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New efficient visible light photocatalyst based on heterojunction of BiOCl–bismuth oxyhydrate

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ABSTRACT

A novel active photocatalyst, which is a heteroconjuction of a bismuth oxyhydrate and BiOCl, has been synthesized by a simple hydrothermal method. The photocatalytic activity of the new material was measured in the degradation of Rhodamine B (RhB) and Acetophenone (AP) and in the photocatalytic oxidation of iodide in water under UV–vis and visible light irradiations respectively. The heterojunction between bismuth oxyhydrate and BiOCl provided exceptional photocatalytic activity, whereas both the individual bismuth oxyhydrate and BiOCl showed a negligible efficiency. Compared to Degussa P25, the new composite material demonstrated 5 times higher activity in removing aqueous RhB under visible light ($\lambda \geq 420$ nm) irradiation. The chemical composition and crystal structure were investigated using powder X-ray diffraction, scanning and transmission electron microscopy, and thermal methods. The preliminary study has revealed the bismuth oxyhydrate has tetragonal crystal structure with unit cell parameters $a = b = 5.674$ Å, $c = 10.353$ Å, unit cell volume $V = 333.3$ Å^3 and possible P4/mmm (No. 123) space group. Temperature behavior of new photocatalyst has been investigated. It was found that at heating to 550 °C for 45 min the new phase transforms into well-known monoclinic Bi_2O_3.

1. Introduction

The development of visible light induced photocatalysts is of great importance for the efficient utilization of solar energy or indoor artificial light in the photocatalytic degradation of organic pollutants and splitting of water [1,2]. TiO_2 has proven to be the most effective photocatalyst for the oxidative decomposition of numerous compounds. However, its photocatalytic activity in visible light is extremely low due to its wide band gap (3–3.2 eV) that limits its further applications in the visible region, thus making impractical overall technological process based on TiO_2 [3,4].

Nowadays, two strategies have been employed in the design of visible-light-driven photocatalysts. First strategy employs modification of TiO_2 by doping or by producing heterojunction between TiO_2 and another material (that is making the interface between the semiconductors with unequal band gaps as opposed to a homojunction). Doping by foreign elements is one of the most successful ways to alter the structure of the host semiconducting material and improve its properties. For example, doping by nitrogen or transition metal cations was used to extend the optical absorption of TiO_2-, ZnO- and Bi_2O_3-based systems to visible-light region and to improve their photocatalytic properties and structural stability [5–20]. The second approach involves exploration of novel semiconductor materials capable of absorbing visible light [21]. Chemical compounds containing Bi(III), such as $BiVO_4$ [22], Bi_2WO_6 [23], $CaBi_2O_4$ [24], $PbBi_2Nb_2O_9$ [25], $Bi_4Ti_3O_{12}$ [26], and others [27–29] have been reported to be promising photocatalysts under visible light irradiation.

Recently, bismuth oxyhalides also have been established as effectual photocatalysts for the degradation of aqueous dyes under UV irradiation [30–35]. Bismuth oxyhalides can be applied as chemical catalysts [36,37], ferroelectric materials [38,39], and pigments [40]. Bismuth oxychloride is one of the simplest members of the Sillen family phases which is expressed either as $[Bi_2O_2][Cl_m]$ or $[Bi_3O_{4+n}][Cl_m]$ ($m = 1 \div 3$) where bismuth oxide based fluorite-like layers, $[Bi_2O_2]$ or $[Bi_3O_{4+n}]$, are inter-grown with double chlorine layers [41]. Bi-based oxychlorides have drawn considerable attention due to their potential application as novel photocatalysts owing to their unique layered structures and high photocorrosion stability [42–45]. BiOCl was the first oxyhalide to be used as photocatalyst [30]. Many routes have been applied to synthesize these compounds. Zhang et al. prepared BiOCl powders by acid hydrolysis of Bi_2O_3 in excess HCl and reported the photocatalytic activity for Methyl Orange degradation under UV light to be higher than Degussa P25 (TiO_2) [41]. Wang and co-workers reported the photocatalytic degradation of RhB over BiOCl and Bi_2O_3 nano-fibers obtained by electrospinning [45]. However, BiOCl is a wide band gap (indirect 3.46 eV) semiconductor with a band gap higher than

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