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A green approach for degradation of organic pollutants using rare earth metal doped bismuth oxide

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ABSTRACT

Much effort has done for the development of novel semiconductor photocatalyst with enhanced visible light photocatalytic activity. Bismuth based oxide have attracted significant attention in the field of photocatalysis due to its narrow band gap hence, harvest more visible light. Therefore, a strategy for the design of efficient heterogeneous semiconductor photocatalyst is propose. In this connection, we have synthesized the modified bismuth trioxide using sol gel method with excellent photocatalytic activity for degradation of three different organic dyes. The fabricated samples were characterized by using standard analytical techniques, such as XRD, SEM, TEM, BET, PL and UV–vis/DRS spectroscopy. All doped-Bi_2O_3 photocatalysts exhibit higher photodegradation of dyes as compared to pure Bi_2O_3 under visible light illumination, while the highest efficiency was found at 3.0% La doped Bi_2O_3 and 1.2 g L^{-1} dose. The enhanced photocatalytic activity of modified Bi_2O_3 photocatalyst can be ascribed predominantly due to their improved visible light absorption property and efficient charge separation. The photodegradation of dyes follow pseudo first-order kinetic in the presence of synthesized materials. Furthermore, the fabricated rod can be reused with little loss in photocatalytic efficiency. The results of scavengers study suggest that holes, hydroxyl and superoxide radicals play a significant role for photodegradation of dyes. The modified bismuth based oxide approach will open new avenues for the development of efficient photocatalyst for environmental remediation and energy conversion.

1. Introduction

In the recent years, environmental destruction and energy shortage are the major problems worldwide. Therefore, a lot of studies have been done on semiconductor photocatalysts, which considered as a green technique employed for environmental remediation and solar energy conversion by utilizing sun light [1]. TiO_2, is one of the most popular heterogeneous semiconductor considered as an outstanding candidate and used as reference material in photocatalysis. However, the large band gap of TiO_2 (3.2 eV) and relatively high electron hole pairs recombination rate, limits its particle applications. Therefore, it is big challenge to scientific community to design an efficient visible light-induced photocatalyst. Recently, great efforts have been devoted for the extension of absorption spectra of semiconductor photocatalysts in to visible region for the better utilization of solar energy by band gap engineering through doping of various metal and non-metals or coupling with other semiconductors [2]. Another approach to find the narrow band gap semiconductor photocatalysts, which can work under visible light illumination. [3,4]. Bi_2O_3 has attracted growing attention due to many promising applications in gas sensing, solid oxide fuel cells, ceramic glass manufacturing, optical coating and catalysis [2]. Moreover, the bismuth oxide is a p-type semiconductor with a direct band gap of 2.8 eV with suitable band edge potentials for water oxidation leading to some reactive species which can initiate oxidation reactions [5]. The various shapes of Bi_2O_3 such as micro and nanostructure has been reported as good candidate for degradation of various dyes (rodamine B [6,7], methylene Blue [8], CBBG-250 [9], methylene orange [10], malachite green [11], etc) acetaldehyde [12], 4-chlorophenol [1], drugs [13], and gases [14]. Unfortunately, Bi_2O_3 exhibit low catalytic activity when used alone [15]. Since the lack of the ability of CB electron to reduce oxygen due to CB edge at (E_{cb} = 0.33 V vs NHE) resulting a fast recombination rate of the photo-excited electron and hole pairs. Many strategies have been employed for the development of visible light induced photocatalyst by designing the oxygen reduction sites on the semiconductor surface. Recently, a lot of work has been done to enhanced the photocatalytic activity of TiO_2 and ZnO

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photocatalyst by doping of rare earth metals such as La, Nd and Ce on the surface of TiO_2 and ZnO [16–19]. Considering these in mind, we expect that the doping of rare earth metal in to Bi_2O_3 could be a promising route for enhancing the visible light activity of Bi_2O_3. The rare earth metal ions have received much attention due to their unique d and f electron orbital structure. The doped Bi_2O_3 impart a different type of electron transfer process as compared to pristine Bi_2O_3 leading to improved electron hole pairs separation and thereby improving its photocatalytic activity [20]. Furthermore, the rare earth metal ions easily dissolve in to matrix of Bi_2O_3 due to comparable ionic radius size with bismuth ion, therefore, providing another efficient route for enhancing the photocatalytic activity [21–23].

The morphology, size and crystalline structure also have a great effect on photocatalytic activity of semiconductor photocatalyst. Therefore, from the last few years, a lot of interest has been devoted on the controlling the size, morphology and crystalline microstructure of materials. Different chemical methods has been reported for the fabrication of bismuth trioxide to achieve this goal. Among them, sol gel method is a facile, simple and cost effective method, which produce uniform size and shape powder, and considered as one of the most efficient approach [24–26].

In the present work, we report the fabrication of pure and La/Er doped Bi_2O_3 nanoparticles with a uniform morphology and good structural stability by using sol gel method. The photocatalytic activities of the as prepared material was tested by studying the degradation of targeted dye derivatives under visible light illumination as a function of illumination time.

2. Experimental

2.1. Reagents and chemicals

Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$) was taken from Otto India Pvt. Dyes derivative Acid Yellow 29 (AY-29), Coomassie Brilliant Blue G250 (CBBG-250), and Acid Green 25 (AG-25) used for the degradation study were obtained from Sigma-Aldrich. Nitric acid, (HNO_3, 98 wt%), sodium hydroxide (NaOH), surfactant (Triton-x) Potassium iodide (KI) and isopropanol (IPA) were obtained from Merck private limited Mumbai. The dopant precursors, Lanthanum nitrate hexahydrate and Erbiuum nitrate hexahydrate were obtained from Central drug house (CDH) New Delhi, India. Benzoquinone (BQ) was obtained from alfa aesar. The water used in all experiment was double distilled. All Chemicals were pure and analytical grade.

2.2. Synthesis of pure and doped Bi_2O_3 photocatalysts using sol–gel method

In this paper, we use sol gel method for the preparation of pure and modified bismuth trioxide nanoparticles. In a typical procedure, (0.97gm) of $Bi(NO_3)_3 \cdot 5H_2O$ bismuth nitrate pentahydrate and (0.1gm) surfactant were dissolved in 10 ml Nitric acid (1.12 mol/L in water) in a round bottom flask and magnetically stirred to form a homogeneous solution at room temperature. An aqueous solution of sodium hydroxide (100 ml, 0.2 mol/L) was added dropwise into the above solution to give white precipitate. Which was heated at 90 °C for 3 h, and then the colour of solution changed from white to yellow. The yellow precipitate was filtered and washed thoroughly with water and ethanol which was dried at 80 °C for 3 h to give pure bismuth oxide photocatalyst which was taken as reference to compare the photocatalytic activity with rare earth metal doped Bi_2O_3.

The bismuth oxide powder was doped with different concentration of Lanthanum and Erbium by adding a solution of known concentrations of Lanthanum nitrate hexahydrate varying from 0 to 4% and Erbium nitrate hexahydrate varying from 0% to 1.2% in sodium hydroxide solution. The schematic flow chart for the preparation of doped Bi_2O_3 is shown in Fig. 1. The formation of Bi_2O_3 nanoparticle by the sol–gel method generally undergoes solvation, hydrolysis and then transferred into Bi_2O_3 nanoparticles [27]. Bismuth nitrate ($Bi(NO_3)_3$ precursor was first solvated and then strongly hydrolysed in water where the formation of slightly soluble colloidal–gel of $BiONO_3$ Eq. (1) takes place and finally in the presence of sodium hydroxide $BiONO_3$ transformed into Bi_2O_3 Eq. (2).

$$(Bi(NO_3)_3 + H_2O \rightarrow Bi^{3+} + H_2O + NO_3^{-} \rightarrow BiONO_3 + 2H^{+} \quad (1)$$

$$2BiONO_3 + 2OH^{-} \rightarrow Bi_2O_3 + 2NO_3^{-} + H_2O \quad (2)$$

2.3. Characterization

The fabricated materials were characterized by standard analytical techniques such as UV–vis/DRS, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) Photoluminescence (PL) and Brunauer–Emmett–Teller (BET). The XRD analysis was carried out in the 2θ range of 20–60° using a wide-angle X-ray diffractometer (XRD, PANalytical) equipped with a Cu Ka radiation (1.54 A). The UV–vis measurements were made using Shimadzu UV–vis spectrophotometer (Model 1601) at room temperature. The morphology of the particles was examined using SEM analysis (JSM-6700F) with applied voltage of 2 kV and 3–8 mm working distance using conducting graphite block. TEM characterizations were carried out using JEOL JEM-2100F at an accelerating voltage of 80 kV. The Brunauer–Emmett–Teller (BET) was done using Belsorp Max.

2.4. Photocatalytic experiments

The photocatalytic performance of the prepared materials was tested by studying the degradation of three different chromophoric dye derivatives, such as AY-29, CBBG-250 and AG-25 in aqueous suspension. For irradiation experiment, an immersion well photochemical reactor made of Pyrex glass and a tungsten halogen linear lamp (500 W, 9500 Lumens) was used as visible light source. The lamp was poured inside a cylindrical reactor, which surrounded by a circulating water jacket for cooling during experiment. An aqueous solution of dye was taken in the reactor and required amount of photocatalysts (Bi_2O_3/doped-Bi_2O_3,) was poured into the reactor, which was sonicate in the dark for 30 min. The suspension was stirred and bubbled with atmospheric oxygen throughout the irradiation experiment. The zero time reading is taken for a blank solution kept in the dark, but otherwise treated similarly to the irradiated solution. Sample (5 ml) was collected at regular intervals during the irradiation and centrifuged before analysis to remove the photocatalyst. The degradation of dye derivatives was monitored by measuring the absorbance at their λ_{max} using UV–vis spectrophotometer.

The degradation% (η) was calculated by Eq. given below.

$$\eta = \frac{C_0 - C}{C_0} \times 100\% \quad (3)$$

Where C_0 is the initial concentration and C is concentration at time t.

3. Results and discussion

3.1. XRD analysis

The phase structure and purity of the as prepared material was investigated with the help of XRD. The XRD pattern of pure and modified Bi_2O_3 is shown in Fig. 2. It could be seen from the figure that the XRD patterns of pure and modified bismuth trioxide reveal the peaks related to the single monoclinic phase and indicate crystalline nature. The XRD patterns of modified trioxide showed no impurity peaks indicating that the products being in pure monoclinic phase. The metal ion concentration does not affect the crystal of Bi_2O_3. There are no characteristic XRD peaks related with La_2O_3 & Er_2O_3 in the doped materials. The average crystallite size of pure and modified Bi_2O_3 nanoparticles