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Synthesis, characterization and photocatalytic performance of visible light induced bismuth oxide nanoparticle

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ABSTRACT

Pure and doped Bi_2O_3 nanoparticles were synthesized by sol gel method. The synthesized nanoparticles were characterized by X-ray diffraction (XRD), UV–Visible Spectroscopy, Scanning Electron Microscopy (SEM), Thermogravimetry/Differential thermal analysis (TGA/DTA), potentiostat/galvanostat (CV), Electron-spin resonance (ESR) and Fourier transform infrared spectroscopy (FTIR). The XRD patterns of the fabricated Bi_2O_3 nanoparticles exhibited only the characteristic peaks of well crystallized monoclinic α–Bi_2O_3 and were in pure state. It was found that the crystallite size of doped Bi_2O_3 nanoparticles decreases with increase in dopant concentration up to certain limit and then decrease. The SEM image depicts that pure and doped Bi_2O_3 nanoparticles displayed nanorod like morphology; on doping the surface becomes rough. The UV–Vis absorption spectra of synthesized nanoparticles revealed that absorption edge shifts towards the longer wavelength after doping and it is highly beneficial for absorbing more visible light in the solar spectrum. FTIR spectra of doped Bi_2O_3 nanoparticles showed an additional absorption band. The photocatalytic performance of the as prepared photocatalyst was evaluated by degradation of three different organic dyes as a function of irradiation time.

1. Introduction

Photocatalysis is an important research topic due to its great application in environmental pollutant degradation, energy yield, conversion of photon energy into chemical energy [1]. Photocatalysis is a surface phenomenon and take place as the photogenerated charge carriers diffuse to the surface to initiate redox reactions [2–5]. But most semiconductor oxides photocatalyst generally have a wide band gap so active in UV light which restricts the industrial application under visible region by using 3–5% solar light. The recombination rate of electron–hole pairs relatively high, leading to a poor efficiency of photocatalytic reaction. The separation of photo generated charge carrier is the key factor for enhancing the photocatalytic activity of semiconductor photocatalyst [6]. So efficient surface traps are required to reduce the extant of charge carrier separation and reduced the recombination rate for greater photocatalytic activity and better performance. Therefore, the scientific community are looking for the development of visible light active photocatalyst in order to improving the photocatalytic activity of semiconductor either by doping of wide band gap semiconductor to trap the charge carriers or finding other semiconductor with lower band gap for better and larger contribution towards their practical application. Many oxide semiconductors, such as TiO_2, ZnO, CdS, SnO_2 and Bi_2O_3 etc. were used extensively as photocatalysts for photocatalysis purposes [7–13]. But these semiconductors have limitation suffering from the high photogenerated electron–hole recombination rate [15]. So numerous work has been done for enhance the efficiency of photocatalyst by introducing suitable traps at the surface. It can be done by doping of metal or non-metal ions at the surface of the base/bulk photocatalyst with the formation of heterostructures [16,17]. TiO_2, ZnO, WO_3, Bi_2O_3 or CdS are well investigated photocatalyst semiconductor [18,19]. Among various semiconductors a p-type Bi_2O_3 heterogeneous semiconductor was considered as one of the most efficient photocatalyst and important in modern solid state due to its unique structures and physical attribute like high refractive index, high oxygen-ion conductivity, dielectric permittivity and thermal stability, Bi_2O_3 is inert towards neutral water and possess band gap energy in the visible region (2.8 eV) can oxidise water and produce highly reactive species for initiating oxidation

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reaction for degradation of dyes, gases and drugs chemistry [20,21]. Bi_2O_3 is a super ionic conducting electrolyte material, which can be utilized in fuel cell devices such as solid oxide fuel cells [SOFC] [22]. Bi_2O_3 is a good oxide ion conductor due to the high ratio of oxygen vacancies, which can change chemical energy into an electrical energy. This ionic conductor electrolyte is used in high-temperature oxygen pumps and different gas sensors [23]. Pure Bi_2O_3 exists five polymorphisms: α-Bi_2O_3, β-Bi_2O_3, γ-Bi_2O_3, δ-Bi_2O_3, ε-Bi_2O_3 [24]. α-Bi_2O_3 transforms into δ-Bi_2O_3 at 729 °C, upon cooling δ-Bi_2O_3 transfer into β-Bi_2O_3 at 650 °C [24,25]. Among them, high-temperature δ-phase and the low-temperature α-phase are stable whereas β-Bi_2O_3, γ-Bi_2O_3 and ε-Bi_2O_3 forms are metastable [24]. Among all phases the band gap of the low-temperature α phase is [2.8 ev] and therefore found to be active in the visible region [26,27]. However, the photocatalytic activity of bare Bi_2O_3 is not so good as expected owing to rapid recombination of charge carries, photocorrosion, structural transformations and formation of bismuth carbonate, $(Bi_2O_2)CO_3$, during photocatalysis process [28]. Therefore, the pure Bi_2O_3 is not a suitable photocatalyst [29,30]. The photocatalytic activity of pure Bi_2O_3 can be improved by doping of rare earth, metal and transition metal oxides such as Nb_2O_5, Ta_2O_5, WO_3 lattice in order to separate the electron hole pairs and also extend the light response of the photocatalyst [31–36]. In addition very few works on metal doped Bi_2O_3 has been described in the literature [37]. Researchers [38] suggested that ions of rare earth metal have the ability to speed up the absorption of photogenerated electron–hole pairs during the photocatalytic reaction due to presence of special f electron orbital. Herein, we report the synthesis of pure and doped α–Bi_2O_3 nanoparticles by simple one pot sol gel method. The as prepared photocatalysts were characterized by standard analytical techniques such as X-ray diffraction (XRD), UV–Visible Spectroscopy, Fourier transform infrared (FTIR), Scanning Electron Microscopy (SEM), Thermogravimetry/Differential thermal analysis (TGA/DTA), potentiostat/galvanostat (CV) and Electron-spin resonance (ESR). The fabricated material was found to be active under UV as well as visible light illumination. Hence, photocatalytic activity of prepared photocatalyst was evaluated by degradation of three different model pollutant dyes in aqueous solution under visible light illumination as a function of irradiation.

2. Experimental

2.1. Reagents and chemicals

Bismuth nitrate pentahydrate ($Bi(NO3)_3{\cdot}5H_2O$), Phosphate buffer solutions of pH 5.0 and pH 6.0 was purchased from Otto. Dyes derivative Acid Yellow 29, Coomassie Brilliant Blue G250, and Acid Green 25 were obtained from Sigma–Aldrich. Nitric acid, (HNO_3, 98 wt%), sodium hydroxide (NaOH), surfactant(Triton-x) and glucose were obtained from Merck while, Neodymium nitrate, and ammonium ceric nitrate were obtained from Central Drug House, India.

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

In this study, we used sol gel method for preparation of bismuth oxide. All chemicals were of analytical grade and used without further purification. Typically, (0.97 gm) Bismuth nitrate pentahydrate (0.2 mmol) and (0.1 gm) surfactant (Triton-X) were dissolved in 10 ml of Nitric acid (1.12 mol/l in water) in Round bottom flask under vigorous stirring to avoid the hydrolysis of Bi^{3+} ions. The above solution was added dropwise into 100 ml (0.2 mol/l) sodium hydroxide aqueous solution then white precipitate was appeared. Then the mixture was heated at 90 °C for 3 h, after that the yellow colour was obtained. The fabricated yellow precipitate was filtration and washed with double distilled water and ethanol several times to remove possible impurities before being dried in an oven at 80 °C for 3 h in oven. Finally we got yellow Bismuth oxide powder. The synthesized powder was grinding before characterization.

The Bismuth oxide powder was doped with different concentration of cerium and neodymium by adding a solution of known concentrations of ammonium ceric nitrate varying from 0 to 2.5% (w/v) and Neodymium nitrate varying from 0 to 2.0% (w/v) in sodium hydroxide solution. The schematic flow chart for the preparation of doped Bi_2O_3 is shown in Fig. 1.The formation of α-Bi_2O_3 illustrated by the chemical reaction given in equation (1).

$$2Bi(NO_3)_3 + 6NaOH \rightarrow Bi_2O_3 + 6NaNO_3 + 3H_2O \quad (1)$$

2.3. Characterization

The as prepared materials were characterized by using standard analytical techniques such as X-Ray Diffraction (XRD), UV–Vis Spectroscopy, Scanning Electron Microscopy (SEM), Electron-spin resonance (ESR), Fourier transform infrared spectroscopy (FTIR), Thermogravimetry/Differential thermal analysis (TGA/DTA) and potentiostat/galvanostat (CV). The XRD of the as prepared sample was performed in the 2θ range of 20–80° Shimadzu XRD (model 6100) using graphite monochromatic copper radiation (Cu Kα, λ = 1.5418 Å) operated at voltage of 30 kV and current of 15 mA. The UV–Visible spectrum was taken at room temperature using Shimadzu UV–Vis spectrophotometer (Model 1601). The morphology of the fabricated material was examined using SEM and the pictures were taken using a JSM-6700F microscope (JEOL), an

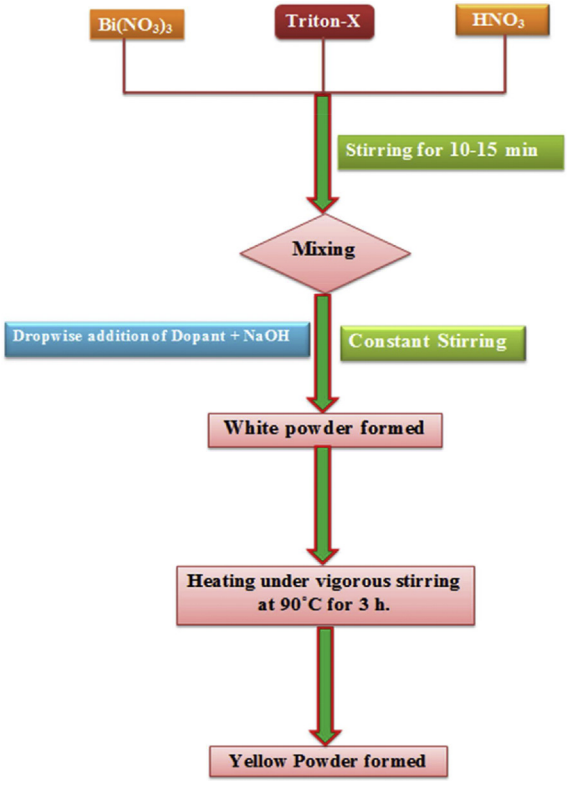

Fig. 1. Schematic flow chart for the fabrication of doped Bi_2O_3 NPs with different dopant concentration.