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ORIGINAL ARTICLE

Preparation, characterization and photocatalytic properties of doped and undoped Bi_2O_3

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Abstract CuO-doped Bi_2O_3 and undoped Bi_2O_3 were prepared using tartaric acid assisted co-precipitation to be applied as nano-photocatalysts for shape controlling Al_2O_3 ceramics. The prepared powders annealed at 300 °C were characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), ultraviolet–visible absorbance spectroscopy (UV–vis) and photoluminescence (PL) spectrophotometry. According to the XRD results the undoped sample consisted of pure β-Bi_2O_3 while the doped one consisted of β-Bi_2O_3–$CuBi_2O_4$. The prepared Bi_2O_3 powders were characterized by band gap energy values ranging from 3.0 to 2.3 eV. The developed $CuBi_2O_4$ was characterized by band gap energy of 1.3 eV. Al_2O_3 ceramics were prepared using a modified polyol method. A marked variation in the microstructure of Al_2O_3 ceramics treated with the different prepared nano-photocatalysts was observed. This variation was referred to the free motions of photocarriers that were the backbone in varying the size, composition and morphology of the particles.

1. Introduction

In recent decades, semiconductor nano-photocatalysis has attracted increasing attention for the solar energy harvest and environmental remediation [1]. Among these semiconductors, bismuth trioxide (Bi_2O_3) and Bi-based oxides have been studied due to their unique properties like large band gap, high oxygen ion conductivity, remarkable photoconductivity and good photoluminescence properties [2]. Bi_2O_3 has been widely used in gas sensors, varistors solid oxide fuel cells, optical coating, electronic ceramics, optoelectronics equipment's, high temperature superconductors and catalysts [1,3–6]. Bi_2O_3 has five main polymorphic forms denoted by: α-Bi_2O_3 (monoclinic), β-Bi_2O_3 (tetragonal), γ-Bi_2O_3 (body centered cubic), δ-Bi_2O_3 (cubic) and ω-Bi_2O_3 (triclinic) [2,7]. Among these polymorphic forms β-Bi_2O_3 has the strongest absorption in the visible light region because it has the smallest band gap (~2.4 eV) and has demonstrated better photocatalytic performance than other phases [7,8]. As the photocatalytic activity of photocatalysts closely interrelates with their sizes, morphologies and microstructures, therefore it is highly desirable to fabricate both doped and undoped Bi_2O_3 with high activity and controllable morphologies that are cost effective and allow large scale production from the practical point of view [9–11].

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In line with the philosophy of green chemistry, an increase in demand was needed to replace the hazardous chemicals by more environmentally friendly alternatives [12]. So it was preferred to prepare Bi_2O_3, a non-toxic material [13], using green methods. Co-precipitation method could be considered as one of the methods that is easy to process, energy saving, environmentally friendly and cost effective as compared with the other methods [14]. There were several technical challenges for wide applications of photocatalysts, including: 1-catalyst optimization to improve quantum yield or to utilize visible light, 2-efficient photocatalytic reactor design and catalyst recovery/immobilization techniques, 3-better reaction selectivity [15]. Especially the practical applications were mainly restricted to photocatalytic water/air purification, hydrogen production from splitting water and high efficiency/low cost solar cells [16]. In the past decades, shape control of nanostructures has been proved extremely important because a wide range of physical and chemical properties of nanostructures depended primarily on their sizes and shapes [17]. The use of Bi_2O_3 as a green photocatalyst for modifying nano-ceramic microstructures has not been discussed before and I tried to spotlight on this new trend. In this study doped Bi_2O_3 with CuO and undoped Bi_2O_3 were prepared using tartaric-assisted co-precipitation technique and applied as photocatalysts for modifying the microstructure of Al_2O_3 ceramics. Al_2O_3 ceramics were prepared using a modified polyol method that is considered as one of the most important derivatives of sol–gel method and has the advantages of simplicity, low cost, relatively low reaction temperatures, and a green method [18]. The interaction of the different prepared photocatalysts with the prepared Al_2O_3 gel under UV light was investigated. A novel mechanism explaining this interaction was also interpreted.

2. Experimental section

2.1. Materials

All chemicals were of the highest purity available and were used as received without further purification; bismuth nitrate pentahydrate Crystal (($Bi(NO_3)_3.5H_2O$, ⩾99.9% Merck, Germany), cupric chloride dehydrate (($CuCl_2.2H_2O$), 98% May & Baker LTD, UK), Tartaric acid ($C_4H_6O_6$, 99% Adwic, Egypt), aluminum nitrate (($Al(NO_3)_3.9H_2O$, 99.5% pure crystal Ridel-de Haën, Germany), glycerol ($C_3H_8O_3$, 99.5% Genchem, China) and the solutions were prepared by using de-ionized water from the Millipore water purification system (18.2 MΩ).

2.2. Photocatalyst preparation

1 mol of bismuth nitrate pentahydrate was dissolved in tartaric acid solution having a molar ratio of (tartaric acid/distilled water: 2:100), respectively, where a white precipitation was formed. The precipitate was aged in its mother liquor at room temperature for 48 h. The aged precipitate was filtered and dried at 100 °C for 48 h then annealed at 300 °C for 3 h using a heating rate of 10 °C min^{-1}, where a yellow powder was obtained. The annealed powder was ground for 30 min using pestle and mortar. The doped powders were prepared by adding bismuth nitrate pentahydrate to cupric chloride dehydrate dissolved in tartaric acid solution taking in mind the stoichiometric ratio of bismuth nitrate pentahydrate to cupric chloride dehydrate as given in Table 1.

Once bismuth nitrate was added to cupric chloride/tartaric acid solution a pale blue precipitate of $Cu(OH)_2$ was formed over the white precipitate of $Bi(OH)_3$. The process was then followed in the same sequence used in the preparation of the undoped Bi_2O_3. The composition and abbreviation of the prepared powders are given in Table 1.

2.3. Al_2O_3 gel preparation

1 mol of aluminum nitrate $Al(NO_3)_3$ś$9H_2O$ was dissolved in an appropriate amount of glycerol. A viscous gel was formed and a complete dissolution of the added precursor occurred through stirring with gentle heating at 80 °C onto a hot plate for a 30 min. The obtained gel was aged for 24 h at room temperature.

2.4. Photocatalytic experiment

The prepared alumina gel was chosen for the photocatalytic applications of the prepared doped and undoped Bi_2O_3 powders. The photocatalytic experiment was carried out for the different prepared powders by adding 0.05 g of the photocatalyst to 10 ml of the prepared gel. It was then stirred in the dark for 30 min using an electrical vibrating system (Ika Vibrational) to attain adsorption–desorption equilibrium. A 125 W UV lamp was used as the light source for the different stirred gels that were exposed to this light for 5 h. Then the prepared gels were filtered and dried at 80 °C for 48 h, 150 °C for 10 h and 200 °C for 10 h then calcined at 400 °C for 3 h in air using a heating rate of 10 °C min^{-1}. After cooling to the room temperature, the calcined powders were ground in an agate mortar for 30 min then pressed into tablets at 20 kN. The different green compacts were thermally treated at 700 °C for 4 h in air using a heating rate of 10 °C min^{-1}. The abbreviations of Al_2O_3 compacts treated with the different prepared photocatalysts are given in Table 2.

2.5. Characterization

Different prepared powders were characterized using X-ray diffraction (XRD) (Philips X'pert multipurpose diffractometer) where the used X-ray tube is a copper-tube operating at 40 kV and 30 mA and the used wavelength is $K_{\alpha 1}$ with wavelength 1.54056 A°. The scan was performed over the range 2θ (10–70) degrees. The identification of the present crystalline phases was done using the Joint Committee on Powder Diffraction Standards (JCPDS) database card numbers.

Table 1 Composition and abbreviation of the prepared powders.

Sample	Composition/(Bi_2O_3:CuO)%	Abbreviation
Bi_2O_3:CuO	100:0	BC0
Bi_2O_3:CuO	99:1	BC1
Bi_2O_3:CuO	97:3	BC3
Bi_2O_3:CuO	95:5	BC5