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# Bismuth oxide nanoplates-based efficient DSSCs: Influence of ZnO surface passivation layer



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#### ABSTRACT

For the first time, bismuth oxide  $(Bi_2O_3)$  nanoplates synthesized by single-step chemical method were envisaged as photoanodes in dye-sensitized solar cells. The structural elucidation demonstrated tetragonal structure with a predominant  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>. The power conversion efficiency (1%) of Bi<sub>2</sub>O<sub>3</sub> nanoplates-based dye-sensitized solar cells was enhanced up to 50% when decorated with zinc oxide thin layer (ZnO). The best performing electrode showed 24% incident photon-to-current conversion efficiency. This high DSSC performance of Bi<sub>2</sub>O<sub>3</sub>-ZnO photoanode is attributed to the increased electron transportation due to the suppression of recombination centers by ZnO passivation layer.

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#### 1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted great scientific attention for sunlight to electricity conversion due to its low cost and high light-harvesting efficiency [1]. DSSCs are composed of a dye-modified semiconductor photoanode, a liquid iodide electrolyte as redox couples, and a counter electrode [2]. Among these, photoanodes of various structures and electronic properties have prime importance due to their different tendency toward dye loading as well as charge transfer characteristics. Along with TiO<sub>2</sub> (one of the highest preferred metal oxides so far), ZnO, Nb<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>,  $SnO_2$ , etc., are also employed as photoanodes in DSSC [3–6]. Each metal oxide has several advantages and disadvantages. For example, ZnO exhibits poor stability in acidic condition. When ZnO was dipped in dye solution such as N3 and N719 (being acidic in nature), it dissolves slowly and aggregates on the surface of electrode. Such aggregation is reported to reduce the electron injection efficiency [7]. In case of  $SnO_2$ , its low  $V_{oc}$  due to a more positive conduction band position is critical to achieve high performance, though the charge carrier mobility of SnO<sub>2</sub> (240 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) is 100 times more than that of TiO<sub>2</sub> [8]. Hence, the design and development of efficient and cost effective photoanode materials are necessary to improve the overall performance of DSSCs.

Many groups have focused their research on improving the efficiency of DSSCs and a maximum of 12.3% efficiency is reported [9]. However, this value is far below the theoretical efficiency of DSSCs which is 30% [10]. One of the factors that limit the efficiency of DSSC is attributed to the presence of trapping states at the interfaces within the photoanode. These surface states act as recombination centers where the photo-injected electrons recombine with redox electrolyte, thereby decreasing the photocurrent as well as cell efficiency. One of the effective ways to suppress the charge recombination is to coat the surface of photoanode with wide band gap materials such as ZnO, Al $_2$ O $_3$ , ZrO $_2$ , MgO, and Nb $_2$ O $_5$  [11–15]. Such a coating acts as a barrier between the injected electrons and electrolyte thus decreasing the rate of charge recombination.

In this study, we have explored bismuth oxide  $(Bi_2O_3)$  as a photoanode for DSSCs applications. This material has several advantages due to its unique electrical, optical and mechanical properties. It exists in four crystal phases i.e., monoclinic  $\alpha$ -Bi $_2O_3$ , tetragonal  $\beta$ -Bi $_2O_3$ , cubic  $\gamma$ -Bi $_2O_3$ , and cubic  $\delta$ -Bi $_2O_3$ . The  $\alpha$ -phase is most stable at relatively low temperatures, while  $\delta$ -phase is stable when the temperature is above 1000 K. The  $\beta$  and  $\gamma$  phases are high temperature metastable phases [16]. Bi $_2O_3$  also exhibits a high refractive index, dielectric permittivity, high oxygen ion conductivity, remarkable photoconductivity and photoluminescence [17–19]. Its band gap energy is commonly observed in the range of 2.5–3.1 eV; mostly depends on the crystal phase type [20]. The narrow band gap of Bi $_2O_3$  makes it suitable for a large range of applications including optical coatings, photovoltaics and microwave integrated circuits superconductor [21–23].

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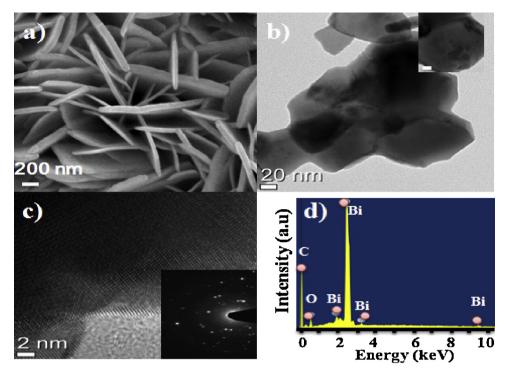


Fig. 1. (a) FE-SEM images, (b) HR-TEM image of the photoanode at low magnification (20 nm) and inset (10 nm), (c) high magnification image (inset SAED pattern), and (d) EDX spectra of Bi<sub>2</sub>O<sub>3</sub> NPLs.

Furthermore,  $Bi_2O_3$  can be grown in numerous forms such as nanoporous, nanoplates, nanoparticles, nanorods, nanotubes, nanolines, etc., depending upon the type of morphology required for a particular application [24–28].

To the best of our knowledge, there is no report in literature regarding  $\rm Bi_2O_3$  as photoanode material in DSSCs. We report for the first time the use of  $\rm Bi_2O_3$  nanoplates (NPLs) as a photoanode in DSSCs which was synthesized by a facile one-step chemical bath deposition method. We demonstrate that the  $\rm Bi_2O_3$  NPLs architecture photoanode supports for dye loading, efficient light harvesting and simultaneously affords a direct conduction pathway for photoexcited electrons. We also investigate the effect of ZnO surface passivation layer on performance of  $\rm Bi_2O_3$  NPLs-based DSSCs and the difference in results is corroborated with other electrochemical measurements.

### 2. Experimental details

Bismuth (III) nitrate pentahydrate (98%), tri-ethanolamine (98%) were purchased from Sigma Aldrich. Sodium hydroxide (97%) was purchased from Junsei. Zinc acetate di-hydrate was purchased from Kanto Chemicals Co. Inc. Ammonia solution (28-30%) was purchased from Samchun Chemicals. The sensitizer dye N719 was obtained from Solaronix SA (Switzerland). All reagents were of analytical grade and used without further purification. Fluorine-tin-oxide (FTO) glass substrates were ultrasonically cleaned sequentially in detergent-added distilled water, acetone and isopropyl alcohol. The Bi<sub>2</sub>O<sub>3</sub> films were deposited from the solution containing 0.1 M bismuth (III) nitrate pentahydrate, triethanolamine and sodium hydroxide [20]. Three clean FTO glass slides were vertically immersed in 100 ml beaker capacity maintained at 50-80 °C for 2h. At higher deposition temperatures loosely bonded Bi<sub>2</sub>O<sub>3</sub> film was grown on FTO substrate. The deposition of Bi(OH)3 on the surface of FTO substrate occurred via heterogeneous reaction. The as-deposited films were annealed in

air at 350 °C for 1 h at 5 °C per min heating rate to obtain  $Bi_2O_3.$  The thickness of film was about 2.8  $\mu m.$ 

Field-emission scanning electron microscopy (FE-SEM) images and energy-dispersive spectrometry (EDS) spectrums were

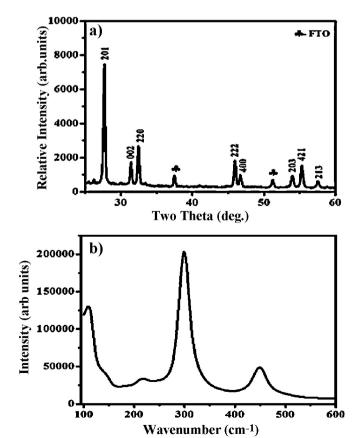


Fig. 2. (a) X-ray diffraction pattern and (b) Raman shift of Bi<sub>2</sub>O<sub>3</sub> NPLs.

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