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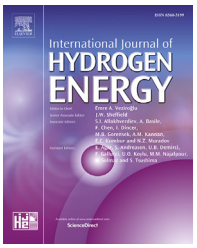

Solution combustion synthesis of heterostructure bismuth titanate nanocomposites: Structural phases and its correlation with photocatalytic activity

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ABSTRACT

Bi_2O_3/TiO_2 nanocomposites were prepared by simple and cost effective solution combustion synthesis route. The structural, textural, surface composition and optical properties of Bi_2O_3/TiO_2 solid solutions are influenced by the type of fuel, *viz.*, urea and glycine used in the combustion process and its concentration. The prepared materials were characterized by powder XRD, SEM, TEM, UV–vis, photoluminescence and N_2 adsorption study. The obtained materials were **evaluated** for the photocatalytic degradation of methylene blue and water splitting reaction for H_2 generation under visible light irradiation. The BT-5 sample **shows** high photocatalytic activity which may be due to the supressed recombination of photo-generated electron hole pairs and the appropriate lattice match by the formation of $Bi_4Ti_3O_{12}$-β-Bi_2O_3 p-n heterojunction phases.

Introduction

Development of visible light driven photocatalysis attracted attention of the scientific community worldwide on finding ways for more effective pollution abatement methods. Searching for efficient heterogeneous semiconductor photocatalyst which utilize visible light is a promising way to solve the environmental problem for water and air purification [1–4]. TiO_2 is a well-known photocatalyst which attracted the attention due to its potential application for the remediation of waste-water containing harmful impurities such as dyes and aromatic organics and removal of various toxic gases in air. The anatase phase of TiO_2 is known to be more active than rutile and brookite phases. The rapid recombination of photo-generated electron/hole pairs and the poor activation of TiO_2 by visible light, limit its activity to the UV range. To overcome these limitations, extensive efforts have been devoted to improve the performance of TiO_2 as a photo catalyst under UV light irradiation and to extend its absorption into the visible light region. The efficiency of TiO_2 can be increased by modification of its surface structure by making composites or by doping of selective metals and non-metals so as to increase its photo response towards visible light [5–11].

In recent years, besides TiO_2 many other catalysts with band gap energies lying in the visible region have also been examined for different photocatalytic reactions. Among them,

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Bi_2O_3 is an important photosensitizer with a direct band gap of 2.8 eV (p-type semiconductor) has attracted special interest due to its strong absorption in the visible light region [12–15]. Bismuth oxide (Bi_2O_3) in association with TiO_2 found to be excellent catalyst for decomposition of dyes as well as photocatalytic water splitting [16–25]. From the earlier finding, we observed that the doping/substitution of Bi species in the TiO_2 matrix could improve the photocatalytic activity of TiO_2, which was attributed to the increase in the efficiency of photoinduced charge separation [16]. **Bian et al.** reported Bi_2O_3/TiO_2 samples with ordered mesoporous structure exhibit high photocatalytic activity under visible light for dye degradation, although Bi_2O_3 **was remained** as a separate phase rather than incorporated into TiO_2 lattice (photosensitization effect of Bi_2O_3) [21].

Bismuth titanate is a large Bi–Ti–O family **that has drawn** much attention due to their several phases such as $Bi_2Ti_2O_7$, $Bi_4Ti_3O_{12}$, $Bi_{12}TiO_{20}$, $Bi_{20}TiO_{32}$ and $Bi_{24}Ti_2O_{40}$ depending upon synthesis condition [26]. Each phase exhibits unique electronic and optical properties. Recent reports suggest that bismuth titania based photocatalysts with different bismuth titania phases viz., $Bi_2Ti_2O_7$ [27], $Bi_4Ti_3O_{12}$ [28–30], $Bi_{12}TiO_{20}$ [31–33] would exhibit remarkable photocatalytic activity under UV as well as visible light irradiation for degradation of dyes. The Bi–O polyhedra in the bismuth titanate compounds were found to be active centers for photocatalysis [30,31]. Bismuth titanate based heterostructured photocatalysts such as $Bi_2Ti_2O_7$–TiO_2 [34], BiOCl–$Bi_4Ti_3O_{12}$ [35] and $Bi_2Ti_2O_7$–$Bi_4Ti_3O_{12}$ [36,37] have been reported to exhibit excellent photocatalytic activity. Remarkably higher photocatalytic activities exhibited by these hetero-structure compounds indicate the efficient electron-hole separation at the interfaces of two semiconductors. The phase selectivity of the bismuth titanate is governed by the synthesis conditions such as temperature and composition [37]. It is, therefore, interesting to see that bismuth titanate based heterostructured photocatalysts fabricated with the different structural phases would exhibit superior photocatalytic activity due to the well alloyed interface and the substantial lattice match between two phases.

In the present paper, we have synthesized Bi_2O_3/TiO_2 nanocomposites by adopting a very simple and cost effective solution combustion route. In addition to this, the effect of different organic species (used as fuels in the solution combustion route) and its concentration on the structural and textural properties of the bismuth titanate solid solutions is investigated. The fuels employed in the present investigation are urea and glycine which are more commonly used in the solution combustion synthesis, as they are readily available and inexpensive. The resulting bismuth titanate samples have been characterized by various physicochemical techniques. A systematic investigation of the different structural phases formed and their correlation with activity data were carried out for the first time in the literature.

Experimental

Preparation of Bi_2O_3/TiO_2 materials

Bi_2O_3/TiO_2 nanocomposite materials were prepared by solution combustion synthesis using urea and glycine as a fuel. The Bi_2O_3/TiO_2 mixed metal oxide samples prepared using urea as a fuel were designated as BT-1, BT-2 and BT-3 while samples prepared using glycine as a fuel were designated as BT-4, BT-5 and BT-6, respectively. In both the cases, the concentration of fuel is varied by increasing proportion with respect to metal ion concentration. The three series of samples were prepared by changing the metal to fuel mole ratio from 1:1:2, 1:1:4, 1:1:6 (Bi:Ti:Fuel) mole for the Bi_2O_3/TiO_2 samples. Titanium tetraisopropoxide (TTIP, Sigma-Aldrich) and bismuth nitrate (Sigma-Aldrich) were used as precursors for Ti and Bi source. In a typical synthesis of Bi_2O_3/TiO_2 nanocomposite samples, 6.06 g bismuth nitrate **pentahydrate (0.0125 mol)** was dissolved in 20 ml water and small amount of HNO_3 in a 250 ml glass beaker. 3.7 ml of TTIP **(0.0125 mol)** dissolved in water with required amount of HNO_3 is added to the bismuth nitrate solution followed by constant stirring for 5 min in order to have a well dispersion of the species ions in solution. **1.5 g** of urea **(0.025 mol)** dissolved in required amount of water and was added to the above solution and the beaker containing this mixture was introduced into a pre-heated muffle furnace at 450 °C. After few minutes the solution starts to dehydrate followed by ignition where fire is observed. This causes the generation of heat which eventually raises the temperature of furnace by 20–30 °C. The complete combustion of the precursors results into the final products Bi_2O_3/TiO_2 single or multiple phases and CO_2, H_2O and N_2 as byproduct of the combustion reaction [38].

Characterization

Powder X-ray diffraction (PXRD) patterns of a series of Bi_2O_3/TiO_2 samples prepared via solution combustion route have been collected within the 2θ range of 10–90° with step size of 0.02° on **Rigaku Miniflex** X-ray diffractometer with Cu source of X-rays (λ = 1.5406 Å). Powder X-ray diffraction is used for studying the structure of the crystalline materials, to identify bulk phases and to determine crystallite sizes. The N_2-adsorption BET surface area of the samples was measured on Quantachrome model NOVA surface area analyzer. The sample was first activated at 573 K to remove moisture and any other volatile matter. The UV–visible diffused reflectance spectra of all the samples were recorded on a Shimadzu model UV-2700 spectrophotometer, using barium sulfate as the standard. SEM micrographs of all the samples were recorded on a **JEOL-JSM-6360 scanning electron microscope** to study the morphology of the oxide particles. TEM micrographs were recorded on a Philips transmission electron microscope (Model CM 200) operated at an accelerated voltage of 20–200 **kV**. The photoluminescence (PL) spectra of the samples were recorded with a Perkin Elmer spectrofluorometer LS 55.

Photocatalytic decomposition of methylene blue

The photocatalytic degradation of methylene blue on Bi_2O_3/TiO_2 samples was carried out in a photoreactor made up of borosilicate glass using 400-W visible light lamp (Philips). 50 mg of photocatalyst sample was dispersed in 200 mL of 10 ppm aqueous methylene blue dye solution. The reaction mixture was first stirred for 30 min in the dark at room

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