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Graphene-like boron nitride modified bismuth phosphate materials for boosting photocatalytic degradation of enrofloxacin

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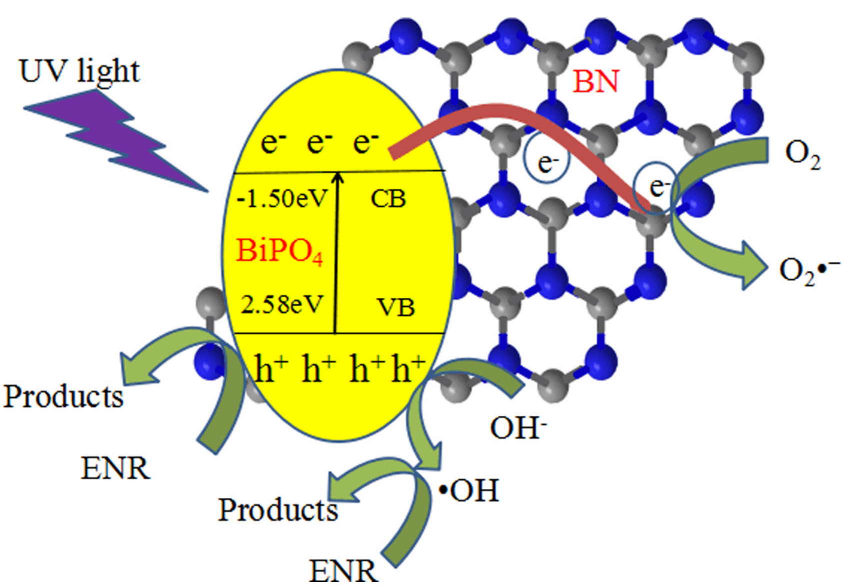
GRAPHICAL ABSTRACT

Graphene-like BN has been employed to modify the $BiPO_4$ to acquire higher photocatalytic activity for the removal of enrofloxacin.



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ABSTRACT

A novel graphene-like BN modified $BiPO_4$ material was prepared for the first time via a simple solvothermal process with the assistance of reactable ionic liquid 1-decyl-3-methylimidazolium dihydrogen phosphate ([Omim]H_2PO_4). The as-prepared photocatalyst was characterized by XRD, FT-IR, Raman, XPS, TEM, DRS, BET, PL, EIS and ESR to investigate the structure, morphology, optical property, surface area, electrical property and active species. The photocatalytic activities of graphene-like BN/$BiPO_4$ materials were evaluated by the degradation of antibiotic enrofloxacin (ENR) under UV light irradiation and the 1 wt% graphene-like BN/$BiPO_4$ displayed the best activity among the BN/$BiPO_4$ composites. The enhanced photocatalytic activity for the removal of enrofloxacin was attributed to higher separation efficiency of

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photogenerated electron-hole pairs, and the generated more $O_2\cdot^-$ and $\cdot OH$ radicals when the BN was modified on $BiPO_4$. Moreover, a probable degradation mechanism was proposed for the improved photocatalytic activity of BN modified $BiPO_4$.

1. Introduction

A range of medicinal materials exists in the environment and their threats have caused special attention [1]. Among these drugs, antibiotics such as fluoroquinolones (FQs) were under intensive study for being regarded as emerging micro-pollutants [2]. Enrofloxacin (ENR), a kind of FQs, was widely applied in the treatment of various infections for animals because of the broad-spectrum activity of ENR against a large amount of pathogenic gram-negative and gram-positive bacteria by selectively inhibiting bacterial DNA synthesis [3,4]. Microscale of enrofloxacin has been found in animal manure may threaten the environment of soil and water [5]. Although the pollutant could be removed in sewage treatment plants, it still persisted in the residual sewage sludge after anaerobic digestion, and then it was transferred to soil which caused secondary pollutants or regarded as fertilizer for plants, creating a risk for health when the plants were used for human consumption [6–10].

Recent years, two-dimensional graphene-like structure materials have aroused massive research interest thanks to their fascinating properties [11–15]. For the photocatalysis field, some graphene-like structure materials have been employed for displaying outstanding photocatalytic activity or been able to enhance the photocatalytic activity of the other semiconductor materials [16–23]. For example, graphene-like carbon nitride (g-C_3N_4) nanosheet has been successful prepared by Niu et al. and displayed advanced photocatalytic hydrogen evolution activity [16]. Dong et al. found that new porous graphene-like carbon nitride ($C_6N_9H_3$) showed excellent ability for NO removal [18]. The fewer layered MoS_2 has been employed to enhance the photodegradation efficiency by coupling with semiconductors such as BiOBr [17], Ag_3PO_4 [19], Ag_3VO_4 [23], and C_3N_4 [22]. Xu et al. has successfully prepared the graphene-like Co_3S_4/Ag_2S which displayed higher photocatalytic activities than the pure Co_3S_4 and Ag_2S under visible light irradiation [21]. These results indicated that the graphene-like structure materials may exhibit superior photocatalytic activity when compared with their bulk counterpart or could serve as effective co-catalysts to boost the photocatalytic activity of primary photocatalysts. By insteading the C atoms of the graphite with B and N atoms, the layered boron nitride (BN) can be obtained with remarkable properties [24,25]. Recent researches have found that when the thickness of BN decreased to few layers, the obtained graphene-like BN could also acted as effective co-catalyst for photocatalysis. Several reports of graphene-like BN based material have been prepared such as BN/WO_3 [26], BN/Ag_3VO_4 [27], BN/BiOBr [28] and the results suggested the introduction of graphene-like BN could effectively promote the visible photocatalytic activity for the degradation of pollutants. However, the relevant information regarding the graphene-like BN based photocatalysts has seldom been reported and no information for the improved photocatalytic activity of antibiotic removal has been reported. It is desirable to construct more efficient graphene-like BN based materials for photocatalytic enrofloxacin removal.

Bismuth phosphate ($BiPO_4$), as a highly efficient oxyacid-type photocatalyst, was first reported by Zhu's group in 2010 owing to its superior activity than P25 (TiO_2) at some aspects [29]. For instance, $BiPO_4$ showed 1–2 times higher photocatalytic activity for the removal of organic pollutant and no deactivation was found during the circulation processes [29–32]. Different methods have been utilized to obtain $BiPO_4$ photocatalyst, such as solvothermal reaction [33], microwave synthesis [34], electrospinning method [35], hydrothermal reaction [29,30] and high temperature hydrolysis [36]. Previous literatures synthesized many $BiPO_4$ based composites, compared the photocatalytic activity and discussed their properties. Pan et al. synthesized the C_3N_4-$BiPO_4$ hybrid photocatalyst to enhance photocatalytic performance towards methylene blue dye degradation [37]. Gawande et al. fabricated graphene@$BiPO_4$ nanocomposite by a simple microwave assisted hydrothermal method to degrade phenol [38]. However, seldom systems have been reported for the antibiotic enrofloxacin removal. Considering the superiority of graphene-like BN and $BiPO_4$, it may further improve the photocatalytic activity by adopting appropriate method to coupling BN with $BiPO_4$. To the best of our knowledge, there has been no report regarding graphene-like BN modified $BiPO_4$ materials or their applications for environment pollutants treatment.

In this study, graphene-like BN modified $BiPO_4$ materials have been prepared for the first time via ionic liquid ([Omim]H_2PO_4) assisted solvothermal method. A series of characterizations were employed to explore the structure, morphology, surface area and photocatalytic performance. The as-prepared graphene-like BN/$BiPO_4$ materials have been demonstrated to display enhanced UV light photocatalytic activity for the degradation of ENR. The possible mechanism for higher photocatalytic activity of the graphene-like BN/$BiPO_4$ was proposed and the main active species were determined.

2. Experimental

2.1. Materials and photocatalyst synthesis

The following chemicals used in this study were analytical grade without further purification. Ionic liquid 1-decyl-3-methylimidazolium dihydrogen phosphate ([Omim]H_2PO_4) was purchased from Shanghai Chengjie Chemical Co. Ltd. Enrofloxacin (ENR), $Bi(NO_3)_3\cdot 5H_2O$ and ethanol were selected from Aladdin industrial corporation, Sinopharm, respectively.

The graphene-like BN was synthesized via calcination with a mixture of boric acid and urea in the mole ratio of 1:24. The white solid was emerged by heating the mixture which was dissolved in 40 mL distilled at 80 °C. Then calcining the above solid at 900 °C for 5 h under nitrogen atmosphere to obtain the graphene-like BN [28,39].

The detailed preparation procedure of graphene-like BN/$BiPO_4$ powder was as follows. 2 mmol [Omim]H_2PO_4 which contains several mass ratios (0, 0.5 wt%, 1 wt%, 2 wt%) of graphene-like BN was immersed in 18 mL ethanol. 1 mmol $Bi(NO_3)_3\cdot 5H_2O$ was added into the above solution under ultrasonic and the suspension was obtained after stirring for 30 min. The above suspension was then transferred to a 25 mL Teflon-lined autoclave and kept at 160 °C for 24 h in oven. After the autoclave was cooled to room temperature, the products were washed with distilled water and ethanol for three times and dried at 60 °C overnight.

2.2. Characterization

The crystal structures and phase data for the photocatalysts were determined by X-ray diffractometry (XRD) on a Shimadzu