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ABSTRACT

Exfoliated g-C₃N₄ (CNs)–BiOBr hybrids with heterojunction structure was fabricated through a chemical deposition–precipitation route. The characterization showed the uniform existence of CNs and BiOBr in hybrids. The fabricated CNs–BiOBr was of enlarged specific surface area, unique optical property, and well-matched energy-band structures. The photocatalytic performance on dye Rhodamine B (RhB) and 2,4-dichlorophenol (2,4-DCP) were dramatically improved. Under identical conditions, sample 0.5CNs–BiOBr and CNs–BiOBr were identified as the best candidate, respectively, for catalytic degradation of RhB and 2,4-DCP. The former could show a reaction rate over RhB about 2.7 and 6.8 times as high as BiOBr and CNs alone, and the later exhibited a reaction rate over 2,4-DCP nearly 7.5 and 2.5 times as high as individual BiOBr and CNs. Finally, a possible catalytic mechanism was also proposed through active species trapping experiments.

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1. Introduction

Semiconductor photocatalysis is regarded as an effective and green technique since it is able to completely decompose a variety of environmental contaminations under mild conditions [1–3]. In

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order to efficiently utilize solar energy, most researchers have devoted many efforts on design and fabrication of visible-light-driven catalysts through various methods, among which construction of heterojunction structures is particularly promising since the integration of semiconductors with suitable energy-band structures favors not only the separation of photoinduced charge carriers but also the visible-light harvesting [4]. The real applications require strong visible-light response, outstanding catalytic performance, and excellent reusability [5]. Thus, it is significant to prepare catalysts with above merits and understand the mechanism of catalysts with heterojunction structures.

BiOBr is a bismuth-based semiconductor with an indirect-transition band-gap, which is propitious to depress the recombination of excited holes and electrons [6]. In addition, it has a layered structure with $[\text{Bi}_2\text{O}_2]$ slabs interleaved by two slabs of bromine atoms, facilitating the light-harvesting by multi-reflection of incident light and efficient migration of reactants and products among layers. These structural virtues together with a suitable band gap around 2.75 eV enable it a reliable candidate for photocatalysis in the visible-light region [7]. However, its catalytic capability is greatly restrained by the high recombination of electron-hole pairs [8,9]. To reduce the recombination possibility and thus enhance the catalytic efficiency, two strategies are generally adopted. The first one is to synthesize pure BiOBr with various architectures, such as lamellas, hierarchical microspheres, microflowers, mesoporous microspheres, and self-assembled 3-D architectures [10–14]. Another alternative is relevant to the fabrication of BiOBr hybrids with other semiconductors of suitable energy-band structures and the obtained hybrids normally own unique optical and catalytic properties, thanking to the formation of a positive synergistic effect between these ingredients [15–19].

Very recently, a novel polymeric material $g\text{-C}_3\text{N}_4$, has been developed and utilized to catalyze the hydrogen evolution by water splitting under visible-light illumination [20]. It is a metal-free organic semiconductor and is composed of only carbon, nitrogen, and a few remained hydrogen atoms in a delocalized π -conjugated structure, ensuring the excellent thermal and photochemical stability [21,22]. $g\text{-C}_3\text{N}_4$ can exert visible light photocatalysis since its band gap is around 2.7 eV. However, the catalytic efficiency is quite low due to the high recombination rate of excited charge carriers. As a result, advancement of $g\text{-C}_3\text{N}_4$ structure is extremely desired to avoid this shortcoming and mainly associates with the construction of mesoporous structure [23,24], doping with metal or nonmetal elements [25–28], composting with other semiconductors [29–33], and exfoliation of bulk form into nanosheets [34–37]. In particular, the exfoliation of bulk $g\text{-C}_3\text{N}_4$ to nanosheets is able to reduce the edge thickness and create new exposed surface, easily leading to the enlarged specific surface area, enhanced charge carriers motilities through reduced migration distances, and variable conduction and valence band positions, which is favorable to the enhancement of photocatalytic performance [34,36].

Energy levels of bulk $g\text{-C}_3\text{N}_4$ and BiOBr are well-matched, and hence several studies have investigated the optical and catalytic properties of BiOBr hybrids with bulk $g\text{-C}_3\text{N}_4$, instead of CNs [38–41]. Whereas, CNs with superior features to bulk $g\text{-C}_3\text{N}_4$, is more suitable to construct hybrids with other semiconductors of visible-light response. Combination of two visible-light-responsive semiconductors with well-aligned straddling band-structures is able to promote separation of charge carriers under visible light, accordingly enhancing the catalytic efficiency. As a result, in this study BiOBr was chosen as a component to construct a series of hybrids with CNs. It was found that the two components coexisted and closely contacted to construct heterojunctions in structures. Besides that, the enlarged specific surface area, favorable optical property, and well-matched band structures assured the enhanced photocatalytic efficiency of as-synthesized hybrids in comparison with bare BiOBr and CNs alone. These hybrids were robust and could be used for several times without loss of catalytic activity. Finally, active species trapping experiments were conducted to propose a possible photocatalytic mechanism.

2. Materials and methods

2.1. Reagents

Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, AR), potassium bromide (KBr, AR), glacial acetic acid ($\text{C}_2\text{H}_4\text{O}_2$, AR), melamine ($\text{C}_3\text{H}_6\text{N}_3$, CP), 2,4-dichlorophenol (2,4-DCP, AR), disodium ethylenediaminetetraacetate (EDTA-2Na, AR), and isopropanol (IPA, AR) were purchased from Sinopharm Chemical

Reagent Co., Ltd (Shanghai, China). All chemicals involved for synthesis and analysis were directly used without further treatments.

2.2. Fabrication of CNs–BiOBr hybrids

Bulk $g\text{-C}_3\text{N}_4$ and its corresponding exfoliated counterpart CNs were prepared according to references except small modifications in the synthetic procedure [34]. Typically, melamine powder (10 g) was put into a semiclosed alumina crucible and annealed in a muffle furnace at 550 °C for 4 h to give a yellow powder as bulk $g\text{-C}_3\text{N}_4$. Subsequently, the resultant bulk $g\text{-C}_3\text{N}_4$ (0.5 g) in an alumina crucible without cover was annealed at 500 °C for 2 h to supply CNs with a thickness of about 1.9 nm, *ca.* six-layered structure, as stated in previous reference [34]. The obtained CNs displayed much higher photocatalytic efficiency upon removal of RhB (30 mg L^{-1}) than bulk $g\text{-C}_3\text{N}_4$ in Fig. S1, which was consistent with previous Ref. [36].

CNs was adopted to fabricate CNs–BiOBr hybrids through a chemical deposition–precipitation method described as follows. A certain amount of CNs and KBr in distilled water (30 mL) was sonicated for 0.5 h to create a suspension A. Meanwhile, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ with a stoichiometric ratio to KBr was introduced into glacial acetic acid (30 mL) and the mixture was stirred at room temperature to achieve a transparent solution B. Solution B was carefully dropped into the suspension A and the resulting mixture was stirred for 0.5 h and aged for 3 h at room temperature prior to the completion of reaction. Finally, the precipitate was collected by centrifugation, washed several times with water and ethanol, and dried at 80 °C overnight to provide target hybrids, which were denoted as xCNs–BiOBr and x hereafter referred to a theoretical mass ratio of CNs to BiOBr. Using an identical protocol, pure BiOBr and bulk $g\text{-C}_3\text{N}_4\text{-BiOBr}$ were also prepared at the absence of CNs and using bulk $g\text{-C}_3\text{N}_4$ instead of CNs, respectively. In addition, a mechanically mixed 0.5CNs–BiOBr was prepared by finely grinding a mixture of CNs and BiOBr.

2.3. Characterization

X-ray diffraction (XRD) patterns of samples were carried out on a Bruker D8 Advance X-ray diffractometer using a Cu K α radiation source ($\lambda = 1.5418\text{ \AA}$). The accelerating voltage and the applied current were 40 kV and 40 mA. General morphology of samples was observed by a Hitachi S-4800 FEG scanning electron microscope (SEM) under a working voltage of 200 kV. Transmission electron microscopy (TEM), elemental mapping, and high-resolution transmission electron microscopy (HRTEM) were obtained on a JEOL JEM-2011 electron microscope. FT-IR spectra were recorded on a Bruker V-70 Fourier transform-infrared spectrophotometer using a KBr pellet technique. Optical property of samples was evaluated on a Shimadzu UV-2600 UV–Vis spectrophotometer with BaSO_4 as a reflectance standard. X-ray photoelectron spectroscopy (XPS) measurements were performed using a RBD upgraded PHI 5000C ESCA System (Perkin Elmer) with an Mg K α (1253.6 eV) radiation. The signal positions were calibrated as the base of C 1s at 284.8 eV. The total organic carbon (TOC) of solution was determined using a TOC analyzer (Analytic Jena multi N/C 3100 TOC, Germany). N_2 adsorption–desorption isotherms were measured on a Micromeritics ASAP 2020 nitrogen adsorption apparatus at 77 K. Thermogravimetric (TG) analyses were recorded on a PerkinElmer STA8000 thermal analyzer with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ in a temperature range from 30 to 800 °C in air.

2.4. Photocatalytic activity measurement

The photocatalytic performance of prepared samples were investigated through decomposing dye RhB and 2,4-DCP in aqueous solutions, using a LIMX-VII apparatus manufactured by Bylabo Precision Instrument Co. Ltd. (Xi'an, China). A 400 W halogen lamp (Institute for Electric Light Source, Beijing) with a 2 M sodium nitrite solution was equipped to provide visible-light illumination with wavelength over 400 nm and eliminate thermal effect. An aqueous solution of RhB (60 mg L^{-1} , 40 mL) or 2,4-DCP (10 mg L^{-1} , 40 mL) was added into quartz glass tubes. A certain amount of catalyst (20 mg for RhB solution and 40 mg for 2,4-DCP solution) was dispersed into the aqueous solutions. Prior to irradiation, the suspensions were magnetically stirred in dark for 0.5 h to reach an adsorption–desorption

equilibrium. During photocatalytic processes, 1 mL of RhB suspension was withdrawn, diluted six times, and centrifuged to remove suspended photocatalyst particles, and then the supernatant was analyzed at the maximum absorption band 554 nm by a UV–Vis spectrophotometer (Purkinje General T6). As to 2,4-DCP degradation, high performance liquid chromatography (HPLC, Waters E2695) was used to analyze the remnant amount. The HPLC was equipped with a water reverse-phase C18 column (4.6 mm $\times$ 150 mm, 3.5 μ m, XBridge, Ireland) and a Waters 2489 UV–Vis detector at 285 nm. The mobile phase was a mixture of methanol and water with a volume ratio of 80:20 and the flow rate was 0.5 mL min⁻¹. 20 μ L of solution was injected for analysis each time.

In order to realize and further propose the photocatalytic mechanism, active species capture experiments were carried out, during which 0.5 mM IPA or EDTA-2Na was dispersed in RhB solution containing 0.5CNs–BiOBr hybrid or 2,4-DCP solution containing CNs–BiOBr hybrid to trap hydroxyl radicals ($\cdot$ OH) or photoinduced holes (h^+), respectively. The catalytic ability measurement and analysis were identical with what we described above.

The stability and reusability of 0.5CNs–BiOBr hybrid were estimated using a procedure as bellow, after each run, the photocatalyst collected from RhB aqueous solution was washed by deionized water and ethanol under sonication for several times, dried at 100 $^{\circ}$ C overnight, and subjected to next recycling test.

3. Results and discussion

3.1. TG analysis

Thermogravimetric analysis was conducted from 30 to 800 $^{\circ}$ C at a heating rate of 10 $^{\circ}$ C min⁻¹ in air atmosphere, aiming to detect the real content of CNs in as-synthesized CNs–BiOBr hybrids. As depicted in Fig. 1, the pure CNs becomes unstable and tends to decompose as soon as the temperature rises over 500 $^{\circ}$ C, revealing that pyrolysis of CNs occurs above such temperature. Complete thermal decomposition of pure CNs is found at nearly 650 $^{\circ}$ C. The phase transformation of CNs is different from the observation of bulk g-C₃N₄ whose pyrolysis happens at temperature arranging from 600 to 750 $^{\circ}$ C [42], mainly ascribing to the structural distinction between exfoliated CNs and bulk g-C₃N₄. As to pure BiOBr, around 71.8 % of original mass was retained beyond 750 $^{\circ}$ C. According to a reported method [41], the measured mass ratio of CNs *verse* CNs–BiOBr in hybrids 0.09CNs–BiOBr, 0.2CNs–BiOBr, 0.5CNs–BiOBr, CNs–BiOBr, 2CNs–BiOBr are about 0.09, 0.2, 0.37, 0.54, and 0.67 basing upon TG analyses, which are quite close to the theoretical values 0.08, 0.17, 0.33, 0.5, and 0.67. As a result, bismuth species in aqueous solution was almost equivalently converted to BiOBr that was *in situ* combined with CNs to fabricate CNs–BiOBr hybrids.

Fig. 1. TG analyses of CNs–BiOBr hybrids, bare BiOBr, and CNs.

3.2. XRD analysis

Fig. 2 shows the XRD patterns of CNs–BiOBr hybrids, pure BiOBr, and CNs. The diffraction peaks of pure BiOBr are in good agreement with the $P4/nmm$ tetragonal phase BiOBr (JCPDS 73-2061) [39]. Sample CNs displays two pronounced peaks in spectrum. The high-intensity peak at around 27.8° corresponds to a characteristic (002) interlayer stacking reflection of conjugated aromatic segments. The low-intensity one centered at nearly 13.3° , indexed as (100), is relevant to the in-plane structural repeating motif in crystal [40]. After hybridization, XRD patterns of CNs–BiOBr hybrids are identical to that of pure BiOBr except the appearance of a small peak at 27.8° from hybrid 0.2CNs–BiOBr to 2CNs–BiOBr, corresponding to the (002) plane of CNs and signed using a dashed line. The intensity of this peak increases with the increase of CNs addition. The presence of these characteristic peaks in hybrids confirms the coexistence of both components CNs and BiOBr whose main phase structures are well maintained after hybridization. Moreover, other diffraction peaks cannot be observable, revealing the high-purity of obtained hybrids without formation of impurities.

3.3. XPS analysis

X-ray photoelectron spectroscopy was conducted to investigate the surface chemical compositions and structural environments of CNs, BiOBr and 0.5CNs–BiOBr hybrid in Fig. 3. Peak positions in all XPS spectra were calibrated with C 1s at 284.8 eV. The appearance of elements Bi, O, Br, C, N in survey XPS spectrum of 0.5CNs–BiOBr hybrid confirms the presence of both components CNs and BiOBr, as shown in Fig. 3A. High resolution spectra of C 1s, N 1s, O 1s, Br 3d, and Bi 4f were displayed in Fig. 3B and D. The C 1s signals are composed of three carbon species for CNs at 284.8 eV, 287.8 eV, and 288.3 eV, corresponding to the adventitious carbon, the sp^3 -coordinated carbon from defects on $g\text{-C}_3\text{N}_4$ surface, and the sp^2 -bonded carbon in N-containing aromatic rings ($\text{N-C}=\text{N}$), respectively [36]. As to the N 1s spectrum of CNs, four nitrogen species can be found at 398.5 eV, 399.7 eV, 400.4 eV, and 404 eV, assigning to the sp^2 -hybridized nitrogen in triazine rings, tertiary nitrogen in N-(C)_3 groups, nitrogen atoms in amino groups, and charging effects, respectively [36,41]. The O 1s spectrum of pure BiOBr can be fitted into two signals at 531.1 eV and 532.6 eV, attributing to the oxygen atoms in crystal lattice (Bi-O) and in surface hydroxyl groups [41]. Two peaks in Br 3d spectrum at 68.2 eV and 69.3 eV are relevant to $\text{Br } 3d_{5/2}$ and $\text{Br } 3d_{3/2}$ in pure BiOBr crystal network. Two signals in Bi 4f spectrum centered at 159.3 eV and 164.6 eV are associated to $\text{Bi } 4f_{7/2}$ and $\text{Bi } 4f_{5/2}$ in pure BiOBr, respectively [11,17]. It is apparent that intensity ratio of C 1s peaks at 287.8 eV and 288.3 eV to 284.8 eV in 0.5CNs–BiOBr hybrid is relatively low in comparison to that of pure CNs, thanking to the relatively low content of

Fig. 2. XRD patterns of CNs–BiOBr hybrids, BiOBr, and CNs.

Fig. 3. X-ray photoelectron spectra of (A) survey scan of 0.5CNs–BiOBr hybrid, bare BiOBr, and CNs; high-resolution spectra of (B) C 1s and N 1s of 0.5CNs–BiOBr hybrid and CNs; (C) O 1s of 0.5CNs–BiOBr hybrid and BiOBr; (D) Br 3d and Bi 4f of 0.5CNs–BiOBr hybrid and BiOBr.

CNs contained [43], which is in good accordance with the XRD pattern. In addition, after hybridization all characteristic signals of both components CNs and BiOBr are present in hybrid 0.5CNs–BiOBr with slight shift in binding energy values, revealing the coexistence of two ingredients with the possible formation of intense interactions between them.

3.4. FT-IR analysis

Fig. 4 displays the FT-IR spectra of BiOBr, CNs, and CNs–BiOBr hybrids. The absorption bands at 3450 cm^{-1} and 1630 cm^{-1} in all spectra correspond to the stretching and bending vibrations of O–H, respectively [43]. Absorption bands ranging from 1200 cm^{-1} to 1600 cm^{-1} are ascribed to the typical stretching modes of CN heterocycles, which are fully present in CNs–BiOBr samples, revealing that the main structure of CNs is well sustained after hybridization. The absorption peak at 810 cm^{-1} belongs to the characteristic breathing mode of s-triazine [39,40]. The intensity of this peak gradually increases from sample 0.09CNs–BiOBr to 2CNs–BiOBr, in good agreement with the variation of CNs addition. Accordingly, the absorption band at 510 cm^{-1} attributed to the Bi–O stretching mode becomes feeble from sample 0.09CNs–BiOBr to 2CNs–BiOBr [39,40]. Based upon TG, XRD, XPS and FT-IR analysis, we can deduce that as-synthesized hybrids consist of two components CNs and BiOBr with original main structures maintained even exposure to hybridization.

3.5. Morphology, microstructure, and N_2 adsorption–desorption isotherms

Cotton-like CNs possess a layered structure in morphology with flat and smooth surface and crimped edges. The BiOBr have a flower-like three-dimensional structure and the solid interior was

Fig. 4. FT-IR spectra of CNs-BiOBr hybrids, BiOBr, and CNs.

assembled by nanosheets with sizes of several hundred nanometers and thicknesses about 40 nm, as seen in Fig. S2 and inset. The SEM images of CNs-BiOBr hybrids are exhibited in Fig. 5 and pure BiOBr is also supplied for comparison. Clearly, hierarchical flower-like units with several tens of micrometers in size are still maintained in 0.09CNs-BiOBr hybrids. With the increase of CNs addition from hybrids 0.2CNs-BiOBr to CNs-BiOBr, BiOBr nanosheets can be recognized as before in spherical units that are gradually coated with the cotton-like CNs. Further addition of CNs amount beyond mass ratio of 1 causes the total packages of BiOBr nanosheets without exposure. BiOBr spherical units with CNs coating in the outermost region are observable in corresponding TEM images in Fig. S3. To clarify microstructures, pure CNs, BiOBr, and hybrid 0.5CNs-BiOBr were subjected to sonication treatment in ethanol for recording TEM images, as shown in Fig. 6. A lamellar structure with flat surface and wrinkles at the edge is found in pure CNs in Fig. 6a, in accordance with the SEM result in Fig. S2. Fig. 6b displays plenty of nanosheets with irregular shapes and variable sizes in pure BiOBr. In Fig. 6c, the CNs as the ellipse labeled in white and BiOBr nanosheets as the ellipse labeled in black are easily found in an intimate contact manner in hybrid 0.5CNs-BiOBr. As to the HRTEM image of 0.5CNs-BiOBr hybrid in Fig. 6d, two different lattice images are found with d -values of 0.282 nm and 0.325 nm, corresponding to the (102) plane of BiOBr and the (002) plane of CNs, respectively. Formation of intimate interfaces between CNs and BiOBr phases facilitates the migration and transfer of photogenerated charge carriers, thus the inhibition of recombination possibility and in turn the increase of catalytic efficiency [41]. Moreover, TEM elemental mapping in Fig. 7 was recorded to show the distribution of both components BiOBr and CNs in 0.5CNs-BiOBr hybrid. Five elements C, N, Br, O, and Bi are evenly dispersed in the testing region, revealing the coexistence of two ingredients in a uniform manner.

The Nitrogen adsorption-desorption isotherm of pure CNs belongs to the type IV with a H_3 hysteresis loop at a high relative pressure range of 0.7–1.0 [43,44], confirming the existence of slit-like pores in Fig. S4. The isotherms of hybrids are similar to that of pure BiOBr, except that adsorption ability of these samples gets increase with the increase of CNs addition, which agrees well with the variation of specific surface area listed in Table 1. CNs with *ca.* six-layered structure has the largest S_{BET} value 202.5 m² g⁻¹ and flower-like pure BiOBr has the smallest value 10.1 m² g⁻¹. S_{BET} values of CNs-BiOBr series are between CNs and BiOBr and increase with the increment of CNs addition. Enlarged specific surface area benefits not only the sufficient light-harvesting achieved, but also abundant active sites exposed [36].

3.6. Optical property

Optical properties of pure CNs, BiOBr, and CNs-BiOBr series were measured by UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS), as seen in Fig. 8A. CNs shows a fundamental absorption edge

Fig. 5. SEM images of CNs–BiOBr hybrids and BiOBr.

rising at ~ 424 nm, while BiOBr holds an onset of absorption at ~ 444 nm. The band gap energy of both pure semiconductors can be estimated through the following formula [45]:

$$\alpha h\nu = A(h\nu - E_g)^{\frac{n}{2}}$$

where α , h , ν , E_g , and A are absorption coefficient, Planck constant, light frequency, band gap energy, and a constant, respectively; n is defined according to the type of optical transition of a semiconductor ($n = 1$ for direct transition and $n = 4$ for indirect transition). Values of n for pure BiOBr and CNs are adopted as 4 and 1 as reported [11,34]. From Fig. 8B, E_g values of pure BiOBr and CNs are calculated as 2.73 eV and 3.05 eV by means of $(\alpha h\nu)^{n/2}$ versus $h\nu$ plots. After hybridization, main absorption edges of these CNs–BiOBr series were well distributed between BiOBr and CNs in Fig. 8A, revealing that these

Fig. 6. TEM images of (a) CNs, (b) BiOBr, and (c) 0.5CNs–BiOBr hybrid; HRTEM image (d) of 0.5CNs–BiOBr hybrid.

hybrids pose structural features of both components. In addition, as seen in inset of Fig. 8A, unique absorption ability in the visible light region is observed in sample CNs–BiOBr that is slightly superior to both 0.5CNs–BiOBr and 0.2CNs–BiOBr. As to sample 2CNs–BiOBr, visible-light adsorption rapidly decreases over 450 nm. Corresponding E_g of these hybrids were estimated and collected in Table 1. It is reasonable to speculate that both 0.5CNs–BiOBr and CNs–BiOBr hybrids are good candidates for the further photocatalytic evaluation under visible light illumination because of the appreciate SBET values, favorable optical properties, and intimate interfaces along two component boundaries, which ensure abundant active sites exposed, sufficient absorption of visible light, and efficient separation of charge carries through intimate interface of well-aligned straddling band-structures.

3.7. Photocatalytic performance

Photocatalytic evaluation of as-synthesized CNs–BiOBr hybrids was accomplished using dye RhB and 2,4-DCP as target pollutants under visible light illumination and shown in Fig. 9. As depicted in Fig. 9A, degradation of RhB without catalysts cannot occur, which excludes the possibility of self-photolysis [41]. After irradiation for 100 min, pure CNs and BiOBr can render merely 50% and 78% catalytic degradation of RhB, respectively, which is much lower than those of CNs–BiOBr hybrids. The photocatalytic capability of hybrids is closely relevant to the mass ratio of CNs to BiOBr since an appropriate CNs addition is beneficial to construction of heterojunctions with favorable physiochemical properties. With the increase of mass ratio from 0.09 to 0.5, catalytic efficiency of corresponding

Fig. 7. TEM elemental mapping images of 0.5CNs–BiOBr hybrid.

Table 1
 S_{BET} values, E_g , and reaction rate constant k_{RhB} and $k_{2,4-DCP}$ of CNs–BiOBr hybrids, BiOBr, and CNs.

Sample	S_{BET} (m^2/g)	E_g (eV)	k_{RhB} ($\times 10^{-2}$)	$k_{2,4-DCP}$ ($\times 10^{-3}$)
BiOBr	10.1	2.73	1.46	1.02
0.09CNs–BiOBr	24.9	2.81	2.73	1.56
0.2CNs–BiOBr	38.3	2.84	3.81	2.96
0.5CNs–BiOBr	53.3	2.85	4.01	3.91
CNs–BiOBr	82.3	2.87	2.62	7.6
2CNs–BiOBr	95.2	2.81	1.45	6.76
CNs	202.5	3.05	0.59	3.06

Fig. 8. (A) UV-vis diffuse reflectance spectra of CNs-BiOBr hybrids, BiOBr, and CNs (inset is enlarged image of UV DRS for clarity); (B) $(zhv)^2$ or $(zhv)^{1/2}$ versus E_g plots of bare CNs and BiOBr.

Fig. 9. (A) Photocatalytic activity for the degradation of RhB on CNs-BiOBr hybrids, BiOCl, CNs, mechanically mixed 0.5CNs-BiOBr, and bulk $g\text{-C}_3\text{N}_4\text{-BiOBr}$; (B) Photocatalytic activity for the degradation of 2,4-DCP on CNs-BiOBr hybrids, BiOCl, CNs, and bulk $g\text{-C}_3\text{N}_4\text{-BiOBr}$.

catalysts is gradually getting improved. Nevertheless, further increment of mass ratio contrarily leads to a decrement of photocatalytic outcome. Apparently, among all samples hybrid 0.5CNs-BiOBr is the best candidate since it can exert complete removal of RhB after 100 min irradiation. Mechanically mixed 0.5CNs-BiOBr was exposed to the photocatalytic evaluation under an identical condition and displayed a catalytic efficiency even worse than bare CNs and BiOBr, revealing the real presence of heterojunctions in hybrids instead of physical mixtures [39]. Photocatalytic efficiency of bulk $g\text{-C}_3\text{N}_4\text{-BiOBr}$ is much lower than that of CNs counterpart, indicating that CNs with favorable structural features is more suitable to fabricate heterojunctions with other semiconductors than bulk $g\text{-C}_3\text{N}_4$ in terms of photocatalysis [35,36]. The blue shift of characteristic adsorption peak of RhB during photocatalysis is observed in Fig. S5 and is attributed to the deethylation phenomenon [46]. The experimental data were subsequently fitted by a pseudo-first-order model to study reaction kinetics of the RhB degradation and the corresponding apparent reaction constants (k) were listed in Table 1. The hybrid 0.5CNs-BiOBr, regarded as the best catalyst toward RhB removal, shows the highest reaction constant that is nearly 2.7 and 6.8 times as high as those of BiOBr and CNs alone.

The visible-light-driven photocatalytic capability of synthesized samples was further proven through degradation of 2,4-DCP, a colorless and toxic contaminant, as seen in Fig. 9B. Direct photolysis of 2,4-DCP is almost negligible. The catalytic ability of hybrids enhances with the increase of mass ratio up to 1. Sample CNs–BiOBr shows the highest catalytic efficiency among hybrids and the corresponding reaction constant is around 7.5 and 2.5 times as high as those of bare BiOBr and CNs. Similar to the result in Fig. 9A, appreciate amount of CNs in hybrids is favorable to construct hybrids with suitable structures and optical properties, ensuring the acquisition of enhanced catalytic performance. In addition, TOC analysis was also checked and shown in Fig. S6. Degradation of RhB over 0.5CNs–BiOBr through UV–Vis and TOC analysis is around over 98% and 40%, respectively. As to 2, 4-DCP, removal efficiency by CNs–BiOBr through HPLC and TOC analysis is nearly 80% and 43.9%, respectively. The results indicate that partial pollutants can be mineralized to small molecules upon measured conditions.

As stated above, as-synthesized hybrids display dramatically enhanced photocatalytic ability in comparison with pure CNs and BiOBr, mainly attributing to the suitable structures and optical properties. On the one hand, the hybrids with enlarged specific surface areas benefit the efficient utilization of visible light upon abundant active sites, hereby generating more holes and electrons that readily participate degradation reactions. In addition, shrinkage of band gap of CNs–BiOBr is obtained by combining with BiOBr, leading to the enhancement of catalytic efficiency compared with CNs. On the other hand, appreciate mass ratio of CNs to BiOBr is crucial to construct CNs–BiOBr heterojunctions that are featured with good dispersion and intimate contact of both components [17]. Through smooth interfaces along phase boundaries in well-matched band structure, electron and holes tends to transfer and accumulate in different components, greatly inhibiting recombination possibility and raising photocatalytic efficiency. Self-aggregation of some phase tends to occur if mass ratio is less or higher than the suitable one, accordingly destroying the synergistic effect of both components toward removal of organic molecules.

The reusability and durability are important parameters to explore real applications of catalysts. As a result, 0.5CNs–BiOBr hybrid was specifically chosen for successive catalytic estimations in Fig. 10. There is no obvious decrease of photocatalytic efficiency over RhB for four cycling runs under visible light, possibly linking to the well-maintained chemical composition and phase structures, evidenced by the XRD and FT-IR analysis before and after catalytic reactions in Fig. S7.

3.8. Photocatalytic mechanism proposed

To fully understand the photocatalytic process and further propose a reasonable mechanism, hydroxyl radicals and holes trapping experiments were conducted to realize roles of both oxidative

Fig. 10. Reusability of 0.5CNs–BiOBr hybrid over RhB degradation.

Fig. 11. (A) Active species trapping experiments by sample 0.5CNs-BiOBr over degradation of RhB and (B) active species trapping experiments by sample CNs-BiOBr over degradation of 2,4-DCP.

species through addition of a desired amount of IPA [46,47] and EDTA-2Na [38,39,46], respectively. From Fig. 11A, the catalytic degradation efficiency of 0.5CNs-BiOBr hybrid over RhB is somewhat restrained upon addition of IPA, revealing that hydroxyl radicals $\cdot\text{OH}$ exert a minor effect on the process. On the contrary, the photocatalytic performance is greatly inhibited as soon as EDTA-2Na was added, indicating that holes are crucial active species during catalysis. The result is in good agreement with previous results [38,39]. As to the photocatalytic degradation of 2,4-DCP over CNs-BiOBr hybrid, a different phenomenon was observed. The presence of EDTA-2Na causes a slight reduction of catalytic efficiency and the involvement of IPA shows a great negative effect on the degradation outcome, revealing that hydroxyl radicals $\cdot\text{OH}$ are dominant oxidative species, which is similar to the report [48].

We have estimated E_g values of pure BiOBr and CNs as 2.73 eV and 3.05 eV in the optical property section. The valence band (VB) edge potential of a semiconductor can be predicted by the following empirical equation [29,40]:

$$E_{VB} = X - E^e + 0.5E_g$$

where E_{VB} is the VB edge potential, X is the electronegativity that is a geometric mean of the absolute electronegativity of the constituent atoms, E^e is the energy of free electrons on the hydrogen scale (around 4.5 eV), and E^g is the band gap energy. The corresponding conduction band edge potential (ECB) can be acquired by $ECB = E_{VB} - E_g$. Accordingly, E_{VB} and ECB values of pure CNs are determined as +1.76 eV and -1.29 eV, and E_{VB} and ECB values of pure BiOBr are +3.07 eV and +0.34 eV. Therefore, energy-band structures of both BiOBr and CNs are matched and favorable to form the well-aligned straddling band-structures.

Basing on the band structures of both semiconductors, a possible photocatalytic mechanism was speculated in Fig. 12. Upon visible light irradiation ($\lambda > 400$ nm), both components are readily excited to generate photoinduced electrons-holes pairs. The electrons are prone to transfer from the CB of CNs to the CB of BiOBr across the intimate interface of well-aligned straddling band structures since the CB potential of CNs is more negative than that of BiOBr. Owing to the less negative CB potential of BiOBr than $E_{(\text{O}_2/\cdot\text{O}_2^-)} = -0.046$ eV/NHE [39,41], these electrons staying on the CB of BiOBr cannot react with oxygen molecules adsorbed on the surface of hybrids to produce radicals $\cdot\text{O}_2^-$ that directly oxidize organic molecules or indirectly oxidize via transforming to $\cdot\text{OH}$ radicals by a two-electron oxidation pathway [39,42]. However, few remainder electrons in CB of CNs are able to undertake the above reaction. In addition, holes in the VB of BiOBr tend to migrate to VB of CNs because of the potential distinction. Holes accumulated in the VB of CNs can mineralize RhB molecules through a direct manner, instead of converting adsorbed H_2O molecules to $\cdot\text{OH}$ (E_{VB} of CNs $< E_{(\cdot\text{OH}/\text{H}_2\text{O})} = +1.99$ eV/NHE)

Fig. 12. Proposed mechanism of CNs–BiOBr hybrids upon visible light irradiation.

[39,41]. Few remainder holes in VB of BiOBr are capable of providing $\cdot\text{OH}$ radicals or directly mineralizing organic molecules. Differentiating from the degradation of RhB, 2,4-DCP is mainly decomposed by $\cdot\text{OH}$ through converting $\cdot\text{O}_2^-$ on CB of CNs or holes on VB of BiOBr as the base of active species capture experiments. As a result, efficient separation of photogenerated hole–electron pairs are achieved by the distribution of electrons and holes on different semiconductors and thus enhanced the corresponding catalytic performance.

4. Conclusions

In this investigation preparation and characterization of exfoliated CNs–BiOBr hybrids were reported. According to structural analyses, as-synthesized hybrids were composed of both components with the maintenance of their original structures. In addition, both components distributed evenly and contact closely to create smooth interface along phase boundaries, through which charge carriers easily migrate across and stayed in different components, resulting into the low recombination possibility and thus enhanced catalytic performance. Together with other merits, such as enlarged specific surface area, unique optical property, and well-matched energy-band structures, these hybrids exhibited greatly enhanced catalytic efficiency toward degradation of RhB and 2,4-DCP. Finally, a possible catalytic mechanism was also proposed through active species trapping experiments.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.spmi.2014.10.002>.

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