Effect of different Bi/Ti molar ratios on visible-light photocatalytic activity of BiOI/TiO₂ heterostructured nanofibers

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1. Introduction

It is well known that environmental pollution issues, in addition to economic development and urbanization in China, are posing an increasing threat. Researchers have reported several advanced oxidation technologies for treating pollutants. Among these technologies, photocatalysis has attracted significant attention. Currently, titanium dioxide (TiO₂) has been extensively used for the treatment of wastewater, attributed to its cost-effectiveness, nontoxicity, and chemical stability [1–3]. However, unfortunately, anatase TiO₂ imposes limitation due to its unsatisfactory quantum efficiency because of its large band gap (3.2 eV). Only ultraviolet (UV) light (λ < 380 nm, less than 5% of solar energy) can be absorbed for realizing the photoelectric effects [4,5]. Moreover, the obstacle of separating the photocatalysts from the reaction system for recycling is a major limitation for their large-scale industrial application [6,7]. Therefore, it is imperative to improve the quantum efficiency and solve the recyclability issue of TiO₂.

For improving the photocatalytic activity of TiO₂, so far several methods have been employed, such as doping with impurities or combining with heterogeneous semiconductors [8–11]. The manipulation of semiconductor heterostructures has attracted significant attention as an effective approach to efficiently improve photocatalytic activity. As compared to single-phase photocatalysts, heterostructures are superior because they exhibit enhanced reactivity in both UV and Vis-light regions as well as the advanced separation of photoelectrons and holes. This result is attributed to the fact that when a semiconductor is coupled with another one, the small-band-gap semiconductor serves as a photosensitizer and absorbs a large fraction of the solar spectrum, indicating easy production of more photoelectrons and holes. Moreover, the photoelectrons present on the surface of an excited small-band-gap semiconductor can be transferred to another one, the small-band-gap semiconductor serves as a photosensitizer and absorbs a large fraction of the solar spectrum, indicating easy production of more photoelectrons and holes.

In recent years, bismuth oxyhalides (BiOX, where X=F, Cl, Br, I), which represent semiconductors with a small band gap, have attracted significant interest as a new type of semiconductor photocatalysts, wherein photocatalytic activity is observed in both UV and Vis-light regions [19,20]. Among these oxyhalides, BiOI, with a

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small band gap of approximately 1.79 eV, exhibits the highest photocatalytic activity in the Vis-light region. A BiOI/TiO2 heterogeneous powder has been reported for the treatment of organic pollutants or wastewater under Vis-light irradiation [16]. However, it was difficult to recycle the powder from the reaction system. Nonetheless, compared to the powder, nanofibers can be easily separated from the reaction system.

As a facile, highly efficient method for synthesizing nanomaterials, electrospinning has been widely employed for producing nanostructured materials with different diameters, such as nanofibers and nanotubes [21–23]. Electrospinning-derived TiO2 composite nanofibers are more suitable for environmental management, attributed to their controllable configuration with respect to diameter and length. Compared to powder photocatalysts, TiO2 nanofibers demonstrate more potential for separation from reaction systems. Furthermore, TiO2 nonwoven films can also be efficiently fabricated by electrospinning [24].

In this study, electrospinning and solvothermal methods were employed for synthesizing different stoichiometric amounts of BiOI/TiO2 heterostructured nanomaterials. The photocatalytic activities of these heterostructures were measured by the degradation of methylene blue (MB) under Vis-light irradiation (λ = 420 nm). The result showed that the BiOI/TiO2 heterostructures demonstrated photocatalytic activity significantly higher than those of pure BiOI microflowers and TiO2 nanofibers. Moreover, the 80% BiOIVTiO2 heterostructure exhibited the best photocatalytic activity. Furthermore, the morphology of the crystalline structures was observed, and the surface electronic states as well as the UV–vis diffuse reflectance spectra (UV–vis DRS) of these samples were also measured.

2. Materials and methods

2.1. Preparation of titanium dioxide nanofibers

TiO2 nanofibers were synthesized by electrospinning. In a typical synthesis, 1.5 g of polyvinyl pyrrolidone (PVP) powder (Mc = 1300000, Alfa Aesar) was first added slowly into a 20 mL ethanol solution containing 8 mL tetrabutyl titanate (Sinopharm Chemical Reagent Corp., China) and 5 mL acetic acid. Second, the mixture was stirred for approximately 2 h at room temperature to form a solution. Third, the mixture was aspirated into a 20 mL syringe. The voltage applied to the needle was 15 kV, and the distance between the needle and silver paper was 15 cm. The pump speed was 2 mL h−1. Finally, the TiO2 nanofibers were collected and heated at 500 °C for 1 h in a muffle furnace [24].

2.2. Fabrication of bismuth oxyiodide/titanium dioxide heterostructure nanofibers

The hydrothermal method was employed for synthesizing BiOI/TiO2 heterostructured nanofibers. In a typical synthesis, different stoichiometric amounts of Bi(NO3)3·5H2O (Aladdin) were first added into a 10 mL ethylene glycol solution and constantly stirred using a magnetic stirrer for 20 min to form a solution. Second, 0.6 mmol of TiO2 nanofibers was added into the Bi(NO3)3·5H2O solution. The Bi/Ti molar ratio was controlled at 0, 0.20, 0.50, 0.80, and 1. Third, 10 mL of a potassium iodide (Sinopharm Chemical Reagent Corp., China) solution with equimolar amounts of Bi(NO3)3·5H2O was added dropwise into the Bi(NO3)3·5H2O/TiO2 solution. Next, the mixtures were transferred into an autoclave and heated at 150 °C for 15 h. The final products were collected and washed with ethanol and distilled water several times and dried in a drying oven at 50 °C. The final samples were denoted as 20%, 50%, 80%, and 100% BiOI/TiO2, corresponding to Bi/Ti molar ratios of 0.20, 0.50, 0.80, and 1, respectively. For comparison, pure BiOI powders were synthesized by the same method.

2.3. Characterization

Powder X-ray diffraction (XRD) was employed for observing the crystalline structures of the as-prepared samples using a P-general XD-3 XRD with Cu Kα radiation (λ = 1.5406) at 40 mA and 40 kV. Scanning electron microscopy (SEM) was employed for examining the morphology of the photocatalysts using a Zeiss Supra 55 instrument. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were employed for examining the sample microstructures using an FEI Tecnai G2 F30 instrument. X-ray photoelectron spectroscopy (XPS) (Escalab 250 Xi, Thermo Scientific) was employed for observing the surface electronic states of the as-prepared samples. The UV–vis DRS of the photocatalysts were recorded on a Varian Cary 5000 UV–vis spectrophotometer.

2.4. Photocatalytic activity measurements

The photocatalytic activities of the samples were evaluated by the degradation of MB in aqueous solutions under Vis-light irradiation (500 W Xe lamp) with a cut-off filter of 420 nm, which can prevent UV irradiation. First, 0.05 g of photocatalyst was added in a quartz tube containing a 50 mL MB aqueous solution at a concentration of 10 mg L−1. Before irradiation, the solutions were stirred using magnetic stirrers for 30 min in the dark to attain adsorption–desorption equilibrium. At every 30 min, 2 mL of the solution was collected and centrifuged to obtain supernatants. The solution concentration was measured on an INESA LS 5 UV–vis spectrophotometer.

3. Result and discussion

3.1. Scanning electron microscopy images

SEM images were recorded for investigating the structure and morphology of the pure TiO2 nanofibers, pure BiOI nanosheets, and BiOI/TiO2 heterostructured nanofibers with varying Bi/Ti ratios. Fig. 1a shows that pure-phase TiO2 nanofibers exhibit a smooth surface with diameters of approximately 200–300 nm. After the introduction of different concentrations of the Bi(NO3)3·5H2O precursor into the system, as shown in Fig. 1(b)–(e), the TiO2 nanofibers were covered with disk-like BiOI nanosheets after solvothermal treatment, in which the BiO1 nanosheets were approximately 800–1000 nm in length or width. By increasing the precursor concentration ratio of Bi/Ti from 20% to 100%, the nanosheets were still uniformly distributed over each fiber without aggregation, and the density of the nanosheets on the TiO2 nanofibers increased significantly. Notably, compared to the SEM image showing the morphology of BiOI nanosheets without TiO2 nanofibers, a typical SEM image (Fig. 1e) of pure BiOI microspheres exhibited flowerlike morphology, attributed to the self-assembly of BiOI nanosheets, with an average diameter of 4 μm in the absence of TiO2 nanofibers.

3.2. Transmission electron microscopy and high resolution transmission electron microscopy images

Detailed structural information about the BiOI/TiO2 composite samples was further investigated by TEM and HRTEM. Fig. 2a shows the representative TEM images of 80% BiOI/TiO2 heterostructured photocatalysts. Clearly, most of the BiOI nanosheets exhibit a relatively smooth edge, attributed to the layered
Fig. 1. SEM images of TiO$_2$, BiOI, and BiOI/TiO$_2$ heterostructures: (a) pure TiO$_2$ nanofibers, (b) 20% BiOI/TiO$_2$, (c) 50% BiOI/TiO$_2$, (d) 80% BiOI/TiO$_2$, (e) 100% BiOI/TiO$_2$, and (f) pure BiOI.

Fig. 2. (a) TEM and (b) HRTEM images of 80% BiOI/TiO$_2$ heterostructures.
structure of BiOI as reported previously \[6\]. Moreover, disk-like BiOI nanosheets were aligned perpendicular to the smooth surfaces of TiO\(_2\) nanofibers, which was consistent with the SEM results. HRTEM was employed for obtaining more detailed structural characteristics of the 80\% BiOI/TiO\(_2\) heterostructures. Fig. 2b demonstrates two lattice images with d spacing values of 0.35 nm (3.54 nm for 10 lattices) and 1.93 nm, corresponding to the (101) plane of anatase TiO\(_2\) and the (021) plane of tetragonal BiOI, respectively. HRTEM further confirmed the coexistence of BiOI and TiO\(_2\) in the resulting samples.

3.3. X-ray diffraction analysis

Fig. 3 shows the XRD patterns of TiO\(_2\) nanofibers, 20–100% BiOI/TiO\(_2\) composites, and BiOI nanosheets. The TiO\(_2\) nanofibers prepared by electrospinning exhibit diffraction peaks around 20 values of 25.5°, 37.8°, 47.8°, and 55°, indexed to anatase TiO\(_2\) (JCPDS No. 84-1285). The diffraction peak of pure BiOI nanosheets was well indexed to tetragonal BiOI (JCPDS No. 73-2062). The diffraction peaks of BiOI/TiO\(_2\) heterostructures with different Bi/Ti molar ratios exhibited the same diffraction angle as those of pure TiO\(_2\) and BiOI components. Notably, the relative intensity of the characteristic peak of TiO\(_2\) gradually decreased; however, peaks attributed to BiOI gradually increased with the increasing molar ratio of BiOI/TiO\(_2\) in the composite system. This result further indicated that BiOI and TiO\(_2\) coexisted in the BiOI/TiO\(_2\) composites, and their molar ratio showed agreement with the precursor molar ratio, which was consistent with the SEM results discussed previously in Fig. 1.

3.4. X-ray photoelectron spectra

XPS was employed for investigating surface electronic states as well as the chemical composition of the as-prepared samples. Fig. 4 shows the XPS survey and high-resolution XPS spectra of different atoms of the 80% BiOI/TiO\(_2\) heterostructures. Fig. 4a shows that the surface of the 80\% BiOI/TiO\(_2\) heterostructures is covered by BiOI as reported previously \[6\]. Moreover, disk-like BiOI nanosheets were aligned perpendicular to the smooth surfaces of TiO\(_2\) nanofibers, which was consistent with the SEM results. HRTEM was employed for obtaining more detailed structural characteristics of the 80\% BiOI/TiO\(_2\) heterostructures. Fig. 2b demonstrates two lattice images with d spacing values of 0.35 nm (3.54 nm for 10 lattices) and 1.93 nm, corresponding to the (101) plane of anatase TiO\(_2\) and the (021) plane of tetragonal BiOI, respectively. HRTEM further confirmed the coexistence of BiOI and TiO\(_2\) in the resulting samples.

3.5. Ultraviolet–visible diffuse reflectance spectra

The optical absorption of the synthesized photocatalysts was measured by UV–vis DRS. Fig. 5a shows that the absorption edge of TiO\(_2\) nanofibers is 410 nm, which is same as that of anatase TiO\(_2\), revealing the negligible absorbance of TiO\(_2\) nanofibers in the Vis-light region. Pure BiOI exhibited an absorption edge at 650 nm, indicating its optical response in the Vis-light region. Moreover, with increasing BiOI ratio, the light absorption edge of heterostructured photocatalysts was extended to the Vis-light region. For instance, the light absorption edge of 20\% BiOI/TiO\(_2\) heterostructures was observed at approximately 500 nm, indicative of response in the Vis-light region. Notably, 80\% BiOI/TiO\(_2\) heterostructures exhibited better performance with respect to optical response compared to that of 100\% BiOI/TiO\(_2\) heterostructures, which was in good agreement with the results obtained from the photocatalytic activities.

The band gap of the semiconductor synthesized herein can be calculated according to the following equation:

\[
\alpha h\nu = A (h\nu - E_g)^n \tag{1}
\]

where, \(\alpha\), \(h\), \(\nu\), \(E_g\), and \(A\) represent the absorption coefficient, light frequency, band gap, and constant, respectively. Furthermore, \(n\) depends on the characteristics of transition in a semiconductor; i.e., \(n=1\) for a direct transition or \(n=4\) for an indirect transition. For BiOI and TiO\(_2\), the value of \(n\) is 4 corresponding to an indirect transition. Therefore, the band gap energy \((E_g)\) of the photocatalysts can be estimated from a plot \((\alpha h\nu)^{1/2}\) versus photon energy \((h\nu)\), and the band gap energy of the products was well measured by the intercept of the tangent to the X axis. Fig. 5b shows that the band gaps of pure BiOI and anatase TiO\(_2\) nanofibers are approximately 1.9 and 3.2 eV, respectively. With the increase in the BiOI mole ratio from 20\% to 80\%, the band gap of BiOI/TiO\(_2\) heterostructures decreased from 3.0 to 1.95 eV. However, the band gap of 100\% BiOI/TiO\(_2\) heterostructures (2.1 eV) is larger than 80\% BiOI/TiO\(_2\) samples (1.95 eV). The above results showed that the synthesized heterostructures, with a BiOI/TiO\(_2\) mole ratio of 80\%, exhibited the smallest band gap of 1.95 eV. The heterostructures with smaller band gap have the higher valence band and lower conduction band, indicating easy production of more photoelectrons and holes.

3.6. Photocatalytic activities of bismuth oxyiodide/titanium dioxide heterostructures

MB is a type of stable organic dyestuff, which can be often used as a model pollutant for evaluating photocatalytic activity. In our experiment, the photocatalytic activities of TiO\(_2\) nanofibers, BiOI nanosheets, and BiOI/TiO\(_2\) heterostructures were measured by the degradation of MB under Vis-light irradiation \((\lambda > 420\ \text{nm})\). Fig. 6 shows the result of photocatalytic measurements. Before Vis-light irradiation, the reactor was placed in the dark and stirred for 30 min to attain adsorption–desorption equilibrium. After 30 min of reaction in the dark, the degradation of MB over TiO\(_2\) nanofibers was merely 5%. Notably, with increasing BiOI nanosheets coupled with the TiO\(_2\) nanofibers, the concentration of MB solution rapidly decreased. Moreover, when pure BiOI nanosheets were dispersed
into the reactor, 46% of MB was adsorbed during 30 min of the reaction in the dark. After Vis-light irradiation for 180 min, the degradation of MB over pure TiO$_2$ nanofibers and BiOI nanosheets was barely 1% and 4%, respectively. Furthermore, the heterostructured photocatalysts exhibited photocatalytic activity higher than those of single-phase TiO$_2$ and BiOI in the Vis-light region. For example, 27% of MB was degraded by 20% BiOI/TiO$_2$ in 180 min under Vis-light irradiation. With increase in the stoichiometric ratio of BiOI to 50%, only 45% of MB was degraded in 180 min 60% of MB was degraded by 100% BiOI/TiO$_2$ heterostructures in 180 min. However, 80% BiOI/TiO$_2$ exhibited the best photocatalytic activity. The efficiency for the degradation of MB increased to 83% under Vis-light irradiation for 180 min over the 80% BiOI/TiO$_2$ heterostructure. Therefore, the 80% BiOI/TiO$_2$ heterostructure exhibited the photocatalytic activity better than the other heterostructures in our experiment.

For quantitative analyses of the kinetics of MB photodegradation, wherein the pseudo-first-order model was utilized, which is widely applied for photocatalytic degradation with the objective of calculating photodegradation data. The prerequisite for using this model is low initial pollutant concentration, and this model is expressed as Eq. (2).

$$\ln \left( \frac{C_0}{C} \right) = kt + b$$

where, $k$ is the degradation rate constant, $C_0$ and $C$ are the concentrations of MB and dye in the solution at a reaction time $t$, respectively.
respectively. Fig. 7a shows that the slope of the line corresponds to the photodegradation rate. The 80% BiOI/TiO2 heterostructure exhibited the highest degradation rate. Fig. 7b shows the comparison of the degradation rate of the as-prepared photocatalysts. The results showed that the photocatalytic degradation rate of the 80% BiOI/TiO2 heterostructures was approximately 20 times greater than that of pure BiOI, and the degradation efficiency of pure TiO2 nanofibers under Vis-light was negligible.

4. Conclusions

In summary, the BiOI/TiO2 heterostructures with Bi/Ti molar ratios of 0.20–1 were synthesized by electrospinning and hydrothermal methods. These heterostructures exhibited photocatalytic activity significantly higher than those of pure TiO2 nanofibers and BiOI nanosheets for the degradation of methylene blue under visible light irradiation. Among the as-prepared photocatalysts, the 80% BiOI/TiO2 heterostructures exhibited the highest efficiency, and the degradation rate of 80% BiOI/TiO2 heterostructures was 20 times greater than that of pure BiOI. The characterization results confirmed the formation of heterojunctions and revealed that the 80% BiOI/TiO2 heterostructures exhibited the best band gap structure among these heterostructures, leading the enhanced photocatalytic activity.
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