Fabrication of SnO₂ Nanoparticles/BiOI n−p Heterostructure for Wider Spectrum Visible-Light Photocatalytic Degradation of Antibiotic Oxytetracycline Hydrochloride

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ABSTRACT: In this work, n−p heterostructure SnO₂/BiOI photocatalyst was successfully fabricated through a facile chemical bath method. The photocatalysts was applied to minimize antibiotic oxytetracycline hydrochloride (OTTCH) and methyl orange (MO) under visible light irradiation. SnO₂/BiOI composite exhibited excellent photocatalytic performance for the refractory pollutant OTTCH and MO decomposition. The sample of 30 wt % SnO₂/BiOI possessed the best photocatalytic performance in all the obtained catalysts. Several reaction parameters affecting OTTCH degradation such as initial concentration, ion species, and concentration were investigated systematically. The optical and electrical properties of materials demonstrate that the transfer rate of electron−hole pairs dramatically improve though forming an n−p junction in SnO₂/BiOI hybrid. Moreover, the energy band alignments of SnO₂/BiOI junction were confirmed via combining DRS and XPS analysis, which provided strong support for the proposed mechanism. This work could provide a new approach to construct new p−n junction photocatalysts and a reference for the study of other heterojunction catalysts.

KEYWORDS: SnO₂, BiOI, p−n junction, Photocatalysis, Oxytetracycline hydrochloride

INTRODUCTION

Oxytetracycline hydrochloride (OTTCH) is one of the broad-spectrum antibiotics, especially employed in veterinary medicine. Because of its high stability, a large amount cannot be biologically degraded or eliminated in treatment plants, ending up in effluents of lakes and rivers. It can seriously pose a threat to a large number of living organisms. Besides, it is refractory to disposal via traditional treatment processes. Thereby, it is strongly desired to search for an efficient and cost-effective method to destroy its complex structure and remove its biotoxicity. Photocatalytic degradation has become a target method to destroy its complex structure and remove its biotoxicity. Photocatalytic degradation such as initial concentration, ion species, and concentration were investigated systematically. The optical and electrical properties of materials demonstrate that the transfer rate of electron−hole pairs dramatically improve though forming an n−p junction in SnO₂/BiOI hybrid. Moreover, the energy band alignments of SnO₂/BiOI junction were confirmed via combining DRS and XPS analysis, which provided strong support for the proposed mechanism. This work could provide a new approach to construct new p−n junction photocatalysts and a reference for the study of other heterojunction catalysts.

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enhancing the photocatalytic efficiency, for example, SnO2/g-C3N4,19,20 Ag3PO4/SnO2,21 SnO2/Cu2O,22 and SnO2/Co3O4.23 All in all, SnO2 may be a good candidate for fabricating p–n junction toward BiOI.

We successfully fabricated SnO2/BiOI n–p heterojunction by means of loading SnO2 nanoparticles on the surface of BiOI nanosheets. The SnO2/BiOI composites display enhanced photocatalytic performance toward MO and OTTCH degradation under visible-light irradiation. Subsequently, microstructure, surface chemical states, specific surface area, and optical and photoelectrocatalytic properties of the heterojunction system were systematically studied. Meanwhile, several factors that affect OTTCH degradation have also been investigated in detail. The synergistic interaction and an alternative visible-light-induced photocatalytic mechanism were also discussed.

**EXPERIMENTAL SECTION**

Materials. Bismuth nitrate pentahydrate (Bi(NO3)3·5H2O), tin chloride pentahydrate (SnCl2·5H2O), sodium hydroxide (NaOH), poly(vinyl alcohol) (PVA), ethylene glycol (EG), ethanol, sodium sulfate (Na2SO4), potassium iodide (KI), isopropyl alcohol (IPA), sodium oxalate (Na2C2O4), 5-benzoxquinone (BQ), methyl orange (MO), and octetetraycline hydrochloride (OTTCH) were all purchased from Shanghai chemical Reagents Co., Ltd. All ultrapure water used in all the experiments was obtained from a Milli-Q ultrapure water system.

**Synthesis of Pure SnO2.** SnO2 was synthesized via a hydrothermal method according to following procedure. First, 10 mmol of SnCl2·5H2O and 50 mmol of NaOH dissolved in 50 mL of deionized water, respectively. After the two solutions were mixed, 50 mL of ethanol was added dropwise to get a clear yellow solution. Then, this solution was added dropwise to a Thermo ESCALAB 250X. UV–vis diffuse reflectance spectra (DRS) were measured on Hitachi U-4100 using with BaSO4 as a reference material. The PL spectra were recorded using a PerkinElmer (LS 55) fluorescence spectrophotometer. The zeta potentials were determined using a Zeta-sizer Nano-ZS (Malvern). The electron spin response (ESR) signals of radicals spin-trapped by spin-trapped reagent 5,5-dimethyl-l-pyrroline N-oxide (DMPO) were examined on a Bruker ER200-SRC spectrometer under visible light irradiation (λ > 420 nm).

**Photocatalytic Activity Tests.** MO and typical antibiotic OTTCH were used to evaluate the photocatalytic activities. The visible light was provided through a 300 W Xe lamp (Zhong jiao jin yuan, CEL-HXF300) with a UV Cut-off filter (UVCUT420). Briefly, 50 mg of catalyst was added into MO (50 mL, 10 mg/L, pH 6.15) and OTTCH (50 mL, 10 mg/L, pH 5.49) solutions. Before turning on the light, the suspensions were placed on a magnetic stirrer in the dark for 30 min to reach adsorption–desorption equilibrium. During the irradiation, approximately 3.0 mL of suspension was sampled and separated at given time intervals to measure the changes of the pollutants concentration. The concentration of the MO and OTTCH were measured with a UV–vis spectrophotometer at their maximum absorption wavelength (464 nm for MO, 356 nm for OTTCH). The amount of adsorption is excluded when the degradation efficiency is calculated. The degradation efficiency could be calculated according to the following equation:

\[
\text{Degradation Efficiency} = \left(1 - \frac{C_t}{C_0}\right) \times 100\%
\]

where \(C_0\) and \(C_t\) represent the concentrations of target pollutant at irradiation times 0 and \(t\), respectively. \(A_t\) and \(A_0\) are the corresponding values for target pollutant absorbance.

**Electrochemical Measurements.** Electrochemical measurements were performed in a three-electrode system using a CHI660E electrochemical workstation with a standard three-electrode. The reference and counter electrodes were Ag/AgCl and platinum wire, respectively, and we used 0.2 M Na2SO4 aqueous solution as the electrolyte. The work electrodes were prepared according to following procedure: First, the FTO substrates were cleaned in acetone, absolute ethanol, and distilled water for 30 min, respectively. Then, 10 mg of
sample powder was dispersed into 100 \( \mu \)L of 25% PVA solution under ultrasonication for 1 h to obtain slurries. The as-prepared slurries were dropped onto a 1 cm \( \times \) 2 cm FTO slice with an effective working area of 1 cm\(^2\) and dried at 80 °C for 6 h. A 300 W Xe arc lamp (CEL-HXF300, Beijing) was utilized as a light source with a cut-off filter (\( \lambda > 420 \) nm). Electrochemical impedance spectroscopy (EIS) was recorded by using an alternating voltage of 5 mV amplitude in the frequency range of \( 10^5 \)–\( 10^{-2} \) Hz with the open-circuit voltage in 0.2 M Na\(_2\)SO\(_4\). Mott–Schottky plots of the samples were carried on the same standard three-electrode at a frequency of 1 kHz.

**RESULTS AND DISCUSSION**

The crystal structure of the SnO\(_2\) as well as those of BiOI and 30 wt % SnO\(_2\)/BiOI composites were analyzed using XRD, as displayed in Figure 1. All the XRD peaks of pure SnO\(_2\) corresponded well to that of the tetragonal phase (Powder Diffraction File (PDF) 01–0625, Joint Committee on Powder Diffraction Standards (JCPDS), 2004).\(^{24}\) In pure BiOI, the XRD peaks could be indexed to the tetragonal BiOI (PDF 73–2062, JCPDS, 2004).\(^{25}\) For the patterns of composites, some new typical diffraction peaks can be observed at \( 2\theta = 26.2, 33.6, \) and 51.4°, which were ascribed to the (110), (101), and (211) crystal facets of SnO\(_2\) phase, respectively. It is noteworthy that with increasing SnO\(_2\) weight the diffraction peak of SnO\(_2\) became more remarkable. However, the intensity of diffraction peaks of SnO\(_2\) is weak, which is due to lower crystallinity. The average crystallite size of the pure SnO\(_2\) was calculated by Scherrer’s formula:

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

where \( D \) is the average crystal size, \( K \) is the constant (0.89), \( \lambda \) is the wavelength of the Cu K\(_{\alpha}\) radiation (1.54), \( \beta \) is the full width at half-maximum for the (101) plane, and \( \theta \) is the diffraction angle. The particle size of the pure SnO\(_2\) is calculated to be about 4.3 nm. From XRD analysis, we can conclude that SnO\(_2\)/BiOI composites were successfully obtained. Furthermore, no other miscellaneous peaks are observed, indicating the high purity of these heterojunctions.

The surface chemical states of 30 wt % SnO\(_2\)/BiOI were analyzed via the X-ray photoelectron spectroscopy (XPS). Bi, Sn, I, O, and C elements can be seen in Figure 2a, indicating that there is no impurity in the composites. In Figure 2b, two peaks located at 159.02 and 164.32 eV indicate that Bi exists as Bi\(^{3+}\) in the composite.\(^{26}\) The peaks at 487.24 and 495.72 eV can be attributed to Sn 3d\(_{5/2}\) and Sn 3d\(_{3/2}\), indicating that the chemical state of Sn in SnO\(_2\) is +4.\(^{27,28}\) In Figure 2c, we can observe two strong peaks at 618.92 and 630.42 eV, corresponding to I 3d\(_{5/2}\) and I 3d\(_{3/2}\), respectively.\(^{29}\) The O 1s spectrum can be divided into two peaks as exhibited in Figure 2e. The peak at 529.88 eV corresponds to the Sn–O bonds; the other peak at 531.52 eV is due to Sn=O in the sample, respectively.\(^{28,30}\) The XPS results further confirm the formation of SnO\(_2\)/BiOI heterostructures and intimate integration has been achieved.

The typical morphologies and structure images of 30 wt % SnO\(_2\)/BiOI, BiOI, and SnO\(_2\) were displayed in Figure 3. The morphology of pure SnO\(_2\) presented nanoparticles with diameters ranging from 3 to 6 nm, and aggregation phenomena between SnO\(_2\) nanoparticles was observed (Figure 3a,b). The morphology of bare BiOI showed smooth nanosheets (Figure 3b). After decoration with SnO\(_2\) nanoparticles, some SnO\(_2\) nanoparticles can be obviously observed on the surface of BiOI (Figure 3c,d). Meanwhile, the aggregation of SnO\(_2\) nanoparticles was hindered severely in the SnO\(_2\)/BiOI composite, which can greatly provide the chance for the formation of the heterojunction and then accelerate the transfer of charge carrier. The morphologies and structure of BiOI and SnO\(_2\) in 30 wt % SnO\(_2\)/BiOI have no change, revealing that the structure of SnO\(_2\)/BiOI composites is stable.

Figure 4 is the SEM-EDS elemental mapping of the 30 wt % SnO\(_2\)/BiOI. As shown in Figure 4b–f, the Bi, Sn, O, and I elements were well-distributed throughout the whole material. Moreover, ICP-MS was performed in order to estimate the real...
mass ratio of SnO$_2$ to BiOI in SnO$_2$/BiOI composites. As shown in Table S1, it was observed that the real content of SnO$_2$ in the composite is slightly lower than the nominal ratios, which may be due to the incomplete reaction and loss of the samples during the experiment.

An in-depth investigation about the morphology and micro-structural details of the 30 wt % SnO$_2$/BiOI sample was obtained using TEM and HRTEM technique and shown in Figure 5. The TEM images (Figure 5a) clearly indicates the SnO$_2$ nanoparticles dispersed over the surface of BiOI, coinciding with the results from SEM images. The inset in Figure 5 shows that the size of the SnO$_2$ is 3–6 nm, which is consistent with the XRD analysis. Four distinct lattice fringes with different distances can be observed in Figure 5b. Two interplanar distances of 0.283 and 0.303 nm belong to the BiOI (110) and (102) planes, respectively. Analogously, the interplanar spacing of lattice fringes with two different directions was both calculated to be 0.339 and 0.267 nm, which are compatible with the interplanar spacing of (110) and (101) planes of SnO$_2$. The TEM and HRTEM images further implied that SnO$_2$ nanoparticles accreted on the surfaces of the BiOI nanosheets.

Figure S1 illustrates the nitrogen adsorption–desorption isotherms for SnO$_2$, BiOI, and SnO$_2$/BiOI composites. The BET specific surface areas and pore volumes of the catalysts were summarized in Table 1. As listed in Table 1, the BET specific surface area of BiOI is about 2.430 m$^2$ g$^{-1}$. With increasing SnO$_2$ content, the BET of the composites becomes larger, which facilitates the contaminants’ contact with the catalyst and enhances the photocatalytic degradation. Among them, 60 wt % SnO$_2$/BiOI has the largest specific surface area, but its catalytic.

Figure 2. XPS patterns of 30 wt % SnO$_2$/BiOI composite: (a) survey; (b) Bi 4f; (c) Sn 3d; (d) I 3d; and (e) O 1s.
Figure 3. Typical SEM images of (a) SnO₂; (b) BiOＩ; and (c, d) 30 wt % SnO₂/BiOI.

Figure 4. (a) SEM-EDS mapping image for 30 wt % SnO₂/BiOI sample; EDS mapping images of (b) Bi, (c) I, (d) O, and (e) Sn.

Figure 5. (a) TEM image of 30 wt % SnO₂/BiOI; (b) HRTEM image of 30 wt % SnO₂/BiOI.
ability is not the best, which may be due to excess SnO₂ preventing visible light from reaching the surface of BiOI. Therefore, the appropriate loading of SnO₂ is important for the photocatalytic performance of the catalyst.

The adsorption capabilities of the samples for MO were studied and shown in Figure 6a. It was found that the adsorption capability of the composites increases first and then decreases with the amount of SnO₂ increasing. The main reasons may be as follows: Originally, with the weight ratio of SnO₂ increasing, more reactive sites for the adsorption of MO was formed between BiOI and SnO₂. When the weight ratio of SnO₂ is too much, it can cover the surface of BiOI nanosheets.

The corresponding zeta potential of 30 wt % SnO₂/BiOI as a function of solution pH were displayed in Figure 6b. It can be concluded that zero charge (pHṇzc) of the 30 wt % SnO₂/BiOI composite is close to pH 7. The pH of the MO solution is 6.15, which is less than p Hannah. Thus, as a result of electrostatic adsorption, the catalyst has a certain adsorption capacity for MO, which is consistent with the adsorption results.

It is widely believed that the light absorption ability and energy level of a semiconductor has an important influence on their catalytic activity. UV—vis absorbance of BiOI, SnO₂ and SnO₂/BiOI composites are recorded and shown in Figure 7a. BiOI exhibited light absorption over nearly the entire visible light range, while SnO₂ merely responded to ultraviolet light. After coupling with BiOI nanoplates, a visible light absorbance for SnO₂/BiOI heterostructures was observably enhanced. Therefore, BiOI can act as a good visible light sensitizer for SnO₂. The band gap energy (Eg) values can be obtained by the Kubelka–Munk theorem. According to the calculated Tauc’s plot, the band gaps of SnO₂ and BiOI were 3.48 and 1.70 eV, respectively (Figure 7b).

Incipiently, MO was chosen as a typical refractory dye to assess the photocatalytic performance of the obtained samples. Figure 8a shows a diagram of the degradation of MO using the as-prepared samples. Obviously, all the catalysts have an adsorption to MO to some degree, which is consistent with the results of the previous adsorption experiments. Blank tests confirmed that MO hardly breaks down without the catalyst under visible light irradiation. Pure SnO₂ has no catalytic capacity for MO because of its lack of response to visible light. Under the same condition, about 70% of MO can be degraded within 50 min using BiOI as catalyst. Compared with pure BiOI, the SnO₂/BiOI composites showed enhanced photodegradation of MO. The 30 wt % SnO₂/BiOI composite exhibited optimal photocatalytic activity. Besides, the photocatalytic activity of physically mixed SnO₂ and BiOI is much lower than that of the 30 wt % SnO₂/BiOI composite, implying that intimate interface contact was formed between SnO₂ and BiOI. The 30 wt % SnO₂/BiOI shows the best photocatalytic performance. Moreover, the kinetics of the degradation reaction was investigated by applying the Langmuir–Hinshelwood (L-H) model.31 After fitting, the plots ln(C0/Ct) versus irradiation time t were found to be linear as displayed in Figure 8b, suggesting that the reaction followed the pseudo-first-order model. The apparent reaction rate constants (k) were displayed in Figure 8c. As depicted in Figure 8c, the reaction rate constants for different samples were presented in following order: 30 wt % SnO₂/BiOI > 15 wt % SnO₂/BiOI > 45 wt % SnO₂/BiOI > 60 wt % SnO₂/BiOI > BiOI > SnO₂. It was conspicuous that the reaction rate constant of 30 wt % SnO₂/BiOI is largest, which was about 3.2-fold higher than that of pure BiOI. The time-dependent UV—vis spectral of MO is presented in Figure 8d. As shown in Figure 8d, the characteristic peak intensity decreases with the increase of visible light irradiation time.

Apart from degradation of MO, the obtained samples were further used to eliminate antibiotic OTTCH under visible light irradiation. Figure 9a shows the variation in the concentration of OTTCH during the degradation process. Clearly, it is observed that the concentration of OTTCH decreases with increasing irradiation time. The obtained results indicate that the as-prepared composites have a potential application in the field of wastewater treatment.

### Table 1. BET Surface Area, Pore Volume for SnO₂, BiOI, and SnO₂/BiOI Composites

<table>
<thead>
<tr>
<th>samples</th>
<th>BET specific surface area (m²/g)</th>
<th>pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂</td>
<td>94.34</td>
<td>0.03602</td>
</tr>
<tr>
<td>BiOI</td>
<td>2.430</td>
<td>0.00918</td>
</tr>
<tr>
<td>15 wt % SnO₂/BiOI</td>
<td>37.95</td>
<td>0.01533</td>
</tr>
<tr>
<td>30 wt % SnO₂/BiOI</td>
<td>39.19</td>
<td>0.01549</td>
</tr>
<tr>
<td>45 wt % SnO₂/BiOI</td>
<td>64.46</td>
<td>0.02477</td>
</tr>
<tr>
<td>60 wt % SnO₂/BiOI</td>
<td>83.70</td>
<td>0.03408</td>
</tr>
</tbody>
</table>

Figure 6. (a) Absorption ability evaluation of the as-prepared samples for MO under dark condition; (b) zeta potential of the 30 wt % SnO₂/BiOI composite under different pH conditions.
that the decomposition of OTTCH is negligible for the experiment without catalyst via a blank experiment. Obviously, after adding the photocatalysts, OTTCH was removed. Approximately 94% of OTTCH is degraded within 90 min for 30 wt % SnO$_2$/BiOI, while only 84.04, 89.79, 81.87, 64.11, and 11.42% are degraded for 15 wt % SnO$_2$/BiOI, 45 wt % SnO$_2$/BiOI, 60 wt % SnO$_2$/BiOI, BiOI and SnO$_2$, respectively. Therefore, the optimum amount of loaded SnO$_2$ is 30 wt %.

Figure 7. (a) UV−vis absorption spectra of pure BiOI, SnO$_2$ and SnO$_2$/BiOI composites; (b) calculated band gap of pure BiOI and SnO$_2$.

Figure 8. (a) Photocatalytic degradation MO curves; (b) kinetic curves of MO degradation; (c) apparent rate constants for the degradation of MO; and (d) time-dependent UV−vis spectra of MO solution for 30 wt % SnO$_2$/BiOI sample.
Besides, the photocatalytic performance of a mechanical mixture of 30 wt % SnO$_2$/BiOI was also investigated. As shown in Figure 9a, the degradation efficiency (62.28%) is much lower than that obtained by using 30 wt % SnO$_2$/BiOI, suggesting that p−n junction do form between BiOI and SnO$_2$ through the intimate interfacial contact.

Indeed, the initial concentration of the pollutants varies widely in the natural environment. It is significant to investigate the effect of the initial concentration of the pollutants on the catalytic performance of the catalyst. Figure 9b depicts the influence of the initial concentration of OTTCH on the photocatalytic activity of 30 wt % SnO$_2$/BiOI. Clearly, the decomposition efficiencies decreased to a certain extent with the increase of OTTCH concentrations. The main reasons may be summarized as follows: With the pollutant concentration increasing, more intermediates would be generated in the photocatalysis degradation process. Subsequently, these intermediates can compete with the pollutants for contact with the catalyst. Consequently, the number of photogenerated active radicals would decrease.

Wastewater usually contains nitrate ions, so it is necessary to study their effects on degradation of OTTCH. Figure 9c exhibited the effect in the OTTCH degradation under coexistence of NO$_3^-$ with 30 wt % SnO$_2$/BiOI as catalyst. When nitrate ion concentration (NaNO$_3$ as the provider) increases from 5 to 20 mM, the OTTCH removal rate lowers synchronously. The phenomenon might be attributed to the fact that the NO$_3^-$ ions could compete with the pollutants for contact with the catalyst surface and that some active sites on the catalyst surface were covered, resulting in reducing of the photocatalytic activity for OTTCH degradation. Furthermore, we could see that the catalytic performance of the catalyst is not greatly inhibited at low nitrate concentrations, meaning the catalyst has great potential in practical wastewater treatment.

Moreover, actual wastewater may contain different concentrations of salts. As a result, the effect of ionic strength (NaCl, chosen as a reference) on catalyst performance is investigated. Detecting from Figure 9d, OTTCH degradation efficiencies decreased as the NaCl concentration showed less reduction in the range of 0−0.4M. The cause of this phenomenon can be attributed to the following two aspects: first, the electrostatic interaction between OTTCH molecules and the catalyst was hampered due to the electrostatic protection. The other was a competitive adsorption between OTTCH and Na$^+$ ions on the reaction region and this competition would be enhanced with the increase of NaCl strength. Thus, moderate pretreatment of wastewater with high salts level is beneficial to its photocatalytic degradation.

In order to gain insight into the reactive kinetic behaviors of the pollutants degradation in the SnO$_2$/BiOI hybrid, the OTTCH degradation data are further investigated by applying the L-H model. As present in Figure 10a, all of them match well...
with the pseudo-first-order model. In addition, the reaction rate constant (k) values and degradation efficiencies of the obtained samples toward OTTCH are listed in Table 2. Notably, all of the SnO$_2$/BiOI composites exhibit higher photocatalytic efficiency than those of pure BiOI and SnO$_2$. The results apparently demonstrate the heterojunction structure should exist in BiOI/SnO$_2$ composites.

Figure 10b displayed the UV−vis spectra of photocatalytic degradation of OTTCH in the presence of 30 wt% SnO$_2$/BiOI under visible light irradiation. Obviously, the characteristic absorption peak of OTTCH gradually diminishes with the prolongation of light time.

The lifetime of the catalyst is a vital parameter in practical applications. Thus, the stability of the catalysts was evaluated via a cycle experiment using the optimized catalyst 30 wt% SnO$_2$/BiOI. As displayed in Figure 11, the photocatalytic efficiency decreased only 8.16% after 4 cycling runs. Excluding the loss of photocatalyst in the cycling tests, 30 wt% SnO$_2$/BiOI can be considered to be a stable photocatalyst.

The faster photoinduced electron−hole pair transfer and lower photogenerated electrons and holes recombination rate could significantly improve the photocatalytic performance of the catalysts. Photoluminescence (PL) spectrum had a close association with the migration, transfer, and recombination of electron−hole pairs in photocatalysts. Generally, the stronger the PL intensity, the higher the recombination rate of photogenerated charge carriers and the lower the photocatalytic performance.36 As a result, the PL spectra of the catalysts were collected with 390 nm of excitation wavelength and are presented in Figure 12. It can be observed that pure BiOI and SnO$_2$ exhibit higher PL intensity in comparison with that of BiOI/SnO$_2$ samples. After BiOI coupled with SnO$_2$, the PL intensities of BiOI/SnO$_2$ samples weaken, suggesting a lower the recombination rate of photogenerated electron−hole pairs. Moreover, the PL intensity of 30 wt% SnO$_2$/BiOI sample is the lowest, demonstrating that it achieves a fastest separation efficiency of electron−hole pairs, which is in agreement with the photocatalysis performance.

The photocurrent density−time (i−t) curve is a general method to investigate the separation efficiency of the electrons−holes. Figure 13a shows i−t curves of the series of photoanodes prepared via SnO$_2$, BiOI, and 30 wt% SnO$_2$/BiOI under visible light irradiation. As shown in Figure 13a, the photocurrent densities of BiOI are lower than 0.2 μA cm$^{-2}$, while the photocurrent densities of SnO$_2$ are almost zero because it does not respond visible light. However, it is surprising that the photocurrent density of 30 wt% SnO$_2$/BiOI reaches 1.4 μA cm$^{-2}$, almost 7.2-fold that of pure BiOI. This could be attributed to the electric field on the interface between BiOI and SnO$_2$, which greatly promoted the effective separation of electron holes.

SnO$_2$/BiOI composites exhibit higher photocatalytic efficiency than those of pure BiOI and SnO$_2$. The results apparently demonstrate the heterojunction structure should exist in BiOI/SnO$_2$ composites. Figure 10b displayed the UV−vis spectra of photocatalytic degradation of OTTCH in the presence of 30 wt% SnO$_2$/BiOI under visible light irradiation. Obviously, the characteristic absorption peak of OTTCH gradually diminishes with the prolongation of light time.

The lifetime of the catalyst is a vital parameter in practical applications. Thus, the stability of the catalysts was evaluated via a cycle experiment using the optimized catalyst 30 wt% SnO$_2$/BiOI. As displayed in Figure 11, the photocatalytic efficiency decreased only 8.16% after 4 cycling runs. Excluding the loss of photocatalyst in the cycling tests, 30 wt% SnO$_2$/BiOI can be considered to be a stable photocatalyst.

The faster photoinduced electron−hole pair transfer and lower photogenerated electrons and holes recombination rate could significantly improve the photocatalytic performance of the catalysts. Photoluminescence (PL) spectrum had a close association with the migration, transfer, and recombination of electron−hole pairs in photocatalysts. Generally, the stronger the PL intensity, the higher the recombination rate of photogenerated charge carriers and the lower the photocatalytic performance.36 As a result, the PL spectra of the catalysts were collected with 390 nm of excitation wavelength and are presented in Figure 12. It can be observed that pure BiOI and SnO$_2$ exhibit higher PL intensity in comparison with that of BiOI/SnO$_2$ samples. After BiOI coupled with SnO$_2$, the PL intensities of BiOI/SnO$_2$ samples weaken, suggesting a lower the recombination rate of photogenerated electron−hole pairs. Moreover, the PL intensity of 30 wt% SnO$_2$/BiOI sample is the lowest, demonstrating that it achieves a fastest separation efficiency of electron−hole pairs, which is in agreement with the photocatalysis performance.

The photocurrent density−time (i−t) curve is a general method to investigate the separation efficiency of the electrons−holes. Figure 13a shows i−t curves of the series of photoanodes prepared via SnO$_2$, BiOI, and 30 wt% SnO$_2$/BiOI under visible light irradiation. As shown in Figure 13a, the photocurrent densities of BiOI are lower than 0.2 μA cm$^{-2}$, while the photocurrent densities of SnO$_2$ are almost zero because it does not respond visible light. However, it is surprising that the photocurrent density of 30 wt% SnO$_2$/BiOI reaches 1.4 μA cm$^{-2}$, almost 7.2-fold that of pure BiOI. This could be attributed to the electric field on the interface between BiOI and SnO$_2$, which greatly promoted the effective separation of electron holes.

Table 2. Pseudo-First-Order Rate Constants ($k_{app}$) and Degradation Efficiencies for the OTTCH in Different Photocatalytic Systems

<table>
<thead>
<tr>
<th>catalysts</th>
<th>$k_{app}$ (min$^{-1}$)</th>
<th>DE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiOI</td>
<td>0.00966</td>
<td>60.45</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>0.00016</td>
<td>1.42</td>
</tr>
<tr>
<td>15 wt% SnO$_2$/BiOI</td>
<td>0.01835</td>
<td>82.81</td>
</tr>
<tr>
<td>30 wt% SnO$_2$/BiOI</td>
<td>0.03113</td>
<td>94.57</td>
</tr>
<tr>
<td>45 wt% SnO$_2$/BiOI</td>
<td>0.02353</td>
<td>89.11</td>
</tr>
<tr>
<td>60 wt% SnO$_2$/BiOI</td>
<td>0.01734</td>
<td>80.61</td>
</tr>
<tr>
<td>Mixture</td>
<td>0.000886</td>
<td>58.87</td>
</tr>
</tbody>
</table>

Figure 10. (a) Kinetic curves of OTTCH degradation; (b) time-dependent UV−vis spectra of OTTCH solution for 30 wt% SnO$_2$/BiOI sample.

Figure 11. Cycling tests of photocatalytic activity of 30 wt% SnO$_2$/BiOI composite for OTTCH degradation.
and thus leading to the sharp increase of the photocurrent density. All in all, on the basis of the PC results, we can further conclude that the heterojunction was built between BiOI and SnO$_2$ through deposition of SnO$_2$ on the surface of BiOI nanosheets.

Additionally, electrochemical impedance spectroscopy (EIS) measurement could also be applied to investigate the charge separation efficiency. As is well-known, a smaller semicircle radius means higher charge transfer efficiency.$^{37}$ Figure 13b shows EIS Nyquist plots of SnO$_2$, BiOI, and 30 wt % SnO$_2$/BiOI. It is observed that the semicircle of 30 wt % SnO$_2$/BiOI is smaller than those of SnO$_2$ and BiOI electrodes. Such a phenomenon in impedance also has been reported in previous studies.$^{38,39}$ The lowest electron transfer resistance in 30 wt % SnO$_2$/BiOI composites may be ascribed to fabrication of BiOI/SnO$_2$ p–n junction, which can effectively improve the efficiency of electron–hole pair separation, resulting in higher photocurrent response and more excellent photodegradation activity.

In order to ascertain main active groups involved in photodegradation of organic pollutants, 10 mM IPA (*OH quencher), 5 mM Na$_2$C$_2$O$_4$ (h$^+$ quencher), and 0.4 mM BQ (*O$_2^-$ quencher) were added to photocatalytic system as the scavengers during photocatalytic reaction.$^{40,41}$ Figure S2 shows the results obtained from the photocatalytic degradation test in the presence of inhibitors. Apparently, the introduction of IPA does not yield any suppression of the degradation efficiency of OTTCH, indicating the absence of *OH radical in degradation process. Conversely, when Na$_2$C$_2$O$_4$ and BQ were added, the degradation efficiency was thoroughly depressed. Thus, it can be inferred that h$^+$ and *O$_2^-$ radicals are active groups involved in photodegradation of organic pollutants and that h$^+$ play a more important role in the photodegradation reaction than *O$_2^-$ radicals.

Figure 12. Photoluminescence spectra of the obtained samples.

Figure 13. (a) Transient photocurrent response for the pure SnO$_2$, BiOI, and 30 wt % SnO$_2$/BiOI under visible light irradiation; (b) EIS Nyquist plots of the pure SnO$_2$, BiOI, and 30 wt % SnO$_2$/BiOI.
The electron spin resonance (ESR) spin-trap with DMPO technique was employed to detect the reactive over 30 wt % SnO₂/BiOI under dark and visible light irradiation for further confirm the reactive species involved in photocatalytic degradation process. As shown in Figure 14a, no such signals were detected in dark. On the contrary, the signals of DMPO-•O₂⁻ could be clearly observed under visible light irradiation. However, whether in dark conditions or visible light, the characteristic signals corresponding to the DMPO-•OH adduct (as shown in Figure 14b) has never appeared. The ESR results indicate that the •O₂⁻ radicals were produced during the photocatalytic process, while •OH radicals hardly be generated, which are in accordance with the active species trapping experimental.

It is well-known that heterojunction photocatalysts with a staggered band position is more propitious to the separation and transfer of charge carrier. The valence band edge potential (E VB), conduction band edge potential (E CB) and bandgap (E g) of a semiconductor has the following relationship.43,44

\[ E_{VB} = E_{CB} + E_g \]

The band gap energy of the BiOI and SnO₂ is calculated to be 1.70 and 3.48 eV as shown in Figure 7b. The E VB of BiOI and SnO₂ could be confirmed to be 1.94 and 3.48 eV via XPS.
technique, respectively. From the above formulas, $E_{CB}$ of BiOI and SnO$_2$ were estimated to be 0.24 and 0 eV, respectively.

In the light of the above analysis, a possible mechanism for the degradation of pollutants is proposed as outlined in Scheme 2. According to the calculated band position, the band positions of BiOI and SnO$_2$ are shown in Scheme 2a before having any contact. As illustrated in Scheme 2a, pure BiOI and SnO$_2$ show a nested band array, which seems adverse to the transfer of photogenerated carriers. However, it is worth noting that based on the Mott–Schottky plots, BiOI is confirmed as a p-type semiconductor (Figure S3b), while SnO$_2$ was identified as an n-type semiconductor due to the positive slope in the same plot (Figure S3a). The Fermi level of SnO$_2$ is located near the CB while that of the BiOI close to the VB. As the Mott–Schottky plots of 30 wt % SnO$_2$/BiOI present an inverted “V”-shape (Figure S3c), the p–n junction was constructed in SnO$_2$/BiOI composites. The Fermi level achieves equilibrium. Meanwhile, an inner electric field will be built in the interface, which induces the region of BiOI to be negatively charged, and the region of SnO$_2$ to be positively charged. Once SnO$_2$/BiOI composites were exposed to visible light, only BiOI can be excited to generate the electrons and holes. The electrons in the CB of BiOI can easily transfer to the CB of SnO$_2$ with the assistance of the internal electric field. Simultaneously, holes were concentrated on the VB of the BiOI. After that, electrons capture O$_2$ to generate “$^{*}$O$_2$” and involve the degradation of pollutants. Meanwhile, plenty of holes retained on the VB of the BiOI further participated in photocatalytic reactions. Through this route, the photogenerated carriers could be separated efficiently, and the photocatalytic activity was greatly improved, which is in accordance with the PL and Photocurrent results.

The band alignment of the SnO$_2$/BiOI composites can further proved the above proposed mechanism. The $\Delta E_{\text{VBO}}$ and $\Delta E_{\text{CBO}}$ of the SnO$_2$/BiOI heterostructure was calculated according to following equation.  

$$\Delta E_{\text{VBO}} = (E_{\text{V, Bi}}^{\text{BiOI}} - E_{\text{V, Bi}}^{\text{pure}}) - (E_{\text{V, Sn}}^{\text{SnO}_2} - E_{\text{V, Sn}}^{\text{pure}}) + \Delta E_{\text{CL}}$$

$$\Delta E_{\text{CBO}} = E_{\text{CBO}}^{\text{BiOI}} - E_{\text{CBO}}^{\text{SnO}_2} + \Delta E_{\text{VBO}}$$

Herein, the core level positions and the VBM positions of SnO$_2$ and BiOI were also determined via XPS technique. $\Delta E_{\text{CL}} = (E_{\text{Sn, 3d}} - E_{\text{Bi, 4d}})$ is the energy difference between Bi 4f and Sn 3d core levels in the SnO$_2$/BiOI heterostructure. $E_{\text{Bi, 4d}}$ and $E_{\text{Sn, 3d}}$ are the binding energies of the pure BiOI and SnO$_2$, respectively; $E_{\text{V, Bi}}$ and $E_{\text{V, Sn}}$ are the VB of the BiOI and SnO$_2$, respectively. $E_{\text{CB}}^{\text{BiOI}}$ and $E_{\text{CB}}^{\text{SnO}_2}$ are the band gap of SnO$_2$ and BiOI, respectively. Figure S4 show the XPS core-level positions for pure SnO$_2$, BiOI, and SnO$_2$/BiOI heterojunctions. The binding energy values for the core-level, VBM, and band gap energy of pure SnO$_2$, pure BiOI, and SnO$_2$/BiOI heterojunctions were summarized in Table S3. On the basis of the above equations, the $\Delta E_{\text{VBO}}$ and $\Delta E_{\text{CBO}}$ values for SnO$_2$/BiOI heterojunctions could be calculated as 0.86 and 2.64 eV, respectively. A proposed energy band diagram for the SnO$_2$/BiOI heterojunctions was displayed in Scheme 3. Only BiOI could be excited to produce electron–hole pairs under visible light illumination. $\Delta E_{\text{CBO}}$ is the driving force that can promote the photogenerated electrons to transfer from the BiOI to the SnO$_2$. The results further indicate a p–n junction existed between BiOI and SnO$_2$.

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**Scheme 3. Energy Band Diagrams of SnO$_2$/BiOI Heterojunctions**

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**CONCLUSION**

SnO$_2$/BiOI n–p junctions were triumphantly fabricated with the loading of SnO$_2$ nanoparticles on the surface of BiOI nanosheets. The SnO$_2$/BiOI composites showed obviously superior photocatalytic activity and stability for the photodegradation of methyl orange and oxytetracycline hydrochloride under visible-light irradiation. Transient photocurrent response and PL spectrum indicate that a higher photoinduced charge separation efficiency exist in SnO$_2$/BiOI composites. Active species trapping experiments and ESR analysis confirmed that h$^+$ and “$^{*}$O$_2$” were two main active groups involved in photodegradation of organic pollutants. In summary, the remarkable photocatalytic performance can be ascribed to construction of p–n junction which then tremendously quickens the separation of electron–hole pairs. Moreover, the energy band alignments of SnO$_2$/BiOI composites were confirmed via combining DRS and XPS analysis, which provided strong support for the proposed mechanism. This work could provide a new approach to construct new p–n junction photocatalysts and a reference for the study of other heterojunction catalysts. Additionally, this catalyst can be a candidate that can be used in more refractory pollutant degradation as well as other environmental remediation applications.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b00501.

Nominal and real mass ratio of SnO$_2$ to BiOI of the samples; nitrogen adsorption–desorption isotherm of the prepared composites; various degradation values of 30 wt % SnO$_2$/BiOI after introduction of difference scavengers; Mott–Schottky curves of SnO$_2$, BiOI, 30 wt % SnO$_2$/BiOI; XPS core-level and valence band spectra obtained from SnO$_2$, BiOI, 30 wt % SnO$_2$/BiOI; XPS binding energies of the core levels, VBM and the band-gap energy for SnO$_2$, BiOI, and SnO$_2$/BiOI photocatalysts (PDF)
Notes
The authors declare no competing financial interest.

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