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Preparation of a p-n heterojunction BiFeO₃@TiO₂ photocatalyst with a core-shell structure for visible-light photocatalytic degradation

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ABSTRACT

Magnetically separable bismuth ferrite (BiFeO₃) nanoparticles were fabricated by a citrate self-combustion method and coated with titanium dioxide (TiO₂) by hydrolysis of titanium butoxide (Ti(OBu)₄) to form BiFeO₃@TiO₂ core-shell nanocomposites with different mass ratios of TiO₂ to BiFeO₃. The photocatalytic performance of the catalysts was comprehensively investigated via photocatalytic oxidation of methyl violet (MV) under both ultraviolet and visible-light irradiation. The BiFeO₃@TiO₂ samples exhibited better photocatalytic performance than either BiFeO₃ or TiO₂ alone, and a BiFeO₃@TiO₂ sample with a mass ratio of 1:1 and TiO₂ shell thickness of 50–100 nm showed the highest photo-oxidation activity of the catalysts. The enhanced photocatalytic activity was ascribed to the formation of a p-n junction of BiFeO₃ and TiO₂ with high charge separation efficiency as well as strong light absorption ability. Photoelectrochemical Mott-Schottky (MS) measurements revealed that both the charge carrier transportation and donor density of BiFeO₃ were markedly enhanced after introduction of TiO₂. The mechanism of MV degradation is mainly attributed to hydroxyl radicals and photogenerated electrons based on energy band theory and the formation of an internal electrostatic field. In addition, the unique core-shell structure of BiFeO₃@TiO₂ also promotes charge transfer at the BiFeO₃/TiO₂ interface by increasing the contact area between BiFeO₃ and TiO₂. Finally, the photocatalytic activity of BiFeO₃@TiO₂ was further confirmed by degradation of other industrial dyes under visible-light irradiation.

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1. Introduction

The rapid consumption of fossil fuels will lead to both environmental pollution and an energy crisis. One promising solution to lower the demand for fossil fuels is the efficient use of solar energy, which is abundant and clean [1]. Current solar

energy applications include solar cells [2], water splitting [3–5], photocatalytic CO₂ reduction and hydrogen production [6–9], as well as removal of environmental pollutants [10–13]. TiO₂ is one of the most popular photocatalysts in solar-energy utilization because of its high chemical stability, low toxicity, and low cost [14]. However, the wide band gap (E_g) of TiO₂ of 3.2 eV

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means it only absorbs ultraviolet light, which constitutes just 4% of solar radiation. Therefore, fabrication of efficient visible light-active photocatalysts that strongly absorb visible light is of great importance. Another major bottleneck limiting the practical use of photocatalysis is the low quantum yield caused by rapid recombination of the photogenerated electron–hole pairs [15]. Various TiO₂ modification strategies have been developed to overcome the above limitations; for example, dye sensitization [16], impurity doping [17,18], and metal oxide coupling [19]. Among these strategies, heterogeneous coupling has proved to be a promising and practical approach to improve photocatalytic activity by lowering the recombination rate of photogenerated carriers [20–22]. For instance, Luo et al. [23] used Fe₂O₃ and BiFeO₃ to sensitize SrTiO₃ to visible light. Nanocomposites with a core–shell structure containing a magnetic material as the core and TiO₂ as the shell are attracting research interest for use as photocatalysts [24–26].

As a typical perovskite material, BiFeO₃ exhibits both ferroelectric and magnetic polarization [27–30]. The internal polarization of BiFeO₃ usually leads to band bending, which subsequently drive photogenerated carriers in opposite directions [31–33] to inhibit their recombination, thus enhancing photocatalytic efficiency. In addition, BiFeO₃ responds to visible light because of its relatively narrow E_g of 2.2–2.7 eV [34]. Zhang et al. [35] fabricated TiO₂/BiFeO₃ heterostructures in which BiFeO₃ helped slow the recombination of photogenerated electrons and holes. Li and colleagues [36] synthesized BiFeO₃@TiO₂ with a unique core–shell structure via a hydrothermal method. This nanocomposite displayed higher photocatalytic activity than that of pure BiFeO₃ under visible-light irradiation. It was believed that a heterojunction structure formed that promoted interfacial charge transfer in BiFeO₃@TiO₂. Zhu et al. [37] prepared a BiFeO₃/TiO₂ nanotube array composite electrode and found that surface modification with BiFeO₃ nanoparticles improved the photochemical properties of TiO₂ nanotubes because of the increased absorption of visible light. However, the exact photocatalytic mechanism of BiFeO₃@TiO₂ core–shell nanocomposites is not clear; further experimental and theoretical studies need to be conducted to better understand the intrinsic relationships between its high photocatalytic activity and interfacial structures.

In this work, core–shell-structured BiFeO₃@TiO₂ nanocomposites with different mass ratios are synthesized by a citrate self-combustion method and TiO₂ coating procedure controlled by the hydrolysis of Ti(OBu)₄. The crystal structure, optical properties, and morphologies of the nanocomposites are systematically characterized. The photocatalytic performance of the nanocomposites is studied via photocatalytic oxidation of methyl violet (MV) under both ultraviolet- and visible-light irradiation. The photoelectrochemical properties of the nanocomposites are studied to confirm the formation of a p–n heterojunction interface between p-BiFeO₃ and n-TiO₂. A series of quenching tests are conducted to investigate the mechanism of dye photodegradation. The optimal reaction conditions for MV degradation under visible-light irradiation are evaluated. The core–shell-structured BiFeO₃@TiO₂ nanocomposites are also used to degrade other dye pollutants.

2. Experimental

2.1. Materials

MV, methyl orange (MO), and Congo red (CR) (all AR grade from Tianjin Chemical Company, China) were chosen as the model pollutants.

Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O; 99%, AR, Xilong Chemical Corporation), iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O; 98.5%, AR, Nanjing Chemical Company), anhydrous ethanol (C₂H₅OH; 99.7%, Jiuyi Chemical Reagent Co. Ltd., China), nitric acid, ammonium hydroxide (AR, Nanjing Chemical Company), citric acid (AR, Guoyao Group Chemical Reagent Co. Ltd.), polyethylene glycol (PEG; CP, Xilong Chemical Corporation), tetrabutyl orthotitanate (Ti(OBu)₄; AR, Jiangsu Yonghua Chemical Company), and acetylacetone (AR, Jiangsu Yonghua Chemical Company) were used to fabricate the BiFeO₃@TiO₂ catalysts. Deionized (DI) water was used in all experiments. Benzoquinone (BQ; 98%), ammonium oxalate monohydrate (AO; 99.0%) and *tert*-butyl alcohol (TBA; 99.5%) were purchased from Sigma-Aldrich.

2.2. Sample preparation

BiFeO₃ nanoparticles were fabricated by a citrate–nitrate combustion method [38]. In a typical synthesis, equimolar amounts of Fe(NO₃)₃·9H₂O and Bi(NO₃)₃·5H₂O were dissolved in nitric acid solution (100 mL, volume ratio of nitric acid to distilled water was 1:5). The solution pH was adjusted to about 4–5 by adding nitric acid and ammonium hydroxide. An equimolar amount of citric acid was then added to the above solution with continual stirring for 30 min at 50 °C. PEG was added to the solution (0.5 g PEG per 2.5 mmol Bi(NO₃)₃·5H₂O) and then it was ultrasonicated for 30 min. The resulting suspension was heated at 80 °C to give a BiFeO₃ xerogel powder. The xerogel powder was annealed at 500 °C for 2 h to provide the BiFeO₃ nanoparticles.

A TiO₂ coating was formed on the BiFeO₃ nanoparticles via hydrolysis of Ti(OBu)₄ according to a published method with minor modification [36]. The starting reaction mixture consisted of solutions A and B. Solution A contained a suitable amount of Ti(OBu)₄ (mass ratios of BiFeO₃ to TiO₂ of 1:2, 1:1, and 2:1 were used) and acetylacetone (2.5 mL) in a mixture of ethanol (100 mL) and DI water (2 mL). Solution B was composed of BiFeO₃ powder (1.2 g) in ethanol (100 mL). The pH of solution B was adjusted to about 5–6 with HNO₃. Then, solution A was slowly added to solution B under vigorous stirring over 2 h in an ultrasonic bath. The resulting suspension was heated under reflux at 80 °C for 2 h to promote the cross-linking of Ti(OH)₄ on the surface of the BiFeO₃ nanoparticles. The products were washed and dried at 70 °C for 24 h. Finally, the as-prepared powders were calcined at 500 °C for 2 h in air to give BiFeO₃@TiO₂ nanocomposites with different mass ratios of TiO₂ to BiFeO₃. Pure TiO₂ nanoparticles were obtained by hydrolysis of the Ti(OBu)₄ solution under the same experimental conditions in the absence of BiFeO₃ powder.

2.3. Characterization techniques

X-ray diffraction (XRD) was used to analyze the crystal structure of the samples, and was conducted with Cu $K\alpha$ radiation in an X'TRA diffractometer (ARL Company, Switzerland). The surface morphology and structure of the catalysts were studied via scanning electron microscopy (SEM; QUANTA FEG 250, US). Morphologies were also observed by a transmission electron microscope (TEM; 200CX, JEOL, Japan). Ultraviolet-visible diffuse reflectance spectra (DRS) of the solid materials were collected on a UV-vis spectrophotometer (UV-2401, Shimadzu) equipped with an integrating sphere. Photoluminescence (PL) spectra of the samples were measured on a fluorescence spectrophotometer (Fluorolog 3-22, Horiba, Japan).

The photoelectrochemical characterization was carried out on an electrochemical workstation (Zahner Zennium, Germany) with a standard three-electrode system. The prepared samples were deposited on clean fluorine-doped tin oxide (FTO) glass (controlled area of 1 cm²) using a dip-coating method to serve as the working photoanode. Pt wire and Hg/Hg₂Cl₂/saturated KCl (SCE) were used as the counter and reference electrodes, respectively. An aqueous solution of Na₂SO₄ (0.05 mol/L, pH = 6.8) was used as the electrolyte. A 300-W xenon lamp (Philips) coupled with an AM 1.5 G filter was used as the simulated sunlight source ($I_0 = 100 \text{ mW/cm}^2$).

2.4. Photocatalytic activity

The photocatalytic activities of the samples were evaluated by the degradation of MV in aqueous solutions under UV light (CEL-LAX Xe lamp, 400 W, UV cut-off filter < 400 nm) and visible light (CEL-LAX Xe lamp, 400 W, visible cut-off filter 350–680 nm). The concentrations of the dye solutions were measured by a UV-vis spectrometer (Perkin-Elmer Lambda 900 UV/vis/NIR, Waltham, MA, USA). Prior to irradiation, the suspensions were magnetically stirred in the dark for 1.0 h to ensure that an adsorption/desorption equilibrium was established. Quenching tests were carried out by addition of the radical scavengers TBA, AO, and BQ under identical conditions. All measurements were performed at room temperature.

3. Results and discussion

3.1. Morphology and structure

3.1.1. XRD analysis

Fig. 1 shows the XRD patterns of the as-synthesized BiFeO₃, TiO₂, and BiFeO₃@TiO₂ nanocomposites with different mass ratios of TiO₂ to BiFeO₃. The obtained TiO₂ sample consisted of both anatase ((101), (004), and (200) planes) and rutile phases ((110), (211), and (220) planes). All the diffraction peaks from BiFeO₃ (Fig. 1(e)) displayed high diffraction intensity and could be ascribed to perovskite-phase BiFeO₃ [39]. Furthermore, the average crystallite size of BiFeO₃ was calculated to be 39 nm from the Scherrer formula [40], assuming that the small crystallite size is the only reason for the line broadening of XRD peaks. As for the BiFeO₃@TiO₂ nanocomposites with different

Fig. 1. XRD patterns of the as-prepared samples.

mass ratios of TiO₂ to BiFeO₃, they exhibited more intense peaks from BiFeO₃ than from TiO₂ nanoparticles. No impurity peaks were observed, which confirms that no impurity phase formed at the interface between the TiO₂ shell and BiFeO₃ core. With increasing TiO₂ content, the relative intensity of the peaks originating from TiO₂ increased obviously, especially that for the rutile (110) crystal plane.

3.1.2. TEM analysis

TEM analysis was carried out to further investigate the interaction between TiO₂ and BiFeO₃ in the BiFeO₃@TiO₂ samples. TEM images of BiFeO₃@TiO₂ with a mass ratio of 1:1 are shown in Fig. 2(a) and (b). The contrast between the dark core and gray shell is clearly observed, indicating that the sample

Fig. 2. TEM (a, b) and HRTEM (c) images of the BiFeO₃/TiO₂ nanocomposite with a mass ratio of 1:1. The inset in (c) is a SAED pattern. Red lines represent BiFeO₃ while white lines represent TiO₂.

Fig. 3. SEM images of pure BiFeO₃ (a) and BiFeO₃@TiO₂ (b) with a mass ratio of 1:1.

possesses a BiFeO₃ core/TiO₂ shell structure; that is, the BiFeO₃ particles have been encapsulated uniformly by TiO₂ crystallites. The thickness of the TiO₂ shell edge on the core BiFeO₃ particles is in the range of 50–100 nm. The high-resolution TEM (HRTEM) image in Fig. 2(c) indicates that the lattice spacings of the crystalline planes were 0.230, 0.250, and 0.320 nm, corresponding to the (006) plane of perovskite BiFeO₃ and (101) and (110) planes of rutile TiO₂, respectively, which is in good agreement with a previous report [41]. The HRTEM image in Fig. 2(c) also reveals that the BiFeO₃ core is surrounded by TiO₂ structures with a distinct junction interface. The selective-area electron diffraction (SAED) pattern in the inset of Fig. 2(c) indicates that the typical crystal planes of TiO₂ correspond with the XRD results in Fig. 1(a).

3.1.3. SEM analysis

The surface morphology and structure of the as-prepared BiFeO₃ and BiFeO₃@TiO₂ with a mass ratio of 1:1 were studied by SEM. Fig. 3(a) reveals that the pure BiFeO₃ nanoparticles possess irregular shapes, uneven surfaces, and are agglomerated to some extent. In contrast, for BiFeO₃@TiO₂ (mass ratio = 1:1), the BiFeO₃ particles are coated with films of uniform spherical TiO₂ particles and have a relatively smooth surface (Fig. 3(b)).

3.2. Optical properties

3.2.1. UV-vis analysis

UV-vis DRS of TiO₂, BiFeO₃, and BiFeO₃@TiO₂ with a mass ratio of 1:1 are shown in Fig. 4. The spectrum of pure TiO₂ reveals its broad band gap with a narrow absorption edge below

Fig. 4. UV-vis diffuse reflectance spectra of TiO₂, BiFeO₃, and BiFeO₃@TiO₂ with a mass ratio of 1:1.

385 nm. Meanwhile, BiFeO₃ is responsive to visible light because it has a narrow band gap. BiFeO₃@TiO₂ shows a red shift and increased optical absorption compared with the features of TiO₂. The spectral response of BiFeO₃@TiO₂ in the visible region is mainly attributed to the photosensitization of TiO₂ by BiFeO₃. When the two semiconductors are in contact, an electronic interaction occurs at their contact point. The internal spontaneous polarization within the ferroelectric domains of BiFeO₃ leads to band bending, which drives photoinduced electrons and holes in opposite directions and effectively inhibits their later recombination, resulting in enhanced photocatalytic efficiency [35]. In the UV region, pure TiO₂ shows the highest light absorption capacity of the sample, while in the visible region, BiFeO₃@TiO₂ (mass ratio = 1:1) displays the strongest photoabsorption, which should lead to higher production of electron–hole pairs. The estimated E_g values of TiO₂, BiFeO₃, and BiFeO₃@TiO₂ (mass ratio = 1:1) were around 2.96, 1.68, and 1.77 eV, respectively. These values were obtained by extrapolating the linear portion of their UV-vis spectra to zero in Fig. 5(a–c). The TiO₂ sample was a mixture of the rutile phase with some anatase; its band gap was consistent with that reported elsewhere [42].

3.2.2. PL spectra

Fig. 6 shows the PL spectra of TiO₂, BiFeO₃ nanoparticles, and BiFeO₃@TiO₂ with a mass ratio of 1:1 measured at an exci-

Fig. 5. Plots of $(ah\nu)^{1/2}$ against the band gap energy ($h\nu$) of BiFeO₃ (a), TiO₂ (b), and BiFeO₃@TiO₂ (c) with a mass ratio of 1:1.

Fig. 6. PL spectra of TiO_2 , BiFeO_3 , and $\text{BiFeO}_3@\text{TiO}_2$ with a mass ratio of 1:1.

tation wavelength of 350 nm. Two main emission peaks were found at about 519 and 564 nm for pure TiO_2 , which were attributed to oxygen vacancies (OVs) [43]. The pure BiFeO_3 sample displayed a main PL peak centered at about 566 nm, which could also be attributed to OV [44,45]. Once BiFeO_3 is coupled with TiO_2 , the PL intensity decreased markedly, which could be caused by the efficient transfer of photoexcited holes and electrons between BiFeO_3 and TiO_2 , leading to a low recombination probability of electron–hole pairs.

3.3. Photocatalytic degradation of MV

3.3.1. Comparison of photocatalytic activities

The photocatalytic activity of the as-synthesized samples was studied using MV as a substrate under UV and visible irradiation separately. All the reactions were conducted using an initial MV concentration of 15 mg/L, catalyst dosage of 1 g/L, pH of 5, and solution volume of 300 mL. Fig. 7(a) presents the photocatalytic degradation of MV using $\text{BiFeO}_3@\text{TiO}_2$ nanocomposites with mass ratios of 1:2, 2:1, and 1:1; pure TiO_2 , and pure BiFeO_3 as catalysts under UV irradiation. Without any catalyst, only 30% of MV was removed. The pure TiO_2 nanopar-

Table 1

Photodegradation rate constants of photocatalysts under UV and visible light.

Light irradiation	Photocatalyst	K_{app} (min^{-1})	R^2
UV	TiO_2	0.0153	0.954
	$\text{BiFeO}_3@\text{TiO}_2(1:1)$	0.0145	0.980
	$\text{BiFeO}_3@\text{TiO}_2(2:1)$	0.0108	0.989
	$\text{BiFeO}_3@\text{TiO}_2(1:2)$	0.0094	0.991
	BiFeO_3	0.0083	0.992
Visible	$\text{BiFeO}_3@\text{TiO}_2(1:1)$	0.0184	0.984
	$\text{BiFeO}_3@\text{TiO}_2(2:1)$	0.0157	0.982
	$\text{BiFeO}_3@\text{TiO}_2(1:2)$	0.0155	0.977
	BiFeO_3	0.0142	0.979
	TiO_2	0.0025	0.988

ticles degraded MV with high performance, removing 89% of MV after 180 min of reaction, showing that TiO_2 is a highly efficient UV-absorbing material with high photocatalytic activity. In addition, TiO_2 displayed the highest degradation rate under UV light among all the photocatalysts, especially during the first 90 min. As for $\text{BiFeO}_3@\text{TiO}_2$ with a mass ratio of 1:1, its initial degradation rate of MV was slower than that of pure TiO_2 , but it removed 93% of MV in total, so it exhibited extremely high photocatalytic activity under UV irradiation, which is in accordance with its UV-vis absorption spectra.

The apparent first-order rate constants (k_{app}) of the photocatalysts were obtained according to pseudo-first-order kinetics [46] to compare their photocatalytic activities. The calculation results based on Fig. 7(a) and (b) are presented in Table 1. These results reveal that the light absorption capacity of the photocatalyst is a major factor determining its final photocatalytic performance. The k_{app} values of the photocatalysts under visible-light irradiation (Table 1) suggest that the activity of TiO_2 was severely hindered by its wide band gap, while BiFeO_3 exhibited much better performance because of its narrower band gap, which strengthened its sensitivity to visible light [47].

Fig. 7(b) shows that all the composite catalysts displayed higher activity than that of pure TiO_2 or BiFeO_3 under visi-

Fig. 7. Photocatalytic activities of different samples for MV degradation under UV-light (a) and visible-light (b) irradiation. $C_0 = 15$ mg/L, catalyst = 1 g/L, pH = 5.

ble-light irradiation. In addition, their photocatalytic activity for MV degradation showed the following order: 1:1 > 2:1 > 1:2. BiFeO₃@TiO₂ with a mass ratio of 1:1 removed nearly 95% of MV after 150 min. The reason with BiFeO₃@TiO₂ with a mass ratio of 1:1 outperforms the composite catalysts with other ratios will be explained later. As a typical perovskite material, BiFeO₃ exhibits both ferroelectric and spontaneous polarization properties that allow the efficient separation of charge carriers. The internal fields in BiFeO₃ effectively inhibit the recombination of charge carriers, leading to enhanced photocatalytic efficiency. More specifically, the number of separated carriers will increase as the space-charge width widens, which will raise the dielectric constant of BiFeO₃ [48]. The BiFeO₃ sample synthesized in this work is different from that in previous reports. Firstly, E_g of the BiFeO₃ in this study (1.68 eV) was narrower than the reported values of 2.1–2.5 eV [47,49]. This tuned decrease in E_g could be caused by the distortion induced in the Fe-O octahedral rearrangement of molecular orbitals [50]. In addition, the particle size of the BiFeO₃ catalyst in this work was small, with an average crystallite size of 39 nm [49]. These two features result in a larger surface area for visible-light absorption as well as a greater number of electrons excited from the valence band (VB), both of which are favorable for generation of reactive species for photodegradation [51].

The core-shell-structured BiFeO₃@TiO₂ shows much higher photocatalytic activity under visible light than those of its components, which is mainly caused by the suppression of charge recombination, its strong photoabsorption ability, and unique core-shell structure. The low electron-hole recombination rate of BiFeO₃@TiO₂ is ascribed to the presence of electronic-accumulation centers formed by the electronic interaction between the two semiconductors. These centers effectively separate the electrons and holes, leading to high quantum efficiency. In addition, the obvious red shift of the photoabsorption spectrum of BiFeO₃@TiO₂ compared with those of its components is mainly induced by Fe or Bi/Ti interdiffusion at the BiFeO₃/TiO₂ interface. Theoretically, an internal electric field from TiO₂ to BiFeO₃ will be generated when p-type BiFeO₃ and n-type TiO₂ come in contact and form a p-n heterojunction interface [52,53]. Driven by this internal electric field, the holes and electrons will flow in opposite directions, thus leading to the efficient separation of photogenerated electrons and holes and enhanced photocatalytic activity.

To further explore the nature of the p-n heterojunction in

BiFeO₃@TiO₂, Mott-Schottky (MS) measurements were performed to study the flat-band potentials V_{fb} of the semiconductors [54]. The resulting plots are shown in Fig. 8. According to Eq. (1) [55], V_{fb} at the electrode-electrolyte interface was estimated from these plots.

$$1/C^2 = (2/\epsilon_r\epsilon_0 e N_d A^2) [(V - V_{fb}) - kT/e] \quad (1)$$

When plotting $1/C^2$ (C is the specific capacity) against V (V is the applied potential), V_{fb} can be easily found by extrapolating the linear portion of the plots to zero. Fig. 8(a) and (b) reveals that the as-synthesized TiO₂ is a typical n-type semiconductor with a MS plot with a positive slope. Meanwhile, for pure BiFeO₃ is a p-type semiconductor, as indicated by the negative slope of its MS plot. V_{fb} of n-type TiO₂ and p-type BiFeO₃ calculated from the corresponding x-axis intercepts were 0.25 and 1.51 V vs. RHE, respectively [54]. More interestingly, once they were coupled to form a heterojunction in BiFeO₃@TiO₂, an inverted V shape appeared in the MS plot (Fig. 8(c)), suggesting a p-n heterojunction formed between the components with different electronic behavior [54]. Based on Eq. (1), the density of charge carriers was calculated from the slopes of the MS plots. The estimated donor densities of n-type TiO₂, p-type BiFeO₃, and BiFeO₃@TiO₂ in the dark were 9.43×10^{18} , 1.969×10^{18} and 3.773×10^{18} , respectively. The higher donor density of BiFeO₃@TiO₂ than that of BiFeO₃ indicates that charge carrier transport in the BiFeO₃ nanoparticles was efficiently enhanced after coating with TiO₂, confirming the formation of a p-n heterojunction interface that acted as a sufficient space-charge layer in BiFeO₃@TiO₂.

To further explore the mechanism of MV degradation by the photocatalysts, quenching tests were conducted to verify the roles of different reactive species. As a typical O₂^{•-} scavenger, BQ was added to the reaction system. The results in Fig. 9 show that the reaction rate did not decrease upon addition of BQ compared with that without any scavenger, considering the amount adsorbed in the dark in the first 60 min. This indicates that no •O₂^{•-} radicals were produced in the reaction solution. Next, TBA and AO were added to trap •OH and holes, respectively. The degradation rate of MV decreased a little upon addition of 0.01 mol/L TBA as a scavenger of •OH, which indicates that the photocatalytic activity of BiFeO₃@TiO₂ heterojunction is suppressed by addition of TBA. However, addition of AO promoted the degradation of MV, with the degradation rate constant increasing from 0.0195 to 0.0254 min⁻¹, which suggests that dye degradation was not achieved via holes. Accord-

Fig. 8. Mott-Schottky curves for TiO₂ (a), BiFeO₃ (b), and BiFeO₃@TiO₂ with a mass ratio of 1:1 (c).

Fig. 9. Photocatalysis quenching tests with addition of TBA, BQ and AO. Conditions: $C_0 = 15$ mg/L, catalyst = 1 g/L, pH = 5, visible-light irradiation.

ing to studies with similar findings [56–58], MV degradation was mainly driven by electrons and $\cdot\text{OH}$. The trapping of holes by AO effectively inhibited the recombination of electrons and holes. Thus, photogenerated electrons play the most important role in the photodegradation process of MV by $\text{BiFeO}_3/\text{TiO}_2$.

Based on the above photophysical and electrochemical characterization results, the energy-band structure and photocatalytic mechanism of $\text{BiFeO}_3/\text{TiO}_2$ are illustrated in Fig. 10. Assuming the gap between flat-band potential and bottom edge of the conduction band (CB) (or top edge of VB for p-type semiconductors) is negligible for n-type semiconductors [59,60], the CB position of TiO_2 and VB position of BiFeO_3 could be estimated, as indicated in Fig. 10. Given the obtained E_g values, it was easy to calculate the VB position of TiO_2 and CB position of BiFeO_3 . BiFeO_3 has a relatively high CB because of Ti doping [23,36]; therefore, electrons can be excited from the partially filled d orbitals of Fe^{3+} to the Ti 3d orbitals of TiO_2 under visible-light irradiation. According to the energy-band structure, electrons from the CB of BiFeO_3 will be transferred to the lower lying CB of TiO_2 to form an electron center, while the holes from the VB of TiO_2 will be transferred to the VB of BiFeO_3 to form a hole center. After coupling of these two semiconductors,

Fig. 10. Schematic diagram of the energy band structure and proposed mechanism of the photocatalysts before contact (a) and after formation (b) of a $\text{TiO}_2/\text{BiFeO}_3$ p-n heterojunction.

an internal electrical field (E_{internal}) will be formed with its direction from TiO_2 to BiFeO_3 , leading to efficient charge separation. As illustrated in Fig. 10, the Fermi level of n- TiO_2 is close to its CB, whereas for p- BiFeO_3 , the Fermi level is close to its VB. After the formation of a p-n heterojunction at the interface between these two semiconductors, their respective VBs and CBs will be realigned through the thermal equilibration of their different Fermi levels [54].

The separated electrons and holes can participate in photocatalytic reactions to directly or indirectly decompose organic compounds such as MV. This process involves holes partially oxidizing H_2O to $\cdot\text{OH}$. Compared with the standard reduction potential of $\cdot\text{OH}/\text{H}_2\text{O}$ (2.27 eV) or $\cdot\text{OH}/\text{OH}^-$ (2.38 eV) [53], the VB potential of BiFeO_3 is only 1.51 eV vs. RHE (1.11 eV vs. NHE), indicating that most of the holes on the surface of BiFeO_3 cannot oxidize H_2O or OH^- into $\cdot\text{OH}$. Fortunately, the VB potential of TiO_2 is 3.21 eV vs. RHE (2.81 eV vs. NHE), which is positive enough to oxidize H_2O or OH^- into $\cdot\text{OH}$. Furthermore, the reduction potential of $\text{O}_2/\text{O}_2^{\cdot-}$ is -0.33 eV [53], so the CB edge potential of TiO_2 (0.25 eV vs. RHE or -0.15 eV vs. NHE) is not negative enough to reduce O_2 to $\cdot\text{O}_2^{\cdot-}$. Most of the electrons will induce dye degradation because of the slow electron-hole recombination, which is further confirmed by the results of quenching tests.

Overall, the enhanced photocatalytic activity of the $\text{BiFeO}_3/\text{TiO}_2$ nanocomposite compared with that of its components can be mainly ascribed to the efficient charge separation and transfer at the junction interfaces formed between the two semiconductors assisted by the internal electric field with the matching band potentials of the two components. As a consequence, the recombination of photogenerated electrons and holes is effectively inhibited, which is also consistent with the PL spectra of the materials. Another factor influencing the performance of $\text{BiFeO}_3/\text{TiO}_2$ may originate from BiFeO_3 as a ferroelectric semiconductor. BiFeO_3 has internal dipolar fields that will facilitate the migration of electrons and holes and may slow their recombination. Electrons generated in BiFeO_3 can be transported to the surface of TiO_2 , which is favored in the ferroelectric domains with their positive polarization pointed toward the surfaces, helping to enhance the photocatalytic oxidation efficiency [35]. Furthermore, the UV-vis DRS showed that $\text{BiFeO}_3/\text{TiO}_2$ strongly absorbed light, with its absorption edge reaching further out into the visible region than that of either BiFeO_3 or TiO_2 . This leads to production of more electron-hole pairs, which is another factor that enhances the photocatalytic activity of $\text{BiFeO}_3/\text{TiO}_2$. In addition, the contact area between TiO_2 and BiFeO_3 is increased by the unique core-shell structure of $\text{BiFeO}_3/\text{TiO}_2$, which also promotes charge transfer at the $\text{BiFeO}_3/\text{TiO}_2$ interface. It can be inferred that TiO_2 shells of different thickness can be achieved by changing the loading amount of TiO_2 in the synthesis process. It is known that only when a suitable amount of TiO_2 is deposited on BiFeO_3 will both BiFeO_3 and TiO_2 efficiently form a p-n heterojunction interface to speed up the photocatalytic process. That is, too much or too little TiO_2 is not favorable to form a $\text{BiFeO}_3/\text{TiO}_2$ core-shell structure with highly efficient charge transfer. These theoretical analyses also coincide with the ob-

served photocatalytic activity of the samples, which revealed that BiFeO₃@TiO₂ with a mass ratio of 1:1 showed the highest photocatalytic performance of the samples. As the content of TiO₂ increases, the excess TiO₂ in the sample may shield the BiFeO₃ core from visible light, resulting in a decrease of photocatalytic activity. However, the exact mechanism of BiFeO₃@TiO₂ is not yet very clear, so further experimental and theoretical work is desirable to fully understand the interfacial electronic structures as well as the detailed effects of the TiO₂ shell thickness on the formation of a heterojunction interface in BiFeO₃@TiO₂.

3.3.2 Influences of reaction conditions on MV degradation

The effect of the catalyst dosage (0.5–1.5 g/L) of BiFeO₃@TiO₂ with a mass ratio of 1:1 on MV decomposition was studied (Fig. 11(a)). The highest degradation efficiency was observed when the catalyst dosage was 1 g/L. Increasing the amount of catalyst particles dispersed in the solution may weaken the penetration of the incident light, thus leading to the decrease of dye decomposition at high catalyst loading (1.5 g/L). Only an appropriate amount of catalyst could facilitate the generation of active species to speed up the rate of dye degradation while retaining high transparency. Based on these results, 1.0 g/L of BiFeO₃@TiO₂ with a mass ratio of 1:1 was chosen as the optimal catalyst dosage under the investigated reaction conditions.

Degradation of MV with initial concentrations from 10 to 20 mg/L is depicted in Fig. 11(b). With increasing initial dye concentration, the degradation rate gradually decreases. The catalyst was efficient at degrading MV when the MV concentration was less than 20 mg/L, with the degradation rate exceeding 80% in this case. Considering the practical application of the catalyst and decolorization efficiency, 15 mg/L was chosen as the initial MV concentration in this study.

The effect of MV solution pH on the photocatalytic reaction is depicted in Fig. 11(c). As the pH was increased from 5 to 7, the degradation rate of MV lowered, which was ascribed to the structure of MV as well as the surface charge of the catalyst. A competitive relationship exists between phenoxide ions and •OH on the surface of TiO₂ particles [61]. Meanwhile, the adsorption of the substrate on the TiO₂ surface will directly affect the interaction between MV molecules and •OH, which may influence the photocatalytic degradation rate. In addition, the

Fig. 12. Degradation of MO and CR with BiFeO₃@TiO₂(1:1). Reaction conditions: $C_0 = 15$ mg/L, catalyst = 1 g/L, pH = 5, visible-light irradiation.

isoelectric points of TiO₂ particles and BiFeO₃ ceramics in water are around 6.8 [62] and 5.1 [63], respectively. Under acidic conditions, the catalyst is easily protonated, which should accelerate the transfer of photogenerated electrons to the catalyst surface. When the pH exceeds the isoelectric point of the catalyst, its surface will become negatively charged, so the number of adsorption sites may decrease accordingly.

3.4 Photocatalytic degradation of other dyes with BiFeO₃@TiO₂

To further demonstrate the superior photocatalytic activity and investigate possible practical applications of BiFeO₃@TiO₂, several experiments were run using other dye pollutants, MO and CR, under the same reaction conditions. Fig. 12 reveals that under visible-light irradiation only, both MO and CR underwent minor changes. Upon exposure to BiFeO₃@TiO₂ with a mass ratio of 1:1 and visible-light irradiation for 150 min, the degradation rates of MO and CR reached 56% and 76%, respectively. As shown in the inset of Fig. 12, after each reaction cycle, the as-synthesized BiFeO₃@TiO₂ nanoparticles were strongly attracted towards a black magnet, allowing simple magnetic recycling in a similar manner to pure BiFeO₃. These results reveal

Fig. 11. Effects of (a) catalyst dosage ($C_0 = 15$ mg/L, pH = 5), (b) initial concentration of MV (catalyst = 1 g/L, pH = 5), and (c) initial solution pH ($C_0 = 15$ mg/L, catalyst = 1 g/L) on MV degradation with BiFeO₃@TiO₂(1:1) under visible-light irradiation.

that the core-shell-structured $\text{BiFeO}_3/\text{TiO}_2$ catalyst could be widely used for dye degradation under visible light. Based on the analysis of the molecular structures of the three dyes (Table 2), it was deduced that the degradation efficiency of the dyes was closely related to the presence of azo functional groups. MV contains no azo groups in its structure, while MO and CR contain one and two azo groups, respectively. The cleavage of the $\text{N}=\text{N}$ bond of azo compounds leads to their decoloration, which is the first step of their oxidative process [64]. Besides the characteristics of the dye structure, the degradation efficiency of dyes also depends on other parameters such as pH and catalyst concentration [65].

4. Conclusions

A citrate self-combustion approach combined with hydrolysis precipitation was developed to synthesize the nanocomposite photocatalyst $\text{BiFeO}_3/\text{TiO}_2$ with a core-shell structure. The $\text{BiFeO}_3/\text{TiO}_2$ heterojunction with a mass ratio of BiFeO_3 to TiO_2 of 1:1 exhibited high photocatalytic oxidation activity towards different dyes (MV, MO, and CR) under visible-light irradiation. Such activity was attributed to the efficient inhibition of charge recombination, strong light absorption ability, and core-shell geometry of $\text{BiFeO}_3/\text{TiO}_2$. Photoelectrochemical measurements confirmed the formation of a p-n heterojunction at the interface between p- BiFeO_3 and n- TiO_2 , which enhanced both charge carrier transport and donor density, leading to

increased quantum efficiency. The mechanism of MV degradation by $\text{BiFeO}_3/\text{TiO}_2$ was attributed to hydroxyl radicals and photogenerated electrons. These nanocomposites represent a new perspective on p-n heterojunction nanomaterials for practical use in solar energy conversion.

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Table 2
Molecular structures and characteristics of dyes.

Molecular structure	Applica- tion	Safety
<p>MO</p>	pH indicator	Mutagenic properties
<p>MV</p>	Purple dye for textiles	Mutagen and mitotic poison
<p>CR</p>	pH indicator	Carcinogenicity and reproductive toxicity

Graphical Abstract

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Preparation of a p-n heterojunction BiFeO₃@TiO₂ photocatalyst with a core-shell structure for visible-light photocatalytic degradation

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BiFeO₃ particles coated with TiO₂ to form a core-shell structure with a p-n heterojunction exhibited high photocatalytic activity in degradation of various industrial dyes under visible-light irradiation because of their rapid charge carrier transport and strong light absorption ability.

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核壳结构p-n异质结复合光催化剂BiFeO₃@TiO₂的制备及其在可见光催化降解中的应用

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摘要: 化石燃料的迅速消耗导致环境污染与能源危机日益加剧. 太阳能高效利用与转换是解决该难题的有效途径之一. 在众多光催化剂中, TiO₂因其高催化活性、高稳定性、低毒性以及低成本等优势而普遍受到关注, 但TiO₂存在着带隙过宽而无法利用可见光的缺陷, 严重制约了其在光催化方向的实际应用.

核壳型复合纳米材料具有较大的比表面积、较高的光吸收能力以及所吸附的污染物分子易于从吸附面扩散到光致降解面等特点, 而表现出较强的有机污染物吸附性能以及良好的光催化活性. 以磁体材料为核将TiO₂包覆于磁体表面, 可以制备具有磁分离特性的磁载光催化剂. 而铁酸铋作为一种在室温下同时具有铁电性和铁磁性的钙钛矿型材料, 由于其较窄的带宽(2.1 eV)在可见光催化氧化方面也受到了极大的关注.

本文首先通过柠檬酸自燃烧法制备了可磁性分离的BiFeO₃粉体, 再用水解沉淀法将TiO₂包裹在BiFeO₃前驱体上形成了不同质量比(1:1, 1:2, 2:1)的核壳结构的BiFeO₃@TiO₂复合粉体, 并以甲基紫为例, 对其在紫外光和可见光照射下的光催化性能分别展开了研究. 结果表明, BiFeO₃@TiO₂复合粉体的光催化性能较单独的BiFeO₃或TiO₂均有所提升. 其中质量比为1:1的BiFeO₃@TiO₂复合粉体(TiO₂壳层厚度为50–100 nm)展现出最强的光催化氧化活性, 且在可见光下有更高的光催化效率. 经表征分析, 该复合粉体光催化性能高的原因可能归结于BiFeO₃与TiO₂两者之间形成了p-n异质结界面, 有效地提高了电荷载流子的传输分离效率, 同时BiFeO₃较窄的禁带宽度拓展了纳米TiO₂的光谱吸收范围, 增强其光吸收能力. 光电化学Mott-Schottky测试结果进一步证实: BiFeO₃粉体在与TiO₂复合之后, 其电荷载流子传输与供体密度均有显著提升. 自由基猝灭实验表明, 在甲基紫光催化降解中起主要作用的为羟基自由基与光生电子, 并结合能带理论与自建电场理论对降解机理进行了阐述. 进一步研究表明, 甲基紫降解效果最优条件为: 复合粉体的投加量为1 g/L, 甲基紫初始浓度为10 mg/L, 初始pH为5. 另外, 质量比1:1的BiFeO₃@TiO₂对甲基橙和刚果红染料废水也具有较好的降解效果, 表现出良好的工业应用前景.

关键词: 铁酸铋; 二氧化钛; 核壳结构; 降解; 光催化; 可见光

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