based on the Langmuir–Hinshelwood model [49]:

$$\ln\left(\frac{C_0}{C}\right) = kt \quad (3)$$

where k is the pseudo-first-order reaction rate constant, t is the irradiation time, C_0 and C are the RhB concentrations in aqueous solution at some initial time (the time required to reach adsorption–desorption equilibrium) and t , respectively. From Eq. 2 and Fig. 7b, the values of k for pure TiO_2 , BiOCl , $\text{Ti}^{3+}\text{-TiO}_2$, TB-0.05, TB-0.1, TB-0.3, TB-0.6, and TB-0.8 are 0.0021, 0.0081, 0.0212, 0.0133, 0.0371, 0.1016, 0.0990, and 0.0590 min^{-1} , respectively, with a sequence of TB-0.3 > TB-0.6 > TB-0.8 > TB-0.1 > $\text{Ti}^{3+}\text{-TiO}_2$ > TB-0.05 > pure BiOCl > pure TiO_2 . Clearly, for the heterojunctions, the PC degradation rate constants are strongly influenced by the molar ratio of Bi to Ti. The highest one from TB-0.3 is about 48.38 and 12.54 times greater than those of pure TiO_2 and BiOCl , respectively. Although the $\text{Ti}^{3+}\text{-TiO}_2$ nanoparticles have more red-shifting and stronger absorption intensity in visible-light range than TB-0.3, TB-0.6 and TB-0.8 heterojunction samples (Fig. 5), its PC activity is lower than these heterojunction samples. This is because the formation of the effective heterojunction that can accelerate the separation rate of electrons and holes [5,12,21,22], so TB-0.3 has the best PC performance.

In the PC degradation process, the larger the formation of $\bullet\text{OH}$ radicals, the higher the separation rate of electron–hole pairs in the photocatalysts [50]. The PL intensity and number of $\bullet\text{OH}$ at approximately 426 nm gradually increased with the irradiation time (Fig. S7). The maximum number of $\bullet\text{OH}$ radicals was formed by using the TB-0.3 heterojunction sample during the PC degradation process, which was in agreement with the results of photodegradation of RhB (Fig. 7a). In addition, PL emission spectra have been widely used to explore the efficiency of charge carrier trapping, migration,

and recombination in order to understand the fate of electron-hole pairs in semiconductor particles [51]. The PL results (Fig. S8) indicated that the PL intensity of the pure BiOCl and TiO₂ are higher than that of the heterojunction samples and Ti³⁺-TiO₂ nanoparticles. For the effective heterojunctions, the photoinduced electrons in the CB of TiO₂ migrate to BiOCl, which prevents the recombination of the electron-hole pairs and results in a quenching of the PL emission [5]. These results indicate that the heterojunction structure with the appropriate Bi/Ti molar ratio enhanced separation of photoinduced electrons and holes. The presence of Ti³⁺, Ti²⁺ and Ov also improved optical absorption capability of the samples.

3.5. Proposed mechanism for the enhanced PC and PEC performances

Based on the above experimental results and discussion, we have concluded that the synergistic effect of reduced TiO_{2-x} and BiOCl could effectively improve the visible light PC and PEC performance in the following respects: (1) the appropriate proportion of reduced TiO_{2-x} and BiOCl in TiO_{2-x}/BiOCl composites is crucial to form high-performance heterojunctions and improve the separation efficient of electrons and holes; (2) the presence of Ti³⁺, Ti²⁺, and Ov extends the TiO₂ absorption range to the visible region and accelerates the electron transfer rate [10,11,52]; (3) the Ov on the particle surface adsorbs oxygen molecules and acts as an electron capture agent, leading to the reduction of the electro-hole pairs recombination rate [8,53]; (4) BiOCl nanosheets increase the contact surface with TiO_{2-x} nanoparticles, facilitating the transportation of reactants and products on photocatalyst surfaces and resulting in facile chemical reactions; and (5) the strong adsorption performance of layered structure BiOCl nanosheets increases both the adsorption amount and adsorption strength for RhB dye. Fig. 8a is a schematic of the CB and valence band (VB) maximum

electrochemical potentials for TiO₂ and BiOCl, as well as the possible charge separation process of the heterojunctions in the PC process.

The VB maximum potential of BiOCl [3.56 eV vs. normal hydrogen electrode (NHE)] is more positive than the oxidative potential of TiO₂ (2.91 eV vs. NHE), while the CB maximum potential of BiOCl (0.16 eV vs. NHE) is more positive than the reductive potential of TiO₂ (-0.29 eV vs. NHE) [22,54,55]. Thus, a type-II heterojunction is formed when TiO₂ and BiOCl are coupled. The energy band alignment of TiO₂ and BiOCl induces the formation of a diffusion potential [19], which acts as an electromotive force to favor electron injection. The localized states under the CB of TiO₂ formed by Ti³⁺, Ti²⁺, and Ov are able to extend the TiO₂ absorption range to visible region. Also, the low-oxidation-state Ti ions and Ov can provide better electron conductivity, resulting in higher electron transfer rate and lower electro-hole pair recombination rate [4,10,53]. Under visible-light irradiation, the electrons are excited from the TiO₂ VB to the **localized** states, progressively shift to the TiO₂ CB, and then transfer from the TiO₂ CB to the BiOCl CB, **thereby inhibiting the recombination of electron-hole pairs (Fig. 8a, step 1)**. The better separation of photoexcited carriers are confirmed by PL spectra (Fig. S8). Meanwhile, the adsorbed RhB molecules are excited to form excited-state RhB* and subsequently injects electrons to the CB of BiOCl (Fig. 8a, step 2) [56,57]. The excited-state electrons transfer to the BiOCl nanosheet surface and react with dissolved oxygen to generate the main active groups of superoxide anion radicals ($\bullet\text{O}_2^-$) (Fig. 8a, step 3), $\bullet\text{O}_2^-$ became a highly oxidative $\bullet\text{OH}$ through a series of oxidation reactions (Fig. 8a, step 4, 5, 6), and to further oxidize RhB [58]. The main active species capture results (Fig. S9, [Supporting information given the detailed experimental process](#)) indicated that the PC activity of the TB-0.3 sample was significantly suppressed by addition of the $\bullet\text{O}_2^-$

scavenger. Thus, $\bullet\text{O}_2^-$ radicals are mainly responsible for RhB photodegradation. In addition, the holes at the VB of TiO_{2-x} can directly oxidize the organic molecules (Fig. 8a, step 7) and simultaneously oxidize the surface OH groups and H_2O to generate $\bullet\text{OH}$ (Fig. 8a, step 8). As a result, these highly active species (e.g., $\bullet\text{O}_2^-$, $\bullet\text{OH}$ and h^+) mainly cause enhanced RhB degradation. If an external voltage was applied, the photogenerated electrons are driven away by the positive bias-potential and travel to the external circuit (Fig. 8b)[16]. In such a way, the photogenerated electron-hole pairs are further effectively separated, resulting in an enhanced PEC performance [59,60]. Furthermore, the reduced TiO_{2-x} possesses higher electron conductivity than that of pure TiO_2 , which is in favor of transporting photogenerated electrons to the counter electrode [10,11,26].

4. Conclusions

Heterojunction photocatalysts consisting of reduced TiO_{2-x} nanoparticles and BiOCl nanosheets with different BiOCl amounts were successfully synthesized by a chemical-reduction precipitation method with subsequent hydrothermal treatment, in which $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ is a key factor as the reductant, complexing agent, and precipitant. In such heterojunctions, the BiOCl nanosheets have exposed {001} crystal facets with high PC activity. In addition, Ti^{3+} , Ti^{2+} , and Ov were formed during the synthesis process, extended the absorption range of TiO_{2-x} to the visible region, and accelerated the electron transfer rate. The heterojunctions with the appropriate Bi/Ti molar ratio efficiently reduced the recombination of photoinduced electron-hole pairs and have higher visible light PC and PEC activities than pure TiO_2 and BiOCl. The results regarding enhanced PC and PEC activities provide significant meaningful guidance for the development of Ti-based PC and PEC materials for degrading organic

pollutants and water splitting under solar irradiation and even for related applications.

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Figure captions

- Fig. 1.** XRD patterns of the reduced $\text{TiO}_{2-x}/\text{BiOCl}$ heterojunctions samples obtained at 160 °C for 24 h: (a) TB-0.05, (b) TB-0.1, (c) TB-0.3, (d) TB-0.6, and (e) TB-0.8.
- Fig. 2.** TEM, HRTEM, and FESEM images of the samples obtained at different molar ratio of Bi/Ti: (a) TB-0.05, (b) TB-0.1, (c, d) TB-0.3, (e, f) TB-0.6, and (g, h) TB-0.8.
- Fig. 3.** High-resolution XPS spectra of (a) Ti 2p, (c) Bi 4f, (d) Cl 2p, and (e) O 1s for samples TB-0.3 and TB-0.6. Fitting results of the experimental data for (b) Ti 2p and (f) O 1s for sample TB-0.6.
- Fig. 4.** ESR spectra for sample TB-0.3, TB-0.6, pure TiO_2 , BiOCl and $\text{Ti}^{3+}\text{-TiO}_2$.
- Fig. 5.** UV-vis spectra of pure TiO_2 , BiOCl , $\text{Ti}^{3+}\text{-TiO}_2$ and reduced $\text{TiO}_{2-x}/\text{BiOCl}$ heterojunctions (Inset: partial enlargement absorbance results).
- Fig. 6.** (a) LSV characteristic curves of pure TiO_2 , BiOCl , $\text{Ti}^{3+}\text{-TiO}_2$ and $\text{TiO}_{2-x}/\text{BiOCl}$ heterojunctions with a scan rate of 5 mV s^{-1} at applied potentials from -0.8 to +1.0 V. (b) comparison of transient photocurrent response of the different photoelectrodes at 0.2 V vs Ag/AgCl under visible light irradiation in 0.5 M Na_2SO_4 solution. (c) EIS spectra of Nyquist plots collected at open circuit potential under visible light illumination. (d) Calculated photoconversion efficiencies for the pure TiO_2 , BiOCl , $\text{Ti}^{3+}\text{-TiO}_2$ and $\text{TiO}_{2-x}/\text{BiOCl}$ heterojunction photoelectrodes as a function of applied potential vs Ag/AgCl.
- Fig. 7.** (a) Photodegradation of RhB solutions by using pure TiO_2 , BiOCl , $\text{Ti}^{3+}\text{-TiO}_2$ nanoparticles and reduced $\text{TiO}_{2-x}/\text{BiOCl}$ heterojunctions as photocatalyst under visible light irradiation in neutral suspension. (b) Variation in the normalized $\ln(C_0/C)$ of the RhB concentration as a function of irradiation time.
- Fig. 8.** Schematic of the energy band of TiO_2 and BiOCl as well as charge migration and separation on reduced $\text{TiO}_{2-x}/\text{BiOCl}$ heterojunctions caused by visible-light irradiation. (a) in the PC process, (b) in the PEC process.

Figures

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.