

Synthesis of Bismuth Oxyhalides and Their Photocatalytic Activity

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Abstract

The present work demonstrates the degradation of dye pollutants present in water resource by synthesizing the photocatalysts Bismuth Oxyhalides (BiOX, X=Br, Cl). The Photocatalysts BiOBr and BiOCl was prepared by a facile solid state method and employed to study the phase structure, morphology and optical property via PXRD, SEM and UV-Vis spectroscopy. The photocatalytic activity of BiOBr and BiOCl was tested on the degradation of Rhodamine b (RhB) dye under the presence of UV and Visible light irradiation. The results showed that RhB do not get degraded under the presence of Visible light due to inadequate amount of energy. When UV light is irradiated RhB starts to degrade and after 60 to 70 minutes RhB degraded completely. Therefore Bismuth Oxyhalides are known as potential photocatalytic materials.

Introduction:

Water is the most valuable natural resource for existence of life on the Earth. Now a day's, Water pollution became severe problem on Earth because enormous amount of pernicious are added to water resource through dumping of wastage (Natarajan et al., 2016). To overcome from this Hazard, Now a day's several techniques like Reverse osmosis, Filtration, Adsorption, Sedimentation, Chemical and Biological treatments, Membrane filtration have been broadly used. Although result of this techniques are not satisfactory for waste water treatment which consists of various contaminants such as pharmaceutical wastes, pesticides, domiciliary chemicals. An alternative solution for this is "Photocatalysis technique" (*Towards Better Photocatalysts: First-Principles Studies of the Alloying Effects on the Photocatalytic Activities of Bismuth Oxyhalides under Visible Light - Physical Chemistry Chemical Physics (RSC Publishing)*, n.d.).

Photocatalysis is a well-known chemical process, as it is known for the complete eradication of toxic chemicals, toxic gas and water pollutants in the environment because of its effectiveness and simple application (Ameta & Ameta, 2016). Photocatalysis involves conversion of solar energy into chemical energy with fast progress in nanotechnology, a number of photo-sensitive metal oxides/sulphides/oxy halides etc., have been synthesized and used as photo catalysts for water purification by many groups (Zhou et al., 2018a).

Importance of Bismuth Oxyhalides:

Bismuth-based materials are less toxic, very abundant, and were proven to be very good photocatalytic material in the visible spectral region, particularly in the application of water purification. Bismuth-based materials become visible active due to the formation of favorable hybridized valence band between Bi 6s in Bi (III) and O 2p levels. Bismuth Oxyhalides, BiOX (X = Cl, Br, I), are the new kind of layered materials exhibiting excellent optical and electrical characteristic and are capable for various applications including photocatalysis. BiOX are a class of V-VI-VII ternary semiconductors, having matlockite structure, in which [X-Bi-O-Bi-X] layers are stacked and held by Vander Walls interaction through the halogen atom, whereas all the atoms within the layer are covalently bonded and this structure leads up to excellent electrical optical and mechanical properties. In each [X-Bi-O-Bi-X] layer, Bi atom is surrounded by four each of oxygen and halogen atoms resulting in asymmetric decahedral symmetry. Many variants are BiOX nanostructures such as nanosheets, nanobelts, nanofibers, nanowires, and nano-flowers have been synthesized using various chemical routes (Sharma et al., 2019).

Although, BiOX materials are proven to be the excellent photocatalysts, their photocatalytic behaviors highly depend on their structural characteristics like size, shape, dimensions, and crystal phases. Hence, achieving such BiOX material with remarkable photocatalytic attributes depends on the different methods of syntheses which are adopted to get the well-defined nanostructures such as one-dimensional, two-dimensional, three-dimensional, hierarchical, and



hallow nanostructures that result in suitable band structure to absorb radiation to initiate the photocatalytic reaction(Gondal et al., 2017).

Applications of Bismuth Oxyhalides:

Degradation of Dyes, Organic, Inorganic pollutants and Microorganisms:

One of the major applications of BiOX is their function as photocatalyst in the degradation of organic/inorganic pollutants and deactivation of the microorganisms present in the water and the degree of this photocatalytic activity is usually evaluated by degradation rate of pollutants or inactivation efficiency of pathogens. The most common pollutants present in drinking water are noble metallic ions like Cr^{VI} ; organic dyes like tetrabromobisphenol A, methyl orange and neutral red (NR); noxious gas like NO and 2-propanol; and pathogens like *Micrococcus lylae* and *Escherichia coli*.

Applications of XRD:

- XRD is a non- destructive technique.
- To identify crystalline phases and orientation.
- To determine structural properties, lattice parameters strain, grain size.
- To measure thickness of thin film and multilayer.
- To determine atomic arrangement.
- Obtain XRD pattern.
- Measure d- spacing.
- Obtain integrated intensities.

Photocatalysis:

The photocatalytic activities of BiOBr and BiOCl compounds were measured by examining the degradation of Rhodamine B dye under visible-light, in each experiment, about 10 mg of photocatalysts was added into 25 ml of Rhodamine B solution with a concentration of 5 ppm. Prior to Visible illumination, the suspensions were magnetically stirred in the dark for 30 minutes to ensure an adsorption-desorption equilibrium. Then, the stable aqueous dye solution was exposed to visible light for 150 minutes. During the photoreaction, about 1.5 ml of suspension was collected at different time intervals and centrifuged to remove the catalyst. The transparent solution was analyzed using a UV-Vis spectrophotometer, and the absorbance was measured at a wavelength of 554 nm, which corresponds to the maximum absorption wavelength of Rhodamine B. According to Beers- Lamberts law, absorbance is directly proportional to concentration. Absorbance is almost same for all the dye solution collected at different intervals of time as shown in Fig-3.4.2. Therefore, the dye is not degraded because visible-light of energy is not sufficient. Further, UV-light is irradiated on dye solution and the dye solution was collected at different intervals of time (10 min) up to 70 min. The transparent solution was analyzed using a UV-Vis spectro-photometer, and the absorbance was measured at a wavelength of 554 nm, which corresponds to the maximum absorption wavelength of Rhodamine B. The absorbance value decreases with increase in time as shown in Fig-3.4.3 and Fig-3.4.4 and then finally reaches to very less value (approximately zero) which concludes that dye is successfully degraded.

The degradation efficiency (%) calculated by using formula:

$$\text{Degradation efficiency} = (1 - (A_t/A_0)) \times 100$$

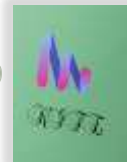
Where A_t and A_0 are the absorbance at time t and at initial time.

The degradation efficiency of BiOBr was found to be 94.52% and BiOCl was 96.80%.

CONCLUSION:

Bismuth Oxychloride and Bismuth Oxybromide are successively synthesized via facile solid state method using Ammonium Bromide, Ammonium Chloride and Bismuth trioxide. When comparing with other methods, it is simple, quick and inexpensive method involving simple steps of preparation.

PXRD, UV-Vis, SEM techniques were utilized to characterize the formed Bismuth Oxyhalides (BiOX X=Br, Cl).XRD data reveals the Phase purity of BiOBr and BiOCl and through XRD



data the structural parameters were refined by Rietveld method this results confirms that the compounds were crystallized in **tetragonal phase** with space group ***P4/nmm***.

SEM analysis provides the Plate-like morphology of BiOBr and BiOCl this verify that Bismuth Oxyhalides are layered semiconductors[X–Bi– O–Bi–X].

By UV-Vis spectroscopy analysis, the optical band gap of BiOBr=2.96eV and BiOCl=3.30eV was found. The band gap of BiOCl was greater than BiOBr so BiOBr is more preferable than BiOCl.

The Dye was not degraded in the visible light due to inadequate amount of energy which is required by electrons. But in the presence of UV-light the photocatalysis takes place and the dye was degraded completely. Therefore they are known as potential photocatalytic materials.

Reference:

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