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Unique layered structured bismuth oxyhalides photocatalyts : A review on photocatalytic performance

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ABSTRACT

Bismuth–based semiconductors (e.g. Bi_2O_3, Bi_2WO_4, $BiVO_4$, $Bi_2O_2CO_3$, BiOX, $BiOIO_3$) have captivated much recognition for their promising application in environmental remediation because of having many properties, such as resistant to photocorrosion, chemical stability, non-toxicity and the most important is superior photocatalytic performance under UV and visible light irradiation. Bismuth oxyhalides, namely BiOX (X=Cl, Br, I) have recently emerged as potentially more effective alternative in the photocatalytic field to the traditional TiO_2 based photocatalysts due to the interesting structure dependent photocatalytic performance that arises from their unique layered structure mediated with $[Bi_2O_2]$ slabs and double halogen atom slabs. Small band gap of BiOX (BiOI- 1.76eV and BiOCl- 3.19eV) than TiO_2 allows it to function near UV and under visible light sources. The intrinsic layered structure creates a strong electric field resulting from the asymmetric charge distribution between the halogen anionic layer and $[Bi_2O_2]$ positive layer both of which facilitates reduction in recombination probability of photo-induced electrons and holes and benefits in displaying enhancement in photocatalytic activity. This review gives an overview of various bismuth oxyhalides, different strategies used for engineering BiOX to improve their photocatalytic activity. This also studies possible mechanism on activity enhancement and details of organic pollutants degraded using bismuth oxyhalides.

Keywords: Bismuth oxyhalides, mechanism, organic pollutants, photoactivity enhancement, unique layered structure

I. INTRODUCTION

Industrial harmful waste products accumulation poses a great deleterious threat to people's health and their surroundings [1, 2]. Over the past years, many methods have been practised for remediation of toxic water

pollutants such as solvent extraction, chemical oxidation, filtration, floatation and photocatalytic degradation. Among these strategies, photocatalytic degradation technology using semiconductor material as photocatalyst is most effective owing to its low-cost, simplicity and efficacious efficiency to degrade organic contaminants [2]. Since 1972, TiO_2 mediated photo-induced water splitting experimentation, by Honda and Fujishima, semiconductor derived photocatalytic processes have drawn widespread recognition in research and industrial work [3].

Besides the most explored photocatalysts like TiO_2 and ZnO, bismuth based semiconductors are less studied. But, Bi based semiconductor materials have emerged as promising photocatalyst due to their low toxicity, earth abundance, strong visible light absorption ability and excellent photocatalytic activity [4, 5]. Among this class of semiconductors one finds BiOX (X=Br, Cl, F and I), $BiFeO_3$, Bi_2S_3, Bi_2WO_6, $BiPO_4$, $BiVO_4$, $BiMoO_6$ [6]. Most of above is that bismuth based oxides are influential under visible light through the alternation of location of valence band or altering the presence of Bi lone pair electrons as a result of interaction between 6s orbitals of bismuth and the 2p orbitals of oxygen [7]. Additionally the strategies such as phase and morphological control, doping, surface sensitization etc. can be adopted to the increase the photocatalyst performance [8].

Recently, bismuth oxyhalides BiOX compounds i.e layered bismuth based semiconductor have established a remarkable interest as effectual photocatalyst for degradation of aqueous dyes owing to their unique layered crystal configuration. Bismuth oxyhalides BiOX (X=F, Cl, Br, I) as a set of main group V-VI-VII ternary oxide compounds which can be applied as chemical catalysts, ferroelectric materials, and pigments [9, 10]. BiOX compounds have an open, layered crystal structure composed of positive $[Bi_2O_2]$ layers interleaved between two negative slabs halogen ions. The sandwiched layered structure builds an internal static electric field perpendicular to each layer, which facilitate effective separation of photoinduced charge carriers [11].

In this paper we propose anovel approach to deal with photocatalytic degradation of organic pollutants using unique layered bismuth oxyhalides. This review intend to overview strategies to modify structure, morphology and surface properties the bismuth oxyhalides to show better photocatalytic degradation efficiency. This review also considers the possible reaction mechanism followed during photocatalytic activity and also compiles the different pollutants studied.

II. PHOTOCATALYTIC DEGRADATION

2.1. Bismuth oxychoride (BiOCl) photocatalyst

Bismuth oxychloride has an indirect transition bandgap in the range of 3.2-3.5 eV, which is similar to that of TiO_2 [11]. BiOCl has anisotropic layered structures consisting of tetragonal $[Bi_2O_2]^{2+}$ layers sandwiched between two Cl^{-1} ion layers [11, 12]. However the band gap of BiOCl makes it useful under UV irradiation and limits its further application.To overcome this, more and more synthesis methods have been explored to degrade pollutants with high efficiency using BiOCl [13]. Most commonly applied methods for synthesis are hydro- and /or solvothermal, which require long preparation time, high temperature and /or toxic organic solvents. In addition to these, other methods used are sonochemical, electrospining and low –temperature chemical vapour

method which require complex equipment [14]. In other to resolve the shortcomings many researchers fabricated well-defined BiOCl nanostructures. For instance, He et al., modified conventional solvothermal method to a simple and environment friendly microwave-assisted method to prepare high-quality BiOCl nanoplates which exhibits high crystallinity and excellent photocatalytic activity under visible light [15]. Some researchers Sarwan et al., have proved that intrinsic BiOCl photocatalyst with oxygen vacancies can absorb visible light and exhibit excellent photocatalytic activity under visible light because of electron trapped by oxygen vacancies [16].

Many efforts have been develop to engineer band gap of BiOCl based photocatalyst by incorporating metal ions or coupling with other semiconductor. Ao et al., proposed p-n heterojunction between p-BiOCl and n-titanium phosphate with strong internal electric field which suppresses recombination of photo-generated charge carriers [17]. Li et. Al., synthesized three dimensional microspheres of bismuth oxychlorides because 3D hierarchical structures possess unique properties such as, improved light harvesting ability, faster infacial charge separation and more reactive sites as compared with 2D nanostructures. Wang et al., reported porous BiOCl microflowers assembled by ultrathin nanosheets exhibited higher photocatalytic activity under visible light through a photosensitization mode [18]. Table 1 includes the various bismuth oxychloride photocatalysts synthesized using different methods and detail of organic pollutants degraded. It also includes the photocatalytic efficiency shown by these semiconductor photocatalyts under UV and visible light irradiation [15-22].

Table 1

Summary of modified BiOCl photocatalysts mediated photocatalytic degradation of different organic pollutants

Photocatalysts	Organic pollutants	Preparation mode	Light irradiation	Photocatalytic degradation efficiency	References
Well defined stacked BiOCl nanoplates	Rhodamine B	Microwave assisted	UV	Followed zero order reaction kinetics. Exhibited strong absorption and photocatalytic activity with absorption capacity of 6.05-8.81 mg RhB/gBiOCl	[15]
Gray BiOCl nanocrystals	Methylene blue	Hydrolysis	Vis	Remarkable decrease in TOC. Gray BiOCl showed highest activity than white BiOCl	[16]
BiOCl nanoflower	Rhodamine B	-	Vis	Degradation rate 2.9 times than sample prepared without L-lysine	[14]

Single crystalline BiOCl	Cr(VI)	-	Laser beam	95% Cr(VI) reduction within short time of laser exposure in presence of BiOCl than compared with P25	[19]
Black BiOCl (plate –like)	Methyl orange	Facile Fe reduction route	Vis	Black BiOCl samples showed higher photocatalytic degradation than white BiOCl	[18]
Uniform BiOCl microspheres	Rhodamine B	Solvotherm al	Vis	3D BiOCl showed faster degradation rate than BiOCl sheets	[12]
BiOCl	Rhodamine B	Solvotherm al	Vis	BiOCl sample prepared in mixed glycol and acetic acid solution for 10 min shows high photocatalytic activity than P25	[20]
BiOCl nanowire arrays (Anodic aluminium oxide AAO, template)	Rhodamine B	Sol-gel	UV	100% degradation after 130 min	[21]
Er^{3+} doped BiOCl hierarchical microspheres	Rhodamine B	Facile solvotherm al	Vis	1.0 mol% Er^{3+} dosage BiOCl samples showed strong photocatalytic activity	[22]
Sheet shaped Yb^{3+} /Er^{3+} doped BiOCl	Rhodamine B	Hydrother mal	Vis	99.5% degradation efficiency in 20 min with 2.0% Yb^{3+} /0.5% Er^{3+} BiOCl sample	[1]
Fe,Nb-doped BiOCl	Rhodamine B	Low temperature	UV and Vis	Better degradation efficiency than BiOCl	[3]

BiOCl modified titanium phosphate nanoplates (BiOCl/TP) composite	Rhodamine B, brilliant red X-3B, methylene blue, ciprofloxacin	In-situ growth	UV	BiOCl/TP exhibited higher activity than pure TP	[17]
BiOCl/TiO_2 heterostructure composite	Rhodamine B	Modified sol-gel	Vis	BiOCl/TiO_2-70% mass ratio composite showed 11 times and 46 times higher activity than pure BiOCl and TiO_2	[11]

2.2. Bismuth oxybromide (BiOBr) photocatalyst

BiOBr has great importance as photocatalyst due high photocatalytic activity, intrinsic lamellar structure and photosatability. The band gap of BiOBr has been evaluated experimentally to be 2.91 eV. But the pure BiOBr has limited absorption ability to visible light for photodegradating organic pollutants [23, 24]. To enhance the photocatalytic performance of BiOBr, a number of different ways have been employed such as impurity doping, formation of semiconductor heterojunctions and surface metallization [25]. Up to now, Graphene/BiOBr, g-C_3N_4/BiOBr, Ag/BiOBr, Bi_2WO_6/BiOBr and TiO_2/BiOBr are different synthesized BiOBr-based heterostructures [26]. BiOBr can work in both UV and visible light irradiation and has been used to photodegradate a variety of organic contaminants polluting water such as microcystin-LR, methyl orange, phenol, rhodamine B, ciprofloxacin, guanine and tetrabromobisphenol A etc. [27]. A number of preparation methods employed for BiOBr includes solvothermal, hydrothermal, thermal photodeposition, double self-assemble and precipitation method [28-37]. Table 2 shows detail of BiOBr photocatalyst, pollutants degraded and their photocatalytic performance.

Table 2

Summary of modified BiOBr photocataysts mediated photocatalytic degradation of different organic pollutants

Photocatalysts	Organic pollutants	Preparation mode	Light irradiation	Photocatalytic degradation efficiency	References
BiOBr	Methyl orange	Solvothermal	Vis	Glycerol mediated BiOBr exhibited strong absorption and photocatalytic activity	[28]
BiOCl nanosquares	Rhodamine B	Hydrothermal	Vis	BiOBr+IL(ionic liquid)+BCA(ammonium	[29]

				bismuth citrate) exhibited excellent photocatalytic activity	
Flake-shape BiOBr	Ciprofloxacin	Hydrothermal	Vis	Better photodegradation as result of direct hole oxidation	[30]
Erbium (Er)-doped BiOBr	Ciprofloxacin	Solvothermal	Vis	3 wt% Er/BiOBr showed highest photocatalytic activity.	[31]
Boron-doped BiOBr	Rhodamine B and phenol	Facile solvothermal	Vis	0.075B-BiOBr possessed superior photocatalytic activity than pure BiOBr	[32]
BiOBr/$CoFe_2O_4$ microspheres	Congo red	Solvothermal	Simulated solar light	Superior absorption and transfer performance than pure BiOBr	[23]
Bi/BiOBr composites	Methyl orange	Facile one-step solvothermal	Vis	Bi/BiOBr composites with 5ml DMSO displayed highest degradation efficiency than pure BiOBr	[25]
Pt-BiOBr heterostructures	p-nitrophenol, tetrabromobisphenol-A	Hydro(solvo) thermal-photodeposition	Simulated sunlight and Vis	Higher photocatalytic activity with respect to P25	[33]
Novel Ti-doped BiOBr microspheres	Rhodamine B	Double self-assemble	Vis	Ti-doped BiOBr exhibited high photodegradation than BiOBr	[34]
N,S-codoped BiOBr	Rhodamine B	Facile solvothermal	Vis	More than 98% Rh B degradation within 60 min	[35]
Hybrid BiOBr-TiO_2	Rhodamine B	Facile one-pot solvothermal	Vis	High photodegradation shown by BiOBr-TiO_2-10 than pure BiOBr	[36]
Ag_3PO_4/BiOBr heterojunction	Rhodamine B	Simple precipitation	Vis	Exhibited better photocatalytic activity than BiOBr	[37]

2.3.Bismuth oxyiodide (BiOI) photocatalyst

The narrow bandgap of BiOI is 1.92 eV which make it one of most attractive visible light driven photocatalyst [38]. The dispersive band of BiOI photocatalyts provide multiple pathways for the excitation of electrons and hence contribute to high photocatalytic performance. But BiOI photocatalyst exhibits low photocatalytic efficiency due to high recombination of photogenerated charge carriers [39]. BiOI shows the photocatalytic performance in visible light and degrades organic pollutants such as bisphenol, rhodamine, tetracycline hydrochloride, methyl orange, phenol and acid orange II [40- 46]. Table 3 shows detailed BiOI photocatalyst with better photocatalytic activity.

Table 3

Summary of BiOI mediated photocatalytic degradation of different organic pollutants

Photocatalysts	Organic pollutants	Preparation mode	Light irradiation	Photocatalytic degradation efficiency	References
3D Hierarchical BiOI	Rhodamine B, bisphenol, tetracycline hydrochloride	Hydrolysis	Vis	$Bi_4O_5T_7$ exhibits highest photocatalytic degradation	[40]
Oxygen deficient BiOI	Methyl orange	Simple glycerol treatment	Vis	Deficient BiOI demonstrated 3.5 times higher photocatalytic performance	[41]
Plate-like BiOI	Methyl Orange	Template free direct hydrolysis	Vis	BiOI samples in acidic conditions shows excellent photocatalytic activity than P25.	[42]
Hierarchical structured BiOI	Phenol	Solid-state reaction with hydrolysis	Vis	BiOI-80 i.e prepared in 80 ml water showed stronger light absorption ability and photocatalytic activity	[43]
$BiOI/TiO_2$	Methylene blue	Hydrothermal	Vis	80%$BiOI/TiO_2$ exhibited 20 times greater degradation than pure BiOI	[44]
BiOI-reduced graphene oxide	Methyl orange	Hydrothermasl	Vis	85% degradation with rGO (4wt%) loaded BiOI photocatalyst	[45]

BiOI – MWCNT composites	Acid orange II	Solvothermal	Vis	Complete degradation with BiOI –MWCNT composites within 180 min.	[46]

Besides above, a number of visible light driven photocatalysts have been synthesized by fixing the composition of any two bismuth oxyhalides to prepare binary BiOX coupled systems such as BiOI/BiOCl, BiOBr/BiOI. For example, Wang et al., prepared xBiOI-(1-x)BiOCl by soft chemical method. The sample showed high photocatalytic activity under visible light irradiation for the degradation of methyl orange [47]. Sun et al., reported $BiOCl_xBr_yI_z$ (x+y+z=1) photocatalyst with band gap range from 1.9 eV to 2.2 eV synthesized using hydrolysis method and showed highly enhanced photocatalytic performance for the degradation of methyl orange under visible light irradiation [48].

III. MECHANISM

The possible photocatalytic mechanism for organic pollutant degradation involves illumination of bismuth oxyhalide photocatalyst under light irradiation which results in excitation of electron from the valence band(VB) to the conduction band(CB) and hence create electron-hole pairs. The photogenerated electrons accumulated on surface and react rapidly with molecular oxygen to form superoxide radicals. But in case of heterostructure, the electron in the conduction band (CB) of BiOX freely migrates to the other layer and hence prevents electron-hole recombination. The holes left in the valence band of BiOX react with water to generate large number of reactive hydroxyl radical, •OH. These hydroxyl and superoxide radical are the reactive species for degradation of toxic pollutants [42, 46].

IV. CONCLUSION

Bismuth oxyhalides exhibits superior photocatalytic performance under UV and visible light irradiation because of self-built internal electric fields in their special layered structure. BiOI and BiOBr semiconductor photocatalyst shows most of their application in visible light irradiation because their narrow bandgap than BiOCl semiconductor photocatalyst. In some cases, these novel class of bismuth based photocatalysts exhibits remarkable photocatalytic activity when compared with extensively employed Degussa P25. The study depicts solvothermal and hydrothermal synthesis of BiOX semiconductors in maximum.

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