



Bi₂O₃/Ni-Bi₂O₃ system obtained via Ni-doping for enhanced PEC and photocatalytic activity supported by DFT and experimental study

Sonal Singh^{a,*,1}, Rishabh Sharma^{b,c,*,1}

^a Shaheed Rajguru College of Applied Sciences for Women, University of Delhi, New Delhi 110096, India

^b Thin Film Laboratory, Department of Physics, Indian Institute of Technology, New Delhi 110016, India

^c Amity Institute of Nanotechnology, Amity University, Sector-125, Noida, Uttar Pradesh 201303, India



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ABSTRACT

In this study, pure and Nickel doped α -Bismuth oxide (Ni-Bi₂O₃) powder were synthesized by simple chemical precipitation method. The resulting samples were analysed using SEM, EDAX, XRD, FTIR, UV-visible, PL and TRPL spectroscopy techniques. EDX and XRD results indicated that Ni was incorporated into the framework of the α -Bi₂O₃. The SEM characterizations revealed rod shape microstructures of the undoped Bi₂O₃ sample, while the Ni-doped product consisted of distorted or broken rod microstructures. Photo electrochemical (PEC) study plainly demonstrated the improved photo current density for Ni-doped sample compared to its pure counterpart. The photocatalytic activities of these samples were evaluated on the degradation of Methylene Blue under irradiation of simulated solar light. The Density Functional theory (DFT) study clearly revealed the formation of intensified energy state level in Ni-Bi₂O₃, supported by PL and UV, which was responsible for the high PEC and photocatalytic efficiency. The experimental results supported theoretical outcomes to conclude that Ni dopant serves as shallow trapping energy sites for photo excited charge carriers and greatly enhances the photoactivity of the catalyst.

1. Introduction

α -Bi₂O₃ is a budding p-type semiconductor material with its strong photocatalytic potential to be included in the capacity of similar narrow band gap semiconductor photocatalyst materials such as BiVO₄ and Fe₂O₃. However, in a quest to overcome its drawback of high rate of electron-hole recombination and extract its full potential as a photoactive material, various methods such as composite-formation, doping, coupled-semiconductor system etc have been adopted [1–5]. Doping of a semiconductor material has always been regarded as one of the most affluent methods for improving the photoactivity of the materials. Doping with C-, S-, Fe-, F-, Cu- and other materials with Bi₂O₃ have been previously reported [6–15]. However, our literature survey suggested that doping of Ni in α -Bi₂O₃ to investigate its photoactivity is still naive and has been explored only for delta (δ) phase of Bi₂O₃ so far, wherein its photoelectrochemical evaluation is particularly missing [16]. Ni²⁺ has been found as an efficient dopant material. In the past, researchers have successfully used Ni as a dopant material in semiconductors such as ZnO, TiO₂, ZnS and CdS to demonstrate their improved hydrogen generation and organic pollutant removal activities

[17–21].

Therefore, in this research contribution, we have successfully fabricated the visible light responsive Ni-doped α -Bi₂O₃ to study their PEC and photocatalytic applications. The photocatalytic activity of Ni-doped Bi₂O₃ samples was studied by analysing the degradation of methylene blue (MB) as a modal contaminant. More importantly, the presence of Ni played a major role in improving the photo response of the material by greatly suppressing the recombination of charge carriers (electron-hole pairs) on the surface of the photocatalyst. The focus of this study is to investigate the influence of Ni doping on the photocatalytic and photoelectrochemical properties of Bi₂O₃. The localized atomic orbital (LCAO) method combined with the supercell model was utilized to calculate the band structure, TDOS and PDOS of α -Bi₂O₃ and Ni-doped α -Bi₂O₃ samples. The experimental evaluation and theoretical calculation results were compared and analysed, ensuring the feasibility of the theoretical calculation. On the whole, this work investigated on a new aspect of Ni-doped Bi₂O₃ for an overall insight in both technological applications and fundamental researches.

* Corresponding author.

** Corresponding author at: Thin Film Laboratory, Department of Physics, Indian Institute of Technology, New Delhi 110016, India.

E-mail addresses: sonal.singh0811@gmail.com (S. Singh), rishabh.rammstien@gmail.com (R. Sharma).

¹ Both the authors have contributed equally to this work.

2. Experimental

2.1. Preparation of Bi_2O_3 and Ni-doped Bi_2O_3 photocatalyst

All chemicals in this study were analytical grade and were used without further purification for synthesis.

Chemical precipitation method was used to synthesize the pristine alpha phase of Bi_2O_3 . The method of synthesis was adapted from Sharma et al. [22]. In brief, 10.78 g of Bismuth Nitrate Pentahydrate, $(\text{Bi}_2(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O})$ was added to 30 ml 1.5 M HNO_3 solution. Then aqueous NaOH (50% W/V) solution was added drop wise to the previous solution until pH reached 13 resulting in the formation of yellow precipitate. It was followed by heating the solution mixture at 80 °C for 2 h. The $\alpha\text{-Bi}_2\text{O}_3$ yellow powder was obtained by centrifugation and washing the powder several times with DI water and ethanol followed by drying at 60 °C in hot air oven for 24 h.

To synthesize Ni-doped Bi_2O_3 , 0.15 g Ni metal powder was dissolved in 4 ml HNO_3 . This mixture was then added in 10.78 g bismuth nitrate solution in 1.5 M HNO_3 . Then aqueous NaOH (50% W/V) solution was added drop wise to the previous solution until pH reached 13 resulting in the formation of green precipitate. It was followed by heating the solution mixture at 80 °C for 2 h. The green powder of $\alpha\text{-Bi}_2\text{O}_3$ was obtained by centrifugation and washing the powder several times with DI water and ethanol followed by drying at 60 °C in hot air oven for 24 h. Fig. 1 shows the change in the colour of the two synthesized powders from yellow to green on doping $\alpha\text{-Bi}_2\text{O}_3$ with Ni.

2.2. Characterization

To determine the crystalline phases of the as-prepared pure and doped catalyst samples, X-ray diffraction (XRD, Rigaku, D2-Phaser, Cu $K\alpha$, $\lambda = 0.15406$ nm) was used. Scanning electron microscope (FEI Quanta 3D FEG 10 kV) was used to investigate the morphologies and structures of prepared samples and to confirm the elemental composition, an energy-dispersive X-ray spectroscopy (EDAX) equipped with the system was used. To record UV absorption spectra, Perkin-Elmer lambda 35 UV-Visible spectrometer within wavelength range of 200–800 nm was used. Perkin-Elmer LS-S5 was used to measure the photoluminescence (PL) emission spectra at the excitation wavelength of 325 nm. Time-correlated single photon counting (TCSPC) was used to collect luminescence lifetime decays at pulsed laser diode of 377 nm

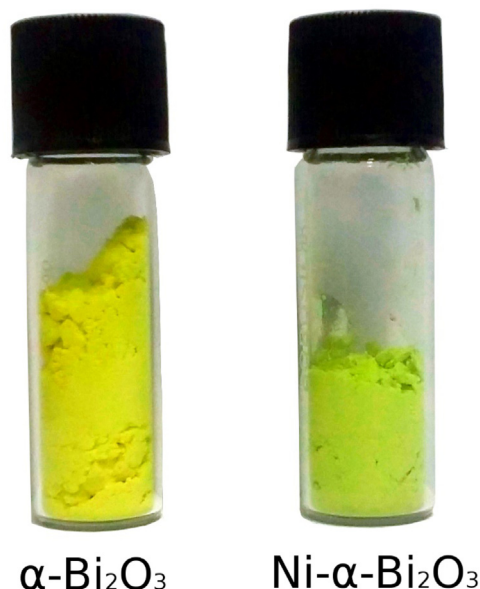


Fig. 1. Figure illustrating change in the colour of the two synthesized powders from yellow to green on doping $\alpha\text{-Bi}_2\text{O}_3$ with Ni.

using Edinburgh FL920 Fluorescence Life Time spectrometer. Thermo Scientific Nicolet IS5 model was used to record Fourier Transform infrared (FTIR).

2.3. Calculation method

Openmx software package was used for density functional theory calculations. Localized atomic orbital (LCAO) pseudo potential approach was used to describe ionic core and valence electron interaction [23]. For exchange-correlation function, generalized gradient approximation (GGA) proposed by Perdew-Burke-Ernzerhof (PBE) was used [24]. For higher accuracy triple zeta basis set is used for individual atoms [25]. Calculations were performed with cut off energy and electronic temperature set to 400 eV and 300 K respectively. Brillouin zone sampling was performed using Monk-horst and Pack scheme [26]. $\alpha\text{-Bi}_2\text{O}_3$ unit cell used for calculations consists of 8 Bismuth atoms and 12 oxygen atoms as shown in Fig. 2(a). One Nickel dopant atom was added substituting one bismuth atom in $\alpha\text{-Bi}_2\text{O}_3$ unit cell shown in Fig. 2(b). To theoretically understand the effect of nickel doping in $\alpha\text{-Bi}_2\text{O}_3$ one Bismuth atom in the unit was substituted with Nickel atom. K-mesh of $2 \times 2 \times 2$ used in calculations was relaxed until the force between atoms was reduced up to 1.0×10^{-4} Hartree/Bohr. BFGS algorithm was used for relaxing the crystal structure. Finally, electronic band structure, total density of states and projected density of states were calculated in reciprocal lattice.

In order to determine whether substituting Ni for Bi lattice sites is energetically more favorable, the formation energies (E_{form}) of doped $\alpha\text{-Bi}_2\text{O}_3$ were calculated. The E_{form} is calculated by following formula [27]:

$$E_{\text{Form}} = E_{\text{doped}} - E_{\text{pure}} - E_{\text{Bi}} + E_{\text{Ni}}$$

$$E_{\text{Form}} = E_{\text{doped}} - E_{\text{pure}} - E_{\text{O}} + E_{\text{Ni}}$$

where E_{pure} and E_{doped} are the total energy of the pure and doped $\alpha\text{-Bi}_2\text{O}_3$. E_{Bi} , E_{O} , and E_{Ni} are the total energy of per atom for Bismuth, Oxygen, and Nickel solids, respectively. The calculated formation energy for Ni replacing O (9.09 eV) is higher than that of Ni replacing Bi (8.16 eV). This clears that Ni prefers to occupy Bi sites rather than O sites.

2.4. Photoelectrochemical activity test

The PEC performance of undoped and Ni-doped Bi_2O_3 samples was evaluated and compared using a three-electrode-electrochemical system. Linear sweep voltammetry (LSV) measurements were carried out under illumination and dark in the potential range of -1–0.25 V vs Ag/AgCl. The samples were prepared over Indium-doped tin oxide (ITO) conducting glass and used in PEC as working electrode keeping Ag/AgCl and Pt electrode as reference electrode & counter electrode respectively. The electrolyte used was 1 M NaOH at pH 14. The film sample was spin coated on ITO substrate/glass at 5000 rpm for 50 s. Frequency range of 100 kHz to 0.1 Hz with open bias AC signal amplitude of 0.01 V was used to perform electrochemical impedance spectroscopy measurements. Xenon arc lamp with AM 1.5 solar illumination at 100 mW/cm^2 was used as a simulated sunlight source.

2.5. Photocatalytic activity test

In order to perform the photocatalytic activities of the as prepared samples, Methylene Blue (MB) was degraded in an aqueous solution under visible-light irradiation. Xenon arc lamp with AM 1.5 solar illumination at 100 mW/cm^2 was used as a simulated sunlight source. All experiments were conducted at room temperature in air. In a typical photocatalytic experiment, into 100 ml of $10 \mu\text{M}$ dye solution, 5 mg of the photocatalyst was added. To uniformly disperse the photocatalyst particles and remove the agglomeration in the solution, suspension was

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