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Design of UiO-66@BiOIO₃ heterostructural composites with remarkable boosted photocatalytic activities in removing diverse industrial pollutants

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	Novel UiO-66@BiOlO ₃ -x composites have been successfully designed for the first time. The as-prepared UiO- 66@BiOlO ₃ -x composites exhibit superior photocatalytic activity for the decomposition of rhodamine B (RhB) and tetracycline (TC), compared with the corresponding BiOlO ₃ . For UiO-66@BiOlO ₃ -30 composite, approxi- mately 93.2% of RhB and 88.4% of TC were decomposed under a 300 W xenon arc lamp light irradiation. Furthermore, the UiO-66@BiOlO ₃ -50 composite presents outstanding oxidative removal activity for gaseous Hg ⁰ . The evident improvement of the photocatalytic property over the UiO-66@BiOlO ₃ -x composites might be ascribed to the promoted separation efficiency of electron–hole pairs and the larger specific surface area. Finally, the electron-hole migration mechanism over UiO-66@ BiOlO ₃ -50 composite is put forward in the light of trapping experiments. This research strategy will provide outstanding development in the application of photocatalysis.			

1. Introduction

In modern society, water pollution of antibiotics and organic dyes has aroused extensive attention [1-3]. Furthermore, as one of heavy metal contaminants, mercury has done great harm to the human health and environment [4,5]. At the present various technologies have been applied for the treatment of antibiotics, organic dyes and mercury pollutants [6–10]. Among these technologies investigated so far, photocatalysis is considered to a promising technology for the removal of the pollutants [11–13].

In the past ten years, Bi-based photocatalysts have been suggested as outstanding photocatalytic materials due to their typical physicochemical properties [14,15]. As a novel bismuth-based material, BiOIO₃ possesses the internal polar and non-centrosymmetrical structure, which consists of polar (IO₃)-groups and the $(Bi_2O_2)^{2+}$ hetero-layered structure, resulting in remarkable photocatalytic activity for the control of contaminants [16,17]. Benefit of its unique crystal configuration and inter-electric field, BiOIO₃ exhibits excellent photoinduced charge carrier separation efficiency. However, the charge migration to the catalytic reaction sites of the photocatalyst is still difficult to achieve. Therefore, the photocatalytic activity is not yet at acceptable levels for the application. Moreover, the specific surface area of BiOIO₃ photocatalyst is relatively lower which causes weak surface adsorption properties for pollutants. It is essential to find a more effective way to improve the charge separation efficiency and increase the surface area of the photocatalyst. Various methods have been studied to improve the charge transfer efficiency of BiOIO₃, including element doping, facet control, polarization, heterojunction formation and defect engineering [18–22].

Constructing heterojunction structure has been regarded as one of the important strategies to improve the charge separation efficiency. Heterostructures integration of MOFs with semiconductor photocatalysts has been recognised as an efficient approach to fabricate high performance photocatalysts. MOFs can supply more pathways which are favourable for the transfer of photogenerated electrons benefit from their high pore volumes [23,24]. This would be in favour of the separation of photogenerated carriers. In addition, the high surface area of MOFs makes it difficult for semiconductor nanoparticles to aggregate. UiO-66(Zr) exhibits better thermal and chemical stability compared with other metal-based MOFs [25,26]. Moreover, UiO-66(Zr) presents excellent structural stability in water, which will in favour of its application in the field of photocatalysis. In this work, UiO-66@BiOIO₃-x composites with different mass ratios (UiO-66 to BiOIO₃ are 30:100 and 50:100, respectively) were synthesised for the first time. The photocatalytic property of UiO-66@BiOIO3-x compared with BiOIO3 is greatly enhanced in the decomposition of rhodamine B (RhB) and tetracycline

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Received 8 September 2020; Received in revised form 12 November 2020; Accepted 10 December 2020 Available online 29 December 2020 0022-3697/© 2020 Elsevier Ltd. All rights reserved. (TC). In addition, UiO-66@BiOIO₃-50 composite exhibits appreciable oxidative removal performance for the gaseous Hg^0 . The potential reaction mechanism of increased photocatalytic activity for UiO-66@-BiOIO₃-x composites was investigated by the active species trap experiments.

2. Experimental

2.1. Synthesis of UiO-66

UiO-66 was synthesized by solvothermal method in the light of the previous report method with slightly modification [27]. Briefly, $ZrCl_4$ (0.233 g, 1 mmol) and 1, 4-benzenedicarboxylic acid (0.245 g, 1 mmol) were dissolved in 60 ml DMF solution. The obtained mixture was then put into an autoclave and performed the solvothermal reaction at 120 °C for 24 h. The obtained powders were filtered and washed with water and absolute ethanol several times. Finally, the samples were then dried at 80 °C for 12 h in air. In order to eliminate occluded DMF molecules completely, the obtained white products were immersed into the methanol solution and shook in constant temperature shaker for 1h. Then the products were filtered, washed and dried according to the above procedure.

2.2. Synthesis of UiO-66@BiOIO3 composites

UiO-66@BiOIO3 composites with different mass ratio of UiO-66 to BiOIO₃ were fabricated via hydrothermal method. Briefly, 0.485g Bi (NO₃) ·5H₂O was dissolved in 30 mL deionized water. In order to inhibit the hydrolysis of bismuth nitrate, 1 ml 67% (w/w) HNO₃ solution was added to the solution. Then 0.12g UiO-66 powder was dispersed into the above solution to form a homogeneous suspension under the condition of magnetic stirring. Subsequently, 0.214g KIO₃ was dissolved with 30 mL deionized water to another beaker. Then the KIO3 solution was dropped into the above suspension. A certain amount of NaOH solution was added to adjust the pH value of the solution. The pH value of the solution was adjusted to ca.3.02 under the stirring condition. The mixture was then loaded into a stainless-steel autoclave and heated at 160 °C for 16 h. And the following operations are the same as the synthesis of UiO-66. The as-synthesised UiO-66@BiOIO3 composite was denoted as UiO-66@BiOIO₃-x (x = 30, where x refers to the mass ratio of UiO-66 to BiOIO₃ was 30%). Another UiO-66@BiOIO₃-50 composite was also prepared taking the similar process by changing the dosage of the Bi (NO₃) ·5H₂O and KIO₃. Pristine BiOIO₃ was obtained via the same procedure except not added UiO-66 power.

2.3. Characterisation

The crystal structure of the samples was measured by a diffractometer with a Cu-Kα radiation (D8 ADVANCE, Bruker). The morphology and microstructure of the samples was characterized by the field emission scanning electron microscopy (FE-SEM, SU-1500, Hitachi) and transmission electron microscope (TEM, JEM-2010, Jeol) operated at 200 kV. The optical absorption property of the samples was recorded by a UV-vis spectrophotometer (UV-2550, Shimadzu). BET specific surface area was counted via N₂ adsorption-desorption with a GeminiVII 2390 instrument. The photoluminescence (PL) spectra was measured using a fluorescence spectrophotometer (RF-5301, Shimadzu). The spectra were excited at 360 nm and photoluminescence spectra were recorded in the range of 400-600 nm. Electron Spin-Resonance spectroscopy (ESR) was measured by using a Bruker EPR A300-10/12 spectrometer at room temperature with the signals of radicals trapped by 5,5-dimethyl-1-pyrroline nitrogen oxide (DMPO) for $\bullet O_2^-$ and 2,2,6,6- tetramethylpiperidine nitrogen oxide (TEMPO) for h⁺. The data were collected with a 300W xenon lamp to simulate solar irradiation at selected time.

2.4. Photocatalytic decomposition of organic pollutants

The decomposition of RhB and TC, at 20 mg/L each with a 300 W xenon arc lamp (Perfect Light Co., PLS-SXE 300, wavelength range 320–800 nm) irradiation was examined to estimate the photocatalytic property of the samples. Generally, 100 mg photocatalyst was dispersed into a 100 mL solution containing one of the pollutants. The solution was stirred for 0.5h under dark to achieve an adsorption–desorption equilibrium between the reagents prior to the irradiation. Next, a few millilitres of suspension were extracted and filtered at regular intervals. Then the solution was analysed to record the concentration by a spectrophotometer.

2.5. Photocatalytic oxidative removal of Hg^0

The oxidized removal of gaseous Hg⁰ was chosen to further assessment the activity of the obtained samples at the laboratory system described in our previous studies [28]. The mercury was generated from the mercury permeation tube which was immersed into a water bath at 55 °C to guarantee an invariable Hg⁰ permeation rate. The entrance mercury concentration was kept about 55 μ g/m³. The concentration of Hg⁰ was measured by an on-line mercury analyzer (RA-915 M, Lumex Ltd., Russia). The device was mainly consisted of three parts: gas system, photocatalytic system and the online mercury analysis. The compressed air was split into two streams and employed two mass flow meters (CS200) to control the velocity of flow. The total velocity was kept at 1.2 L/min and one of the streams with 0.2 L/min run through the Hg⁰ permeation tube to carry Hg⁰ vapor to the system. Firstly, the Hg⁰ stream ran through the bypass. When the concentration of Hg⁰ reached to a constant concentration for a certain time, the gas circuit was changed to the photocatalytic reactor. At the same time, the LED light was turned on. The photocatalytic test was implemented with the photocatalyst(50 mg) loaded on a quartz glass plate. Finally, the gas flowed through the activated carbon system to adsorb the unreacted gaseous Hg⁰ and then discharged. The Hg⁰ removal efficiency can be defined as follows:

$$h_{Hg} = \frac{Hg_{inlet}^0 - Hg_{outlet}^0}{Hg_{inlet}^0} \times 100\%$$

Where, Hg_{inlet}^{0} and Hg_{outlet}^{0} indicate Hg^{0} concentration at the inlet and outlet of the reactor, $\mu g/m^{3}$.

3. Results and discussion

3.1. characterizations of the as-prepared samples

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The XRD patterns of the as-prepared samples are illustrated in Fig. 1. The diffraction pattern of UiO-66 matches well with that reported literatures and no impurity peaks were observed [25,26]. The main diffraction peaks at 7.36°, 8.48°, 12.04°, 22.25° and 25.68° correspond to the (111), (002), (022), (115) and (224) diffraction planes, respectively. For BiOIO₃, the characteristic diffraction peaks match exactly with the orthorhombic structure of $BiOIO_3$ (ICSD # 262019), indicating that pure BiOIO₃ sample was prepared. For the as-prepared UiO-66@-BiOIO₃-x composites, the main diffraction peaks of UiO-66 can be detected evidently. In comparison with pristine UiO-66, the main peak intensity of UiO-66 in UiO-66@BiOIO3-x composites decreased and no extra peaks were checked, verifying that the UiO-66 maintains its crystalline structure during the preparation process of the composites. The diffraction peaks correspond to the (111), (022) and (224) facets of UiO-66 in the composites. These results demonstrated that the UiO-66 particles have been successfully loaded on the surface of BiOIO3 nanosheets.

The morphology structure of the obtained samples was detected by



Fig. 1. XRD patterns of BiOIO₃, UiO-66, and UiO-66@BiOIO₃-x composites.

the FE-SEM and TEM technologies and the results are displayed in Fig. 2 (a–d) and Fig. 3(a–d). The UiO-66 sample exhibits a nanocube structure with the particle size of ca. 200 nm, which is consistent with the results previously reported [29,30]. It can be observed that the BiOIO₃ sample was composed of irregular nanoplates. The SEM micrograph of UiO-66@BiOIO3-x composites (Fig. 2(c), (d)) displays that UiO-66 particles are dispersed on the BiOIO3 nanoplates surface. TEM results (Fig. 3 (c)) clarify that the big nanosheets with the smooth surface are BiOIO₃, and the small particles loaded on the BiOIO3 surface are taken as UiO-66 particles. The interface between BiOIO3 and UiO-66 was observed clearly, which provide the evidence of the UiO-66@BiOIO3-x heterostructure was fabricated. Additionally, the related elemental mapping images of UiO-66@BiOIO₃-50 composite state the existence of all expected elements (Bi, I, O, Zr and C) and the uniform distribution in the composite together. As a result, it is proved that the UiO-66 grains were successfully loaded on the surface of BiOIO3 nanosheets to form a heterojunction, which was beneficial to the transfer of photogenerated charge carriers.

The specific surface area and porosity of the as-prepared samples



Fig. 2. SEM images of UiO-66(a), BiOIO₃ (b) and UiO-66@BiOIO₃-x composites (c, x = 30, d, x = 50).

were investigated by N₂ adsorption-desorption measurement and the corresponding results are presented in Table 1 and Fig. 4. Compared with pure UiO-66, UiO-66@BiOIO3-x samples obtain a decreased surface area and total pore volume. With the increasing of UiO-66 in the composites, the BET value of the UiO-66@BiOIO3-x composites increased (Table 1). It needs to be known that the BET specific surface area of UiO-66@BiOIO₃-50 was much higher than that of BiOIO₃, but lower than that of UiO-66. The total pore volume of UiO-66@BiOIO₃-x composites was higher than that of BiOIO3.The N2 adsorption-desorption isothermal of the UiO-66@BiOIO3-x samples had a type IV loop at a relative pressure range from 0.05 to 1 (Fig. 4). UiO-66 sample possesses the type IV isotherms curves with a H3 typical hysteresis loop. It shows high adsorption at relatively high p/p0 range, which implying the existence of accumulation pores. It can safely deduce that the increased surface area of UiO-66@BiOIO3-x and the porous structure compared to BiOIO3 may favour the transfer of photogenerated electrons and thus promote its photocatalytic activity towards the pollutants' decomposition or oxidation.

The UV–vis diffuse reflectance spectra (DRS) of UiO-66, BiOIO₃ and UiO-66@BiOIO₃-x composites are shown in Fig. 5. It shows that UiO-66 sample exhibits strong absorption in the UV light region of 200–350 nm, with an absorption edge of about 350 nm. The BiOIO₃ and UiO-66@BiOIO₃-x samples possess similar absorption edge and the value is ca. 400 nm, and therefore the bandgap can be estimated to be about 3.10 eV. Moreover, the band gap energy of BiOIO₃ and UiO-66 can be estimated by the following formula:

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

where E_g , α , h, ν , n and A mean the bandgap energy, coefficient of absorption, Planck constant, frequency of light, and a constant, respectively. The n is a constant related to semiconductor transfer properties. BiOIO₃ is an indirect semiconductor and therefore n is taken as 4 while n is taken as 1 for UiO-66 because of its direct transfer feature [31,32]. According to the above equation, the E_g of the pristine BiOIO₃ and UiO-66 are estimated to be 3.13 eV and 3.50 eV (Fig. 6 and Fig. 7), which is similar to the literatures reported previously [33,34].

3.2. Photocatalytic activity

RhB and TC are chosen as contaminants to assess the photocatalytic activities of the samples and the results are shown in Fig. 8. For RhB, the blank experiment exhibited slight photolysis, and only approximately 4.4% of RhB was decomposed after 18 min light irradiation. After adsorption for 30 min, the as-prepared UiO-66@BiOIO3-x composites and UiO-66 showed similar adsorption capacity, and approximately 20% of the RhB molecules were adsorbed. However, the BiOIO₃ sample presents lower adsorption capacity. Pure UiO-66 shows weak photocatalytic activity and finally ca. 30% of RhB are discoloured on the basis of its higher adsorption. The as-prepared UiO-66@BiOIO₃-x composites demonstrate remarkable photocatalytic activity for RhB. The final discoloration rate can reach ca. 94% after adsorption and photodecomposition. The photocatalytic performance can be promoted by the addition of UiO-66 and RhB was almost completely discoloured within 15 min for all UiO-66@BiOIO3-x composites system. UiO-66@BiOIO3-x composites exhibit relatively higher adsorption ability for RhB compared to the BiOIO₃ sample, which might be favourable for the photocatalytic process.

It was found that TC can barely be decomposed under light irradiation in the absence of photocatalyst. UiO-66 and UiO-66@BiOIO₃-x composites demonstrated higher adsorption capacity for the TC molecules (ca. 50%) compared to RhB molecules. Compared to BiOIO₃ and UiO-66@BiOIO₃-x composites, UiO-66 exhibited relatively weak photocatalytic activity for the decomposition of TC. The decomposed rate could reach ca. 89.3% for the UiO-66@BiOIO₃-30 composite, which is much higher than that of BiOIO₃ (69.1%) within 24 min light



Fig. 3. TEM images of UiO-66(a), BiOIO₃ (b), UiO-66@BiOIO₃-50 composite (c, bright field; d, dark field scan) and the elemental mapping images of UiO-66@BiOIO₃-50 composite.

irradiation. It can be inferred that the adhering amount of UiO-66 plays a significant role in the photodecomposition process.

In order to further evaluate the photocatalytic performance of the UiO-66@BiOIO₃-x composites, the Hg⁰ oxidative removal performance was implemented under 24 W LED light irradiation (Fig. 9). The results showed that the UiO-66@BiOIO₃-50 composite possessed relatively higher photocatalytic activity compared with BiOIO₃ and UiO-66. UiO-66 exhibits much lower removal efficiency, and its highest removal efficiency for BiOIO₃ and UiO-66@BiOIO₃-50 composites could reach ca. 54% and ca.

89%, respectively. Note that UiO-66@BiOIO₃-50 composite provides remarkable photocatalytic oxidative removal efficiency for gaseous Hg^0 . These results verify that UiO-66@BiOIO₃-x composites could be used in the field of mercury pollution control. It can be inferred that UiO-66 can be used as a suitable substrate for photocatalysts in pollution control, and it should create the chance for the development of various MOF-based photocatalysts in the future.

The reusability and stability of the UiO-66@BiOIO₃-50 composite was investigated by three consecutive photocatalytic discoloration runs for RhB (Fig. 10). There was no obvious reduction in the

Table 1

The BET surface areas and the photocatalytic decomposition rate of the asprepared samples.

Sample	Total pore volume (cm ³ .g ⁻¹)	BET surface areas $(m^2.g^{-1})$	Decomposition rate	
			RhB	TC
BiOIO ₃	0.03051	9.5054	88.2%	69.1%
UiO-66	0.4197	736.92	33.5%	61.8%
UiO- 66@BiOIO ₃ - 30	0.1144	108.87	95.2%	88.4%
UiO- 66@BiOIO ₃ - 50	0.1293	144.28	94.8%	89.5%





Fig. 4. $\rm N_2$ adsorption-desorption isotherms of UiO-66 and UiO-66@BiOIO_3- x composites.



Fig. 5. UV–vis diffusion reflection spectra (DRS) of $BiOIO_3$, UiO-66, and various UiO-66@ $BiOIO_3$ -x composites.



Fig. 6. BiOIO₃ of plots of $(\alpha h\nu)^{1/2}$ versus photon energy $(h\nu)$.



Fig. 7. UiO-66 of plots of $(\alpha h\nu)^2$ versus photon energy $(h\nu)$.





Fig. 10. Photocatalytic recycling runs(three) for RhB over UiO-66@BiOIO $_3$ -50 composite under the xenon lamp irradiation.

photodiscoloration of RhB, even after three recycles, suggesting the sample owns excellent recyclability in the decomposition reaction.

3.3. Possible photocatalytic mechanism

Trapping experiments were implemented to ascertain the main active radicals during the photodegradation of RhB with the addition in turn of benzoquinone (BQ), isopropyl alcohol (IPA), and ethyl-enediaminetetraacetic acid disodium salt (EDTA-2Na) to quench $\bullet O_2^-$, $\bullet OH$ and h^+ , respectively. As can be seen from Fig. 11, a significant reduce in the discoloration of RhB was observed when EDTA-2Na was used as the scavenger compared with no scavenger. It could be safely concluded that h^+ is the significant active species. In contrast, employing IPA as the scavenger, there was notable decrease in the discoloration of RhB. Moreover, the discoloration rate was also reduced in the presence of BQ. It is suggested that all the oxidative species containing h^+ , $\bullet OH$ and $\bullet O_2^-$ play an obvious role for the photodiscoloration of RhB.

To further prove the above inference, the ESR spin-trapping technique was performed to explore the essence of the reactive oxygen



Fig. 11. Photocatalytic activities of UiO-66@BiOIO $_3$ -50 composite for the degradation of RhB in the presence of different scavengers under the xenon lamp irradiation.



Fig. 8. Photocatalytic activities of the blank (direct photolysis) and samples of $BiOIO_3$, UiO-66 and $UiO-66@BiOIO_3-x$ composites for the degradation of RhB (a) and TC(b) under 300W xenon lamp full spectrum irradiation.



Fig. 9. Removal efficiency of $\rm Hg^0$ for UiO-66, $\rm BiOIO_3$ and UiO-66@BiOIO_3-50 composites under 24W LED light irradiation.



Fig. 12. ESR signals of the TEMPO-h⁺ and DMPO- \cdot O₂⁻ for UiO-66@BiOIO₃- 50 in the dark and under 300W xenon lamp full spectrum irradiation.

species produced for UiO-66@BiOIO3-50 composite under the 300 W xenon lamp and the results are presented in Fig. 12. As shown, the typical peaks of the DMPO- $\bullet O_2^-$ spin adducts were detected in the methanol dispersion under light irradiation. Furthermore, no signals could be detected without light irradiation. It suggests that the generation of $\bullet O_2^-$ under the light irradiation. The obvious characteristic consecutive 1:1:1 triplet signal was observed whether in dark or light condition. The triplet signal originates from the addition of trapping agent TEMPO. There is an obvious reduce in triplet ESR signal strength under light irradiation compared with dark condition. This is because the photogenerated holes react with the electrons that originate from TEMPO molecule. It causes the decrease of triplet signal under the light irradiation and the results are accordance with the literature [35]. Combining the analysis of the trapping experiments with ESR characterisation, it can be safely come to a conclusion that h^+ , •OH and •O₂⁻ are the main active species in the photocatalytic process.

The band structures of the photocatalyst can be calculated according to the following equation:

$$E_{VB} = X - E_e + 0.5E_g$$
 (3)

 $E_{CB} = E_{VB} - E_g$ (4)

Where, X is the absolute electronegativity of the semiconductor, Ee

means the free electrons energy on the hydrogen scale (ca. 4.5 eV) and E_g means the bandgap energy. The E_g value for BiOIO₃ is about 3.13 eV. Consequently, the VB and CB for BiOIO₃ are estimated to 4.10 eV and 0.97 eV (vs NHE), respectively. According to the same way, the LUMO potential and the HOMO potential of UiO-66(Zr) is determined as -0.6 eV and 2.9 eV, respectively. The Eg is estimated to 3.50 eV, which are consisted with the previous report [34,36]. The photogenerated holes may possess higher oxidizing ability as result of the relatively positive level VB potential [33]. It should be noted that the CB potentials of UiO-66 and BiOIO₃ are -0.6 eV and 0.97 eV (vs NHE), correspondingly. On the basis of Nernstian behaviour in aqueous solution, the band edge positions were plotted as a function of the pH solution vs. NHE [37]. The calculated band-edge position for BiOIO3 and UiO-66 perhaps shift to more negative potential (0.56 eV and -1. 01eV) under the photocatalytic reaction experiment (pH \sim 7). The CB potential of UiO-66 was more negative than the standard reduction potential of $O_2/\bullet O_2^-$ ((E₀ $(O_2/\bullet O_2^-) = -0.33$ eV vs. NHE); the excited electrons of UiO-66 can directly reduce molecular oxygen to $\bullet O_2^-$. The VB potential of BiOIO₃ (4.10 eV) may be shift to 3.69 eV (pH \sim 7), which was more positive than the standard oxidation potential of $\bullet OH/H_2O$ (E₀ (H₂O/ $\bullet OH$) = 2.4 eV vs. NHE) [31]; the excited holes can oxidize the adsorbed H₂O molecules to \bullet OH. Also, the induced h^+ in the VB of BiOIO₃ can directly oxidize RhB.

On account of the above mentioned, a plausible photocatalytic mechanism of the UiO-66@BiOIO3-50 composite is proposed and displayed in Fig. 13. Under light irradiation, excited electrons can be migrated from the CB of UiO-66 to that of BiOIO₃. At the same time, the electrons retained on the CB of UiO-66 can reduce the oxygen to form $\bullet O_2^-$. Meanwhile, the holes generated by BiOIO₃ VB can be transferred to the VB of UiO-66. Water molecules also trap the holes to produce •OH. In summary, both $\bullet O_2^-$ and h^+ , as well as $\bullet OH$, are all favourable for the decomposition of RhB. The enhanced photocatalytic property of the UiO-66@ BiOIO₃-x composites is attributed to the existence of energy band cross between UiO-66 and BiOIO₃, improving the transfer efficiency of electrons and holes at the interface and then enhance the photocatalytic performance. This conclusion could be further verified by the photoluminescence (PL) spectra of the as-prepared samples at 360 nm excitation wavelength (Fig. 14). Obviously, the PL emission intensity of UiO-66@ BiOIO₃-x composites was weaker than that of pure BiOIO₃ and UiO-66, which indicates the higher separation efficiency for the UiO-66@ BiOIO3-x composites. This result demonstrates that the separation efficiency of the electron-hole pairs can be promoted with the formation of heterojunction structure.

4. Conclusion

UiO-66@BiOIO₃-x composites have been successfully prepared by a hydrothermal route. The photocatalytic performance of the as-prepared UiO-66@BiOIO₃-x composites was estimated by the decomposition of RhB and TC as well as the oxidative removal of gaseous Hg⁰. Importantly, UiO-66@BiOIO₃-x composites (x = 30 and 50) exhibited similar photocatalytic performance and displayed excellent activity, which is higher than that of UiO-66 and BiOIO₃ samples. The improved photocatalytic activity could be attributed to the boosted separation efficiency of the photogenerated carriers. The results prove that UiO-66 can be used as an excellent substrate in the photocatalysis. This study provides a new route for exploring excellent efficient and stable photocatalysts in many fields.

Credit author contribution statement

- Xuemei Qi: Conceptualization, Methodology, Writing-original draft, Investigation.
 - Qiang Wu: Data curation, Reviewing and Editing. Xiaojian Wang: Supervision. Kexuan Li: Supervision, Validation.



Fig. 13. Schematic illustration of the proposed photocatalytic mechanism.



Fig. 14. Photoluminescence (PL) spectra of the as-prepared BiOIO₃, UiO-66 and UiO-66@BiOIO₃-x composites.

Can Liu: Resources, Validation. **Shiji Li:** Supervision, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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