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Heterostructured BiOI@La(OH)₃ nanorods with enhanced visible light photocatalytic NO removal

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ABSTRACT

Heterostructured BiOI@La(OH)₃ nanorod photocatalysts were prepared by a facile chemical impregnation method. The enhanced visible light absorption and charge carrier separation can be simultaneously realized after the introduction of BiOI particles into La(OH)₃ nanorods. The BiOI@La(OH)₃ composites were applied for visible light photocatalytic oxidation of NO in air and exhibited an enhanced activity compared with BiOI and pure La(OH)₃ nanorods. The results show that the energy levels between the La(OH)₃ and BiOI phases matched well with each other, thus forming a heterojunctioned BiOI@La(OH)₃ structure. This band structure matching could promote the separation and transfer of photoinduced electron-hole pairs at the interface, resulting in enhanced photocatalytic performance under visible light irradiation. The photocatalytic performance of BiOI@La(OH)₃ is shown to be dependent on the mass ratio of BiOI to La(OH)₃. The highest photocatalytic performance can be achieved when the mass ratio of BiOI to La(OH)₃ is controlled at 1.5. A further increase of the mass ratio of BiOI weakened the redox abilities of the photogenerated charge carriers. A new photocatalytic mechanism for BiOI@La(OH)₃ heterostructures is proposed, which is directly related to the efficient separation of photogenerated charge carriers by the heterojunction. Importantly, the as-prepared BiOI@La(OH)₃ heterostructures exhibited a high photochemical stability after multiple reaction runs. Our findings demonstrate that BiOI is an effective component for the formation of a heterostructure with the properties of a wide bandgap semiconductor, which is of great importance for extending the light absorption and photocatalytic activity of wide bandgap semiconductors into visible light region.

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1. Introduction

Since the first report on water splitting with a TiO₂ photoelectrode, semiconductor photocatalysis has received attention for application in solar energy conversion and the removal of

pollutants [1–8]. Currently, the photocatalytic efficiency for most semiconductors is not sufficient for practical application, especially with the use of visible light from the sun [2–4]. The charge separation and visible light absorption are the most important factors to be considered in the development of effec-

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tive semiconductor photocatalysts. Various strategies have been applied to tackle these issues, such as doping with heteroatoms, formation of a heterostructure, microstructure optimization and development of new types of photocatalysts [2–6]. Among the plentiful semiconductor materials, one-dimensional (1D) lanthanide hydroxide ($\text{La}(\text{OH})_3$) nanorods have been receiving increased interest owing to their unique electronic structure and multifunctional properties, especially as an emergent semiconductor photocatalyst [9–11]. However, for a photocatalytic application, the intrinsic wide bandgap of $\text{La}(\text{OH})_3$ allows only a small portion of absorption in the ultraviolet (UV) light region of the solar spectra. The relatively low photocatalytic efficiency and visible light use hinder its practical application. To take full advantage of sunlight, it is imperative to extend the light absorption spectra of $\text{La}(\text{OH})_3$ into the visible light region. Fortunately, hybrid photocatalysts, generally comprising two or more active components, have been developed to address this issue. These hybrid photocatalysts could integrate the synergistic effects of the active components, which may provide the feasibility and versatility to optimize their optical and photocatalytic performance [12–14].

The coupling of two different semiconductors could enhance the transfer of electrons from an excited small band gap semiconductor into another one that is attached in the case of proper band structure matching. This favors the charge carrier separation and thus improves the photocatalytic efficiency. To obtain the desirable heterostructured photocatalysts, two key factors must be considered. One is the interface lattice matching to form a stable heterostructure. The other is the matching of energy levels between the two components so as to promote charge carrier separation. That is, the conduction band minimum (CBM) of the narrow bandgap semiconductor should be higher than the other component with a lower CB [15,16]. In particular, bismuth oxyiodide (BiOI) is an attractive p-type semiconductor with a narrow band gap ($E_g = 1.70\text{--}2.0\text{ eV}$), which means that it exhibits a strong absorption of visible light [17–20]. As a typical p-type semiconductor, BiOI can serve as an effective visible light photosensitizer for semiconductors with a large band gap [21,22]. Therefore, BiOI is a good candidate for coupling with $\text{La}(\text{OH})_3$ to form a $\text{BiOI@La}(\text{OH})_3$ heterostructure with a potentially high visible light photocatalytic activity.

We have developed novel heterostructured $\text{BiOI@La}(\text{OH})_3$ nanorods by a facile method. The introduction of BiOI particles into the $\text{La}(\text{OH})_3$ nanorods was achieved with a facile impregnation method under mild conditions. The $\text{BiOI@La}(\text{OH})_3$ heterostructures exhibited an enhanced visible light photocatalytic activity towards NO removal compared with BiOI and $\text{La}(\text{OH})_3$ alone. The enhanced activity can be ascribed to the highly enhanced visible light absorption owing to the strong interfacial interactions existing in these components, and the significantly improved charge separation and migration. Meanwhile, the effects of BiOI content on the photocatalytic activity of $\text{BiOI@La}(\text{OH})_3$ catalysts were investigated. The $\text{BiOI@La}(\text{OH})_3$ composites exhibited the highest photocatalytic activity when the mass ratio of $\text{BiOI@La}(\text{OH})_3$ was 150%. More importantly, this excellent photocatalyst showed high photochemical stabil-

ity and durability, which is significant for its practical application. The possible photocatalysis mechanism of the $\text{BiOI@La}(\text{OH})_3$ heterojunction is proposed, which could provide new insight into the modification of wide bandgap semiconductors for efficient visible light photocatalysis.

2. Experimental

2.1. Synthesis of $\text{La}(\text{OH})_3$ nanorods

All the chemicals used were of analytical grade and used without further purification. In a typical synthesis, an appropriate amount of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1.083 g) was dissolved in distilled water (30 mL) with continuous stirring. Then, a concentrated ammonia solution (28 wt%, 20 mL) was added with magnetic stirring. Distilled water was added to the above solution, to make a total volume of 70 mL, which was stirred for 30 min. Subsequently, the obtained suspension was transferred to a 100 mL Teflon-lined autoclave. The precursor solution was hydrothermally treated at 180 °C for 8 h. After the hydrothermal reaction, the product was centrifuged and washed with distilled water and ethanol four times and dried at 60 °C to obtain the $\text{La}(\text{OH})_3$ nanorods.

2.2. Construction of $\text{BiOI/La}(\text{OH})_3$ heterostructures

In a typical process, $\text{La}(\text{OH})_3$ (0.54 g) was added into distilled water (50 mL) containing a stoichiometric amount of KI, and then dispersed for 30 min with ultrasound treatment (marked as suspension A). Subsequently, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved into distilled water (50 mL) with acetic acid (5 mL; marked as solution B). Then, solution B was added dropwise into suspension A with magnetic stirring for 30 min. The resulting precipitates were collected and washed with water and ethanol four times, and dried at 60 °C to obtain the final products. The mass ratio of BiOI to $\text{La}(\text{OH})_3$ was controlled at 25%, 50%, 100%, 150% and 200%, respectively. Accordingly, the products were labeled as Bi/La-25%, Bi/La-50%, Bi/La-100%, Bi/La-150% and Bi/La-200%, respectively.

2.3. Characterization

The crystal phases of the sample were analyzed by X-ray diffraction (XRD) with $\text{Cu-K}\alpha$ radiation (model D/max RA, Rigaku Co., Japan). To characterize the morphology and structure of the obtained products, transmission electron microscopy (TEM, JEM-2010, Japan) was used to collect the TEM images. Scanning electron microscopy (SEM, JEOL model JSM-6490, Japan) with X-ray energy dispersive (EDX) mapping equipment was used to characterize the morphology and composition of the samples. The Brunauer-Emmett-Teller (BET) specific surface area and pore structure of the samples were analyzed by nitrogen adsorption-desorption using nitrogen adsorption apparatus (ASAP 2020, USA) with all samples degassed at 90 °C for 12 h prior to the measurements. X-ray photoelectron spectroscopy with $\text{Al-K}\alpha$ X-ray ($h\nu = 1486.6\text{ eV}$) radiation operated at 150 W (XPS, Thermo ESCALAB 250, USA) was used to inves-

tigate the surface properties. The UV-vis diffuse reflection spectra were obtained for the dry-pressed disk samples using a scanning UV-vis spectrophotometer (UV-vis DRS, UV-2450, China) equipped with an integrating sphere assembly, using 100% BaSO₄ as a reflectance sample. The electron spin resonance (ESR) signals of hydroxyl radicals spin-trapped by the spin-trap reagent, 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) in water, were examined on a Bruker model ESR JES-FA200 spectrometer equipped with a Quanta-Ray Nd:YAG laser system as the irradiation source.

2.4. Evaluation of the visible light photocatalytic activity

The photocatalytic activity of the samples was investigated by the removal of NO at ppb levels in a continuous flow reactor. The volume of the rectangular reactor, made of stainless steel and covered with Saint-Glass, was 4.5 L (30 cm × 15 cm × 10 cm). A commercial tungsten halogen lamp (150 W) was vertically placed 20 cm above the reactor. A UV cut-off filter (420 nm) was applied to remove UV light for the test of the photocatalytic activity in the visible light region (420–700 nm), and the average light intensity was 0.16 W/cm². For each photocatalytic activity test, two sample dishes (with a diameter of 12.0 cm) containing the photocatalyst powder (0.1 g) were placed in the center of the reactor. The photocatalyst samples were prepared by coating an aqueous suspension of the samples onto the glass dishes. The coated dish was treated at 70 °C to evaporate the water and then cooled to room temperature before the photocatalytic activity test. The NO gas was acquired from a compressed gas cylinder at a concentration of 100 ppm of NO (N₂ balance). The initial concentration of NO was diluted to 520 ppb by an air stream of purified air. The flow rate of the air stream and NO were controlled at 2.4 L/min and 15 mL/min, respectively. Then, the two gas streams were premixed by a three-way valve. After the adsorption-desorption equilibrium was achieved, the lamp was turned on. The concentration of NO was continuously measured by a chemiluminescence NO_x analyzer (Thermo Scientific, 42i-TL), which monitors NO, NO₂, and NO_x (NO_x represents NO + NO₂) with a sampling rate of 1.0 L/min. The removal ratio (η) of NO was calculated as η (%) = $(1 - C/C_0) \times 100\%$, where C and C_0 are the concentrations of NO in the outlet stream and the feeding stream, respectively.

3. Results and discussion

3.1. Phase structure

The phase and crystal structures of the as-prepared samples were examined by XRD as shown in Fig. 1. The XRD peaks of the La(OH)₃ sample agree well with the standard card of La(OH)₃ (JCPDS-ICDD Card No. 36-1481) and no other impurities are detected, indicating a pure phase. The strongest peak at $2\theta = 27.9^\circ$ is representative for (101) facet reflections. The as-prepared BiOI, with dominant (012) and (110) peaks, can be indexed to tetragonal BiOI (JCPDS-ICDD Card No. 73-2062). Other diffraction peaks are missing owing to the low crystallin-

Fig. 1. XRD patterns of the as-prepared La(OH)₃, BiOI and BiOI@La(OH)₃ heterostructures.

ity of the as-prepared BiOI prepared at low temperature. Based on further observation, the peak intensity of BiOI@La(OH)₃ composites is decreased with an increasing BiOI content, indicating the interaction and intimate contact between BiOI and La(OH)₃ [23,24]. The diffraction peaks of BiOI cannot be obviously observed even for the Bi/La-200% sample, which can be ascribed to the observation that the dominant diffraction peaks of BiOI and La(OH)₃ are overlapped. The formation of BiOI in the composites was determined with SEM and TEM.

3.2. Morphological structure

Fig. 2(a) and (b) show the SEM images of the pristine La(OH)₃, which consists of dispersed 1D nanorods. The average diameter of the La(OH)₃ nanorods was 30–50 nm. The SEM images of the BiOI@La(OH)₃ heterostructures (Bi/La-150%) are depicted in Fig. 2(c) and (d). The morphology of this sample was largely maintained, indicating that the BiOI coupling does not change the structure of the La(OH)₃ nanorods. Further observation implied that some particles were attached on the surface of the La(OH)₃ nanorods. The elemental mapping results (Fig. 2(a) and (b)) reveal that La, Bi, I and O are uniformly distributed, which also indicates that BiOI particles were evenly coupled with the La(OH)₃ nanorods.

The microstructure of La(OH)₃ and Bi/La-150% composites was further investigated by TEM and HRTEM. Fig. 3(a) shows the typical TEM image of La(OH)₃ with a 1D nanorod-like structure. The diameter of the nanorods was 30–50 nm and the length was 40–150 nm. Fig. 3(b) shows the typical HRTEM image of a single La(OH)₃ nanorod. The observed spacing distance between the lattice planes was measured to be 0.565 nm, corresponding to the (100) crystallographic planes of La(OH)₃. According to our previous report, the La(OH)₃ nanorod is polycrystalline [10]. Fig. 3(c) and (e) show the TEM images of the Bi/La-150% composite, in which some nanoparticles were deposited on the surface of the La(OH)₃ nanorod substrate, indicating that the composites have two distinctive morphologies of nanoparticles and nanorods. The HRTEM image of the selected area is given in Fig. 3(d). As can be seen, two sets of

Fig. 2. SEM images of La(OH)₃ (a, b) and Bi/La-150% (c, d), and elemental mapping (e, f, g, h) of Bi/La-150%.

Fig. 3. TEM and HRTEM images of La(OH)₃ (a, b) and the Bi/La-150% heterostructure (c, d, e, f).

different fringes could be observed. The observed distinct lattice fringe of $d = 0.318 \text{ nm}$ on the nanorod matches well with the crystallographic plane (101) of La(OH)₃. From the HRTEM image in Fig. 3, the pure La(OH)₃ nanorod and La(OH)₃ nanorod in Bi/La-150% have different exposed crystallographic planes, which indicates that the deposition of BiOI could affect the exposed facets of the La(OH)₃ nanorod. Note that there were some square nanoparticles observed on the surface of the La(OH)₃ nanorod. The lattice fringe of 0.301 nm corresponds to the (012) crystal plane of BiOI. The results further confirm the existence of BiOI particles on the surface of the La(OH)₃ nanorods. The HRTEM images in Fig. 3(d) and (f) demonstrate the relatively intimate interfacial contact between the BiOI parti-

cles and La(OH)₃ nanorods, which is beneficial for charge separation and transfer.

3.3. BET surface area and pore structure

The N₂ adsorption-desorption measurement was used to study the BET surface areas (A_{BET}) and the corresponding pore size distribution curves of pure La(OH)₃ and BiOI@La(OH)₃ heterostructures. Fig. 4(a) shows that all the samples exhibit typical type-IV adsorption-desorption isotherms with H₃ hysteresis, which is indicative of a mesoporous structure [25,26]. The H₃ hysteresis loops show high adsorption at the high relative pressure (P/P_0) position (approaching 1.0), implying the

Fig. 4. N_2 adsorption-desorption isotherms (a) and pore size distribution curves (b) of $La(OH)_3$ and $BiOI@La(OH)_3$ heterostructures.

formation of large mesopores and macropores. The corresponding pore size distribution (PSD) curves of the samples are shown in Fig. 4(b), the composite samples contain macropores and large mesopores over a broad range with the peak pore sizes centered at around 20–30 and 90–110 nm. These results demonstrate the formation of hierarchical meso/macro porous structures in these samples. The specific surface areas and pore parameters of $La(OH)_3$ and $BiOI@La(OH)_3$ composites are summarized in Table 1. It is observed that $La(OH)_3$ has a surface area of $55.0 \text{ m}^2/\text{g}$, and the specific surface area increased with an increase of the BiOI ratio in the $BiOI@La(OH)_3$ heterostructures. The surface areas of Bi/La-150% and Bi/La-200% are much higher than that of $La(OH)_3$.

3.4. Chemical composition by XPS

The XPS measurements provide further information for the chemical composition and surface chemical states of the $BiOI@La(OH)_3$ heterostructures. The binding energies in the XPS spectra presented are calibrated by using that of C 1s (284.8 eV). As displayed in Fig. 5(a), the Bi 4f spectra for BiOI consist of two peaks with binding energies around 159.8 and 165.2 eV , which correspond to the signals from the doublets of Bi $4f_{7/2}$ and Bi $4f_{5/2}$ in the trivalent oxidation state [27–28]. These two peaks of Bi 4f in Bi/La-150% have a shift of 0.6 eV to the low energy region compared with those for pure BiOI. The XPS spectra of I 3d is shown in Fig. 5(b). The binding energies at 619.1 eV (I $3d_{5/2}$) and 630.6 eV (I $3d_{3/2}$) could be ascribed to the I⁺ ions in BiOI [21,24,29]. These binding energies of

Bi/La-150% exhibit a negative shift of 0.4 eV . Fig. 5(c) shows the typical La $3d_{3/2}$ XPS spectra. A double-peak structure with a peak energy of 838.0 eV and satellite energy of 855.4 eV could be observed. The high binding energy of the satellite can be ascribed to the shake-up process associated with the O $2p$ –La $4f$ charge transfer [30]. The O 1s peaks for the $BiOI@La(OH)_3$ heterostructure in Fig. 5(d) can be fitted to two peaks. The peak at 529.6 eV corresponds to the Bi–O bonds, and the peak at 531.04 eV can be attributed to the La–O bond. Compared with pure BiOI, the O 1s peak exhibits a 0.3 eV shift to a lower binding energy [22,31]. The peaks of Bi 4f, I 3d and O 2p undergo chemical shifts in the heterostructure, which can be attributed to the Bi, I and O bonding with La in $La(OH)_3$. These results suggest an interaction between $La(OH)_3$ and BiOI, confirming the existence of chemical bonds between $La(OH)_3$ and BiOI in the heterostructures, which is consistent with the XRD result.

3.5. Optical absorption property

The pure $La(OH)_3$ and $BiOI@La(OH)_3$ heterostructures with an increasing mass ratio of BiOI show a gradient color deepening from white to yellow. From Fig. 6(a), it can be found that the pure $La(OH)_3$ nanorods display an absorption edge in the UV region, and no absorption in the visible light region. Note that the peak at approximately 270 nm can be ascribed to the oxygen defects in $La(OH)_3$ nanorods [10]. Pure BiOI has a strong absorption in the visible light range with an absorption edge around 560 nm . All the $BiOI@La(OH)_3$ heterostructures exhibit a clear optical response in the visible region owing to the coupling with BiOI. An increase of the BiOI content exerts an obvious influence on the visible light absorption of $BiOI@La(OH)_3$ heterostructures. This interesting observation can arise from the special properties of BiOI with a small band gap, large absorption coefficient and strong absorption in the visible light range. It can be concluded that the introduction of BiOI into $La(OH)_3$ nanorods benefits the optical absorption property and efficiency for visible light. The absorption enhancement in the visible light region is beneficial for an enhancement of the photocatalytic activity.

Table 1

A_{BET} , pore parameters and NO removal ratio of the samples.

Sample	A_{BET} (m^2/g)	Pore volume (cm^3/g)	Peak pore size (nm)	η (NO) (%)
$La(OH)_3$	55.0	0.41	30.07	3.9
Bi/La-25%	55.1	0.41	30.07	21.1
Bi/La-50%	60.4	0.44	29.34	28.9
Bi/La-100%	64.8	0.43	26.31	35.9
Bi/La-150%	74.9	0.44	23.41	50.5
Bi/La-200%	75.2	0.44	23.41	48.6

Fig. 5. XPS spectra of BiOI and the Bi/La-150% heterostructure. (a) Bi 4f; (b) I 3d; (c) La 3d; (d) O 1s.

The band gap energy of a semiconductor could be calculated by the following formula: $\alpha h\nu = A(h\nu - E_g)^{n/2}$, where α , ν , E_g and A are the absorption coefficient, light frequency, band gap and a constant, respectively. Among them, n depends on the characteristics of the transition in a semiconductor, including a direct transition ($n = 1$) or indirect transition ($n = 4$). For BiOI and $\text{La}(\text{OH})_3$, the values of n are both 4 as for the indirect transition. Therefore, the band gap energy (E_g) of the samples can be estimated from a plot of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$). The intercept of the tangent to the plot gives a good approximation of the band gap energy of the sample [Fig. 6(b)] [32,33]. The

band gap of BiOI is evaluated to be approximately 2.0 eV, while of $\text{La}(\text{OH})_3$ is found to be approximately 3.41 eV. The band edge positions adopted can be determined theoretically from the absolute electronegativity, which is a simple method with reasonable results for many photocatalysts [34,35]. The VB edge potential of a semiconductor at the point of zero charge can be calculated by the following empirical equation: $E_{\text{VB}} = X - E_c + 0.5E_g$, where X is the absolute electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms. Herein, the electronegativity of an atom is the arithmetic mean of the atomic electron affinity and

Fig. 6. UV-vis DRS spectra (a) and plots of $(\alpha h\nu)^{1/2}$ versus photon energy (b) of the as-prepared samples.

Table 2

Absolute electronegativity, band gap energy, calculated CB edge, and calculated VB position for BiOI and La(OH)₃ at the point of zero charge.

Sample	Absolute electro-negativity (X) (eV)	Band gap energy (eV)	Calculated CB position (eV)	Calculated VB position (eV)
BiOI	5.99	2.00	0.49	2.49
La(OH) ₃	5.67	3.41	-0.41	2.88

the first ionization energy, E_c is the energy of free electrons on the hydrogen scale (approximately 4.5 eV), and E_g is the band gap energy. Moreover, the conduction band (CB) edge potential (E_{CB}) can be determined by $E_{CB} = E_{VB} - E_g$. The X values for La(OH)₃ and BiOI are 5.67 and 5.99 eV [36,37]. Hence, the E_{VB} of La(OH)₃ and BiOI are calculated to be 2.88 and 2.49 eV, respectively. At last, the E_{CB} of La(OH)₃ and BiOI were estimated to be -0.41 and 0.49 eV. The calculated potentials of the CB and VB of La(OH)₃ and BiOI are listed in Table 2.

3.6. Photocatalytic activity and stability

The as-prepared samples were used for the photocatalytic removal of ppb-level NO in the gas phase to demonstrate their potential capability for use in air purification. Fig. 7(a) shows the variation of the NO concentration (C/C_0) with irradiation time under visible light irradiation. NO could not be photolyzed under light irradiation ($\lambda > 420$ nm). In the presence of photocatalysts, NO reacts with the photogenerated reactive radicals to produce the final product. Fig. 7(a) shows the variation in NO concentration with irradiation time for the seven photocatalysts under visible light irradiation. La(OH)₃ exhibits a negligible photocatalytic activity owing to its large band gap. Meanwhile, the BiOI showed negligible photocatalytic activity owing to the rapid recombination of photoinduced electrons and holes. When a small amount of BiOI was introduced on the surface of La(OH)₃ nanorods, the photocatalytic NO removal ratio could be significantly enhanced. The Bi/La-150% exhibits the highest photocatalytic activity with a NO removal ratio of 50.5%, which is superior to N-doped TiO₂ and g-C₃N₄. Mean-

while, the other BiOI@La(OH)₃ heterostructures showed a slightly lower activity, which was still higher than the pure La(OH)₃ or BiOI sample. The enhanced photocatalytic activity of the BiOI@La(OH)₃ samples could be attributed to the heterostructure with intimate contact resulting in the promotion of charge separation. However, excessive BiOI in the heterostructures might reduce the production of the reactive species owing to the increased charge recombination by BiOI. Similar phenomena have been observed for BiVO₄/Bi₂S₃ and Bi₂MoO₆/BiOCl photocatalysts [38,39]. Note that the decreased activity of Bi/La-100% after 5 min can be ascribed to the accumulation of the reaction products on the catalyst surface.

It is important for the photocatalyst to maintain its stability under recycled runs. Fig. 7(b) demonstrates the cycling runs for the Bi/La-150% sample. After consecutive repeated irradiation, the high NO removal ratio can be maintained, which indicates the high photochemical stability of the BiOI@La(OH)₃ heterostructure. The used catalyst can be regenerated by washing it with water to remove the accumulated species.

3.7. Photocatalytic mechanism of the BiOI@La(OH)₃ heterostructure

It is important to determine the main oxidative species in the photocatalytic process to elucidate the photocatalysis mechanism [41]. ESR is a powerful technique for the detection of photogenerated radicals in the photocatalysis process [41,42]. DMPO is generally used for trapping radicals owing to the generation of some stable radicals, such as the DMPO-hydroxyl radical ($\cdot\text{OH}$) and DMPO-superoxide radical ($\cdot\text{O}_2^-$). The ESR technique is thus employed to monitor the reactive species generated during the light irradiation of the BiOI@La(OH)₃ heterostructure with DMPO in methanol and water, and the results are shown in Fig. 8. The signals of the superoxide ($\cdot\text{O}_2^-$) cannot be obviously observed. However, the signals of the hydroxyl radical ($\cdot\text{OH}$) could be observed when the BiOI@La(OH)₃ suspension is irradiated for 5 min by a pulsed laser system. Besides, the intensity of the $\cdot\text{OH}$ signal from the Bi/La-150% sample increased considerably after ir-

Fig. 7. Photocatalytic oxidation of NO over the as-prepared samples (a), and cycling runs of the Bi/La-150% heterostructure in air under visible light irradiation (b).

Fig. 8. DMPO spin-trapping ESR spectra of the Bi/La-150% heterostructure in a methanol dispersion for $\cdot\text{OH}$ (a) and in an aqueous dispersion for $\cdot\text{O}_2^-$ (b).

radiation for 15 min. Therefore, the hydroxyl radical ($\cdot\text{OH}$) is the main oxidative species for the BiOI@La(OH)_3 system. The NO could react with the photogenerated $\cdot\text{OH}$ radicals generated from the photocatalytic reaction to produce the final products of NO_3^- , which involves the three reactions presented in Eqs. (1)–(3) [43,44].

Based on the above results, the enhanced photocatalytic activity of the BiOI@La(OH)_3 heterostructures can be attributed to the following reasons. First, the photocatalytic reaction is often related to the specific surface areas. High specific surface areas could facilitate the diffusion of reactants and products on the catalyst surface. In our case, the BiOI@La(OH)_3 heterostructures possess higher specific surface areas than the La(OH)_3 nanorods, which favors the photocatalytic reaction. Second, the photocatalysis efficiency is related the band gap energy (E_g) of the photocatalyst to some extent. A small E_g value means that the catalyst can use visible light more efficiently, but also means the redox ability of the photogenerated charge carriers becomes weak. These competitive effects lead to the reasonable result that the photocatalytic activity of BiOI@La(OH)_3 heterostructures does not increase monotonically with the BiOI content, but reaches a maximum with an appropriate amount of BiOI. Third, the enhanced visible light photocatalytic activity of BiOI@La(OH)_3 heterostructures can be mostly ascribed to the efficient separation of photogenerated charge carriers by the heterojunction.

The flowchart of the photogenerated electrons and holes at the heterojunction interface depends on band edge positions of semiconductors. The band alignment of the BiOI@La(OH)_3 heterostructure is schematically given in Fig. 9. The BiOI with a narrow band gap energy (2.0 eV) could easily be excited by visible light ($\lambda > 420 \text{ nm}$, energy $< 2.95 \text{ eV}$) to induce the generation of photoelectrons and holes. However, these photoelectrons and holes might also recombine rapidly because of the narrow energy gap. This is why BiOI shows a poor photocata-

lytic activity. La(OH)_3 could not be excited by visible light irradiation with energy less than 2.95 eV ($\lambda > 420 \text{ nm}$) owing to its wide energy gap of 3.41 eV. When a BiOI@La(OH)_3 heterostructure is formed, BiOI could act as a sensitizer to absorb the visible light. Under visible light illumination with energy of 2.95 eV ($\lambda > 420 \text{ nm}$), electrons in the valence band of BiOI could be excited up to a higher potential edge (-0.56 eV) [21,45]. The reformed CB edge potential of BiOI is more active than that of La(OH)_3 (-0.41 eV). The photogenerated electrons in the CB of BiOI transfer to the CB of La(OH)_3 through the intimate interface, while holes remain in the valence band (VB). The potential of the electrons in the conduction band of La(OH)_3 (-0.51 eV) is more negative than the potential of $\text{O}_2/\cdot\text{O}_2^-$ (-0.33 eV vs NHE), so $\cdot\text{O}_2^-$ should be produced. However, the generated $\cdot\text{O}_2^-$ can be rapidly transformed into $\cdot\text{OH}$. Meanwhile, the potential of the holes at the VB of BiOI (2.49 eV) is more positive than the redox potential of $\text{OH}^-/\cdot\text{OH}$ (1.99 eV), and therefore, the holes could directly oxidize OH^- to $\cdot\text{OH}$. Therefore, the photoinduced electron-hole pairs generated from BiOI could be effectively sepa-

Fig. 9. Photocatalytic mechanism of the as-prepared BiOI@La(OH)_3 heterostructure.

rated, and thus the BiOI@La(OH)₃ heterostructures exhibit a highly enhanced photocatalytic performance for the removal of NO under visible light irradiation.

4. Conclusions

We have developed a facile synthetic approach to construct heterostructured BiOI@La(OH)₃ nanorods. The presence of BiOI could extend the light response of La(OH)₃ from the UV to the visible light region. The heterostructure with an intimate interface and well-matched band position was confirmed by various characterization techniques. This heterostructure could promote the charge separation and transfer, thus leading to an enhanced visible light photocatalytic activity. Among the as-prepared samples, Bi/La-150% showed the highest photocatalytic activity, which suggested that the mass ratio of BiOI plays an important role in enhancing the visible light photocatalysis of the La(OH)₃. A new photocatalysis mechanism for photocatalytic NO purification with the BiOI@La(OH)₃ heterostructure was proposed. Our work could provide new insights into the development and application of heterostructured photocatalysts.

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Graphical Abstract

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Heterostructured BiOI@La(OH)₃ nanorods with enhanced visible light photocatalytic NO removal

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Heterostructured BiOI@La(OH)₃ nanorods with efficient visible light photocatalytic performance are synthesized by a facile chemical impregnation method.

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BiOI@La(OH)₃纳米棒异质结制备及其增强可见光催化去除NO性能

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摘要: 一维La(OH)₃纳米棒具有特殊的电子结构和多功能特性, 特别是作为半导体光催化剂引起了人们极大的兴趣。但La(OH)₃禁带宽度较大, 且只能吸收紫外光, 所以光催化效率较低, 可见光利用能力较差, 限制了La(OH)₃的实际应用。因此, 需要开发一种高效的改进方法来提高La(OH)₃的可见光催化性能。本课题组发展了一种有效的改进La(OH)₃方法, 通过简易的方法将BiOI纳米颗粒沉积在La(OH)₃纳米棒上, 有效增强了对可见光的吸收能力和光生载流子的分离能力。本文采用X射线衍射(XRD)、透射电镜(TEM)、扫描电镜(SEM)、紫外-可见漫反射光谱(UV-Vis DRS)、荧光光谱(PL)、光电子能谱(XPS)、电子自旋共振(ESR)、N₂吸附和元素分析等手段研究了BiOI@La(OH)₃纳米棒异质结的构建原理及增强可见光催化性能的原因。

XRD和XPS结果表明, 通过简易化学沉积法原位构建了BiOI@La(OH)₃异质结, 并且在异质结中没有杂相生成。由SEM图像可见, 原始La(OH)₃由分散的一维纳米棒组成, 平均直径为30–50 nm。通过BiOI与La(OH)₃表面的紧密接触成功构建异质结, 但BiOI纳米颗粒未改变La(OH)₃纳米棒的形貌。由TEM和HRTEM图像可见, La(OH)₃纳米棒的平均长度为30–50 nm, 并且在BiOI@La(OH)₃异质结中可以清晰看出BiOI和La(OH)₃之间紧密接触的界面和晶格间距。N₂物理吸附结果显示, 随着BiOI量的增加, BiOI@La(OH)₃异质结的比表面积增加, 但孔体积未现明显变化。UV-Vis DRS结果显示, 引入BiOI后明显促进了La(OH)₃对可见光的吸收能力和利用效率, 从而有利于增强可见光催化活性。通过理论计算分别得到BiOI和La(OH)₃的价带和导带位置, 表明具有非常匹配的能带结构可以促进BiOI光生电子的有效转移。

可见光催化去除NO测试结果表明, BiOI@La(OH)₃异质结的光催化活性高达50.5%, 明显优于BiOI和La(OH)₃。ESR测试结果显示, BiOI@La(OH)₃异质结可见光催化活性中起主要作用的活性物种是·OH。结合表征结果, BiOI@La(OH)₃纳米棒异质结可见光催化性能增强的原因主要有三个: (1) BiOI@La(OH)₃异质结增大的比表面积有利于反应物和产物在催化剂表面扩散, 同时可提供更多活性位点参与光催化反应; (2) 禁带宽度影响光催化效率, 当BiOI与La(OH)₃达到合适比例时, 既可以促进可见光吸收, 也可以使光生电子具有较强还原能力; (3) BiOI@La(OH)₃异质结有利于光生载流子的分离, 从而显著提高其光催化活性。

关键词: BiOI@La(OH)₃异质结; 纳米棒; 光催化; 可见光; 一氧化氮去除

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