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$BiOBr_xI_{1-x}$/BiOBr heterostructure engineering for efficient molecular oxygen activation

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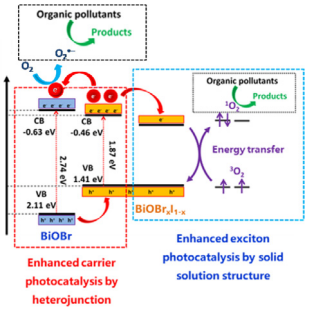
HIGHLIGHTS

- # $BiOBr_xI_{1-x}$/BiOBr heterostructure was in-situ synthesized.
- # $BiOBr_xI_{1-x}$/BiOBr showed effective activity for wastewater treatment.
- # Exciton and carrier photocatalytic processes was found.

GRAPHICAL ABSTRACT

The both enhanced excition and carrier photocatalysis of $BiOBr/BiOBr_xI_{1-x}$ resulted efficient molecular oxygen activation for oilfield waste water treatment and organic pollutants (BPA, RhB and phenol) photodegradation.



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ABSTRACT

The $BiOBr_xI_{1-x}$/BiOBr heterojunction structural photocatalyst was constructed successfully in this work and it was formed by the $BiOBr_xI_{1-x}$ solid solution coupling with the BiOBr monomer, which was determined by efficient characterizations. For the photocatalytic property, The $BiOBr_xI_{1-x}$/BiOBr could degrade some organic pollutants efficiently and the oilfield produced waste water treatment efficiency of it was ideal. The reason for its enhanced photocatalytic property was also explored. Through ESR tests, trapping experiments and other efficient methods, the enhanced molecular oxygen activation capacity of induced $^1O_2$ and $O_2^{\cdot-}$ photogeneration by $BiOBr_xI_{1-x}$ solid solution structure and heterostructure in one photocatalyst was confirmed, respectively. This work provided a new thought for enhanced molecular oxygen activation capacity of bismuth oxyhalide photocatalysts.

1. Introduction

Photocatalysis has been recognized as an efficient technology for environmental remediation [1-4]. The species to which oxygen transformed with high reactivity are generally regarded as reactive oxygen species (ROS), which can degrade the organic pollutants non-

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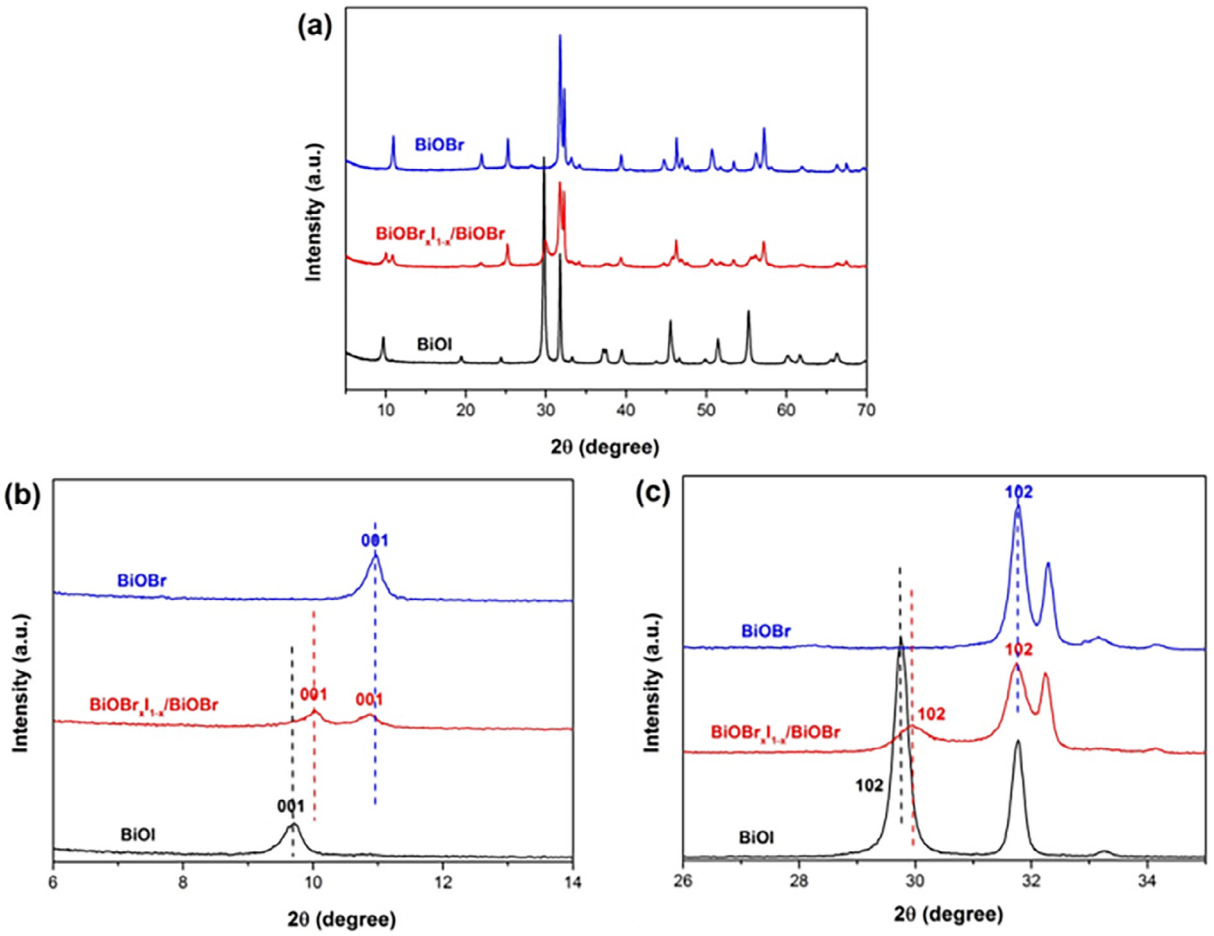

Fig. 1. . XRD patterns of BiOBr, $BiOBr_xI_{1-x}$/BiOBr and BiOI: (a) 5-70°, (b) 6-14°, and (c) 26-35°.

selectively. So, superior photocatalytic degradation performance of a photocatalyst usually depends on the amount and type of the photogenerated ROS, which is also called molecular oxygen activation capacity. In additional, the analysis of the ROS is also important for understanding the photocatalytic mechanism. While, the ROS speciationability is usually determined by the molecular oxygen activation of the photocatalysts. Photocatalysts with high quality can possess excellent molecular oxygen activation capacity under light illumination [5,6]. Therefore, improving the activation capacity of molecular oxygen has become an important factor that should be considered when designing the photocatalytic materials [7,8].

As a kind of efficient strategies for enhanced molecular oxygen activation capacity, forming modified structural photocatalysts have been reported in many researches. Herein, we intend to take bismuth oxyhalide (BiOX (X = Br and I)) as the basic material for further improving the photocatalytic molecular oxygen activation under visible light [9]. In view of the BiOX, the enhanced molecular oxygen activation capacity can be reached by forming solid solution structure and heterostructure according to previous reports [10,11]. In general, through the efficient measurement of the $O_2^{\cdot -}$, more generation of the $O_2^{\cdot -}$ indicates the enhanced molecular oxygen activation capacity by carrier photocatalysis. Besides the $O_2^{\cdot -}$, it has been verified that exciton photocatalytic process of BiOBr photocatalyst also occurred, which was confirmed by the generation of the singlet oxygen ($^1O_2$) [12-14]. In our previous work, we had demonstrated that the exciton and carrier photocatalysis could be enhanced by forming $BiOBr_{0.5}I_{0.5}$ solid solution and BiOBr/BiOI heterojunction, respectively. The enhanced molecular oxygen activation capacity under visible light was approved by the characterizations of the amount and type of the ROS. More $^1O_2$ generated by $BiOBr_{0.5}I_{0.5}$ solid solution and more $O_2^{\cdot -}$ generated by BiOBr/BiOI heterojunction illustrated the enhanced molecular oxygen activation capacity of these two photocatalysts, respectively [15]. Therefore, the molecular oxygen activation capacity can be improved by the modified structures formation of the BiOX (X = Br and I). If the solid solution and heterojunction structures are formed in one BiOX photocatalytic material at the same time, the molecular oxygen activation capacity might be further enhanced. There are many reports for the $BiOBr_xI_{1-x}$ solid solution and BiOBr/BiOI heterostructure, respectively [16,17]. However, a photocatalyst formed by BiOX monomer coupled with the $BiOBr_xI_{1-x}$ has been rarely researched.

Bearing this mind, we firstly in-situ synthesised the $BiOBr_xI_{1-x}$/BiOBr photocatalyst. Through the efficient characterizations we determined the photocatalyst was formed by $BiOBr_xI_{1-x}$ and BiOBr. Through the ESR tests we intuitively confirmed the enhanced molecular oxygen activation ability for both $O_2^{\cdot -}$ and $^1O_2$. Due to the enhanced molecular oxygen activation capacity of $BiOBr_xI_{1-x}$/BiOBr, the ideal efficiency of organic pollutants degradation and oilfield waste water treatment had been achieved. The photocatalytic mechanism of the improved molecular oxygen activation capacity of $BiOBr_xI_{1-x}$/BiOBr was also explored and explained. This work provided a new thought for enhanced the molecular oxygen activation ability of bismuth oxyhalide photocatalysts.

2. Experimental

2.1. Materials

$Bi(NO_3)_3{\cdot}5H_2O$, KBr, KI, ethylene glycol (EG) were of analytical