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### **Influence of Bi-doping on the structure and efficiency of TiO<sub>2</sub> photoanodes**

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#### **ABSTRACT**

Bismuth-doped TiO<sub>2</sub> photoanodes of dye sensitized solar cells were synthesized by using powder bismuth oxide. The effect of bismuth doping on the crystallite size, strain lattice distortion and crystallinity of titanium oxide was investigated and its influence on the photovoltaic behavior of dye sensitized solar cells was studied. The variation in short-current density and open-circuit voltage with Bi-doping was explained in terms of changes in both electron-hole recombination and conduction band edge of titanium oxide, respectively. The prepared photoanodes were characterized by X-ray diffraction and energy dispersive X-ray analyses.

**KEYWORDS:** Bi-doping, crystal structure, DSSC, X-ray diffraction.

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## INTRODUCTION

It is expected that conventional solar cells will be replaced by Dye Sensitized Solar Cells (DSSCs) due to their low cost and simple manufacturing processes<sup>1,2</sup>. Basically, a DSSC consists of photoanode (wide band gap semiconductor oxide(s) on transparent conducting glass), sensitizer, redox electrolyte and counter electrode. Considerable efforts have been devoted on all of these constituents to increase the overall efficiency of DSSC devices. Many studies focus on improving the performance of photoanodes have been published, see for example Refs.<sup>3,6</sup>. More than a few of these studies employed TiO<sub>2</sub> semiconductor because of its high efficiency, low cost, chemical inertness and photostability<sup>7,8</sup>.

The electronic properties of TiO<sub>2</sub> can be modified by doping, either by replacing the Ti<sup>4+</sup> cation or the O<sup>2-</sup> anion<sup>9</sup>. There are different ways for entering the dopant into the TiO<sub>2</sub>-lattice, e.g., mixing TiO<sub>2</sub> precursor solution with the dopant precursor and doping TiO<sub>2</sub> electrochemically by dissolving the dopant in the electrolyte solution<sup>10</sup>. Moreover, coating the photoanodes with another wide band gap semiconductors (such as Al<sub>2</sub>O<sub>3</sub>, ZnO, ZrO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>) to reduce charge recombination were reported<sup>11-14</sup>. Doping TiO<sub>2</sub> photoanodes with Nb<sup>15</sup> and Sb<sup>16</sup> improved the performance of DSSCs due to enhancement of the short-circuit current density. Furthermore, metal doping of TiO<sub>2</sub> with Sn, Zn and W exhibited a positive shift in the conduction band edge that increased the electron injection efficiency and suppressed the carrier recombination<sup>15,17</sup>. Nonmetals such as nitrogen, fluorine, carbon and sulfur also shifted the TiO<sub>2</sub> conduction band edge and decreased the concentration of oxygen vacancies, consequently, reduced the trapping at the defect sites<sup>18</sup>. Rare-earth-doping has been the subject of extensive research as well, e.g. Hafez et al.<sup>19</sup> studied the effect of Eu and Sm doping on the efficiency of DSSCs. On the other hand, cocktail of bi-semiconductors such as TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> were used in the photoanode material and resulted in increasing the performance of the DSSC due to the combined conduction bands<sup>20</sup>. Moreover, photoanodes based on bismuth oxide with  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> morphology prepared by chemical bath deposition method was reported<sup>21</sup>. The DSSC efficiency was enhanced by suppressing charge recombination when another ZnO layer was applied. Bismuth-TiO<sub>2</sub> photoanodes were synthesized mostly via sol-gel method, see for example Refs.<sup>22, 23</sup>.

In this work, we employed powder bismuth oxide via a simple mechanochemical route to dope TiO<sub>2</sub> photoanodes as (Bi<sub>2</sub>O<sub>3</sub>)<sub>x</sub>-(TiO<sub>2</sub>)<sub>1-x</sub> with x=0.0, 0.10 and 0.15. To the extent of our knowledge, there is no reported work on doping titanium oxide with powder bismuth oxide. The employed TiO<sub>2</sub> was prepared as nanoparticles and the used Bi<sub>2</sub>O<sub>3</sub> has the most stable monoclinic  $\alpha$ -phase<sup>24</sup>. The crystal structure of photoanodes with different doping ratios was investigated by

XRD and EDX. Also, the Bi-doping influence on the photovoltaic efficiency of DSSC devices was studied.

## MATERIALS AND METHODS

### *Materials*

Chemical materials of titanium dioxide ( $\text{TiO}_2$ : BHD, 98.0%), Bismuth (III) oxide ( $\text{Bi}_2\text{O}_3$ : Loba Chemie, 99%), acetylacetone ( $\text{CH}_3\text{COCH}_2\text{COCH}_3$ : Loba Chemie, 98.0%), triton X-100 ( $\text{C}_{34}\text{H}_{62}\text{O}_{11}$ : El-goumhouria), Hydrochloric acid (HCl: Elnaser pharm. chem., 30.0-34.0%), Hydrogen peroxide ( $\text{H}_2\text{O}_2$ : PubChem, 50.0%), ammonia solution ( $\text{NH}_3$ : Elnaser pharm. chem., 33.0%), titanium tetrachloride ( $\text{TiCl}_4$ : Loba Chemie, 99.5%), hydrogen hexachloroplatinate (IV) solution ( $\text{H}_2\text{PtCl}_6$ : Sigma Aldrich), absolute ethanol ( $\text{C}_2\text{H}_5\text{OH}$ : Honeywell), pure acetone ( $\text{CH}_3\text{COCH}_3$ : Elnaser pharm. chem.), isopropyl-alcohol ( $(\text{CH}_3)_2\text{CHOH}$ : Elnaser pharm. chem.), ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ : S. D. Fine-Chem Ltd.), iodine resublimed ( $\text{I}_2$ : Elnaser pharm. chem.), potassium iodide (KI: Elnaser pharm. chem., 99.5%), N719 dye (Di-tetrabutylammonium bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II): Dyesol) were used. Also, Fluorine-doped  $\text{SnO}_2$  (FTO: 2.2-mm thick,  $14\Omega/\text{sq.}$ , Pilkington) was utilized as our transparent conducting oxide (TCO) glass.

### *Preparation of $\text{TiO}_2$ nanoparticles*

25 gm of raw  $\text{TiO}_2$  was added to a solution of 25 ml of HCl, 50 ml of  $\text{H}_2\text{O}$ , 12.5 ml of  $\text{H}_2\text{O}_2$  and 6.25 ml of  $\text{NH}_3$  and stirred for 17 h to get a white suspension. Then, the suspension was washed and precipitated by repeated cycles of using distilled water and centrifuge. Lastly, the formed precipitate was dried at  $70^\circ\text{C}$  for 21 h to get  $\text{TiO}_2$  nanoparticles.

### *Preparation of undoped and Bi-doped $\text{TiO}_2$ pastes*

A white solution was made by adding 10 ml of distilled water to 2 ml of  $\text{TiCl}_4$  in an ice bath and kept under stirring until it became colorless. Then, 3 gm of prepared  $\text{TiO}_2$  nanoparticles was added to another beaker with 0.05 ml of triton X-100, 0.1 ml of acetylacetone and 3 ml of distilled water. Lastly, 1.0 ml of the prepared colorless solution was added and the final solution was kept under continuous stirring for 24 h to obtain the  $\text{TiO}_2$  paste. To prepare  $(\text{Bi}_2\text{O}_3)_x\text{-(TiO}_2)_{1-x}$  paste with  $x= 0.10$  and  $0.15$ , bismuth oxide powder was mixed with the previously prepared  $\text{TiO}_2$  nanopowder and rigorously ground to facilitate mechanochemical reaction to take place, then the mixed powder followed the same procedure mentioned above for the preparation of  $\text{TiO}_2$  paste.

### ***Preparation of electrolyte and Pt layer***

To prepare the electrolyte, about 0.6 gm of I<sub>2</sub> was dissolved in 50 ml of ethylene glycol and kept under stirring for 2 h. Then, 4 gm of KI was added to the mixture under continuous stirring for another 2 h and the obtained solution was stored in tight and dark glass container. To prepare the Pt layer of the counter electrode, 20 ml of pure ethanol was added to a beaker containing 0.5 ml of H<sub>2</sub>-Hex-Pt (IV). The acquired solution was dispersed on the FTO substrates and gradually heated to 450 °C for 30 minutes.

### ***Preparation of film electrodes and DSSCs devices***

The prepared paste was spread on the transparent conducting glass using doctor -blade technique and then sintered at 450 °C for 30 min. Subsequently, the film was soaked in ethanol solution of N-719 dye for 24 h at room temperature and then gently washed by ethanol. The DSSC devices were assembled and the electrolyte was introduced into the aperture by repeated addition of electrolyte drops (on a hole in the counter electrode) and air suction to ensure complete filling of the aperture.

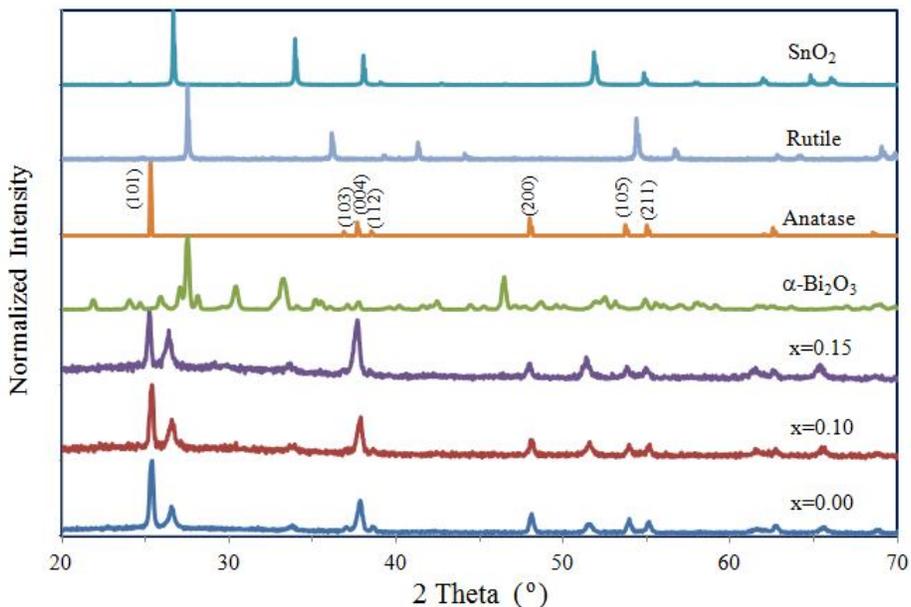
### ***Measurements and characterization***

X-ray diffraction (XRD) of (TiO<sub>2</sub>)<sub>1-x</sub>(Bi<sub>2</sub>O<sub>3</sub>)<sub>x</sub> working electrodes was recorded by using TMR (APD 2000 Pro) diffractometer with Cu-K<sub>α1</sub> radiation ( $\lambda = 1.54056 \text{ \AA}$ ) with  $2\theta$  covering the range from 20° to 70° with an angular resolution of 0.03°. The elemental analysis was carried out by using EDX (Energy Dispersive X-ray analysis) unit attached to SEM model Quanta 250 FEG (Field Emission Gun). The J-V curves of DSSCs were measured by using current amplifier (Kiethley 427), multimeter (Aplab 1087) and data acquisition (DataQ: DI-158U). The DSSCs devices were irradiated with a homemade solar simulator with xenon lamp (35 W), halogen lamp (55 W) and equipped with IR and UV filters to irradiate a DSSC active area of 0.35 cm<sup>2</sup>. The power density of the simulator was 55 mW/cm<sup>2</sup> (measured by using SPM-1116SD Lutron solar power meter) which corresponds to a solar power of about 19 mW for the working active area.

## **RESULTS AND DISCUSSION**

X-ray diffraction (XRD) patterns of (Bi<sub>2</sub>O<sub>3</sub>)<sub>x</sub>(TiO<sub>2</sub>)<sub>1-x</sub> with x=0.00, 0.10 and 0.15 photoanodes and powder Bi<sub>2</sub>O<sub>3</sub> were shown in Figure 1. Also, the standard diffraction patterns of SnO<sub>2</sub> and TiO<sub>2</sub> rutile and anatase phases were given<sup>25</sup>. All charts were normalized and shifted for clarity purposes. The chart of the raw bismuth oxide powder was compared with standard charts and all given peaks matched the peak positions and relative intensities of standard monoclinic ( $\alpha$ -

phase)  $\text{Bi}_2\text{O}_3$ , as referenced in JCPDS 76-1730. All shown diffraction peaks of  $x = 0.0$  photoanode represent pure anatase- $\text{TiO}_2$  phase, in addition to tin oxide (due to FTO: fluorine-doped tin oxide conducting layer) diffraction peaks. It is worth mention that, the small peak at  $33.8^\circ$  belongs to  $\text{SnO}_2$  rather than the monoclinic  $\text{Bi}_2\text{O}_3$ . Before we proceed with XRD discussion for Bi-doped samples, we recall that we applied mechanochemical route in preparing the samples. This method is

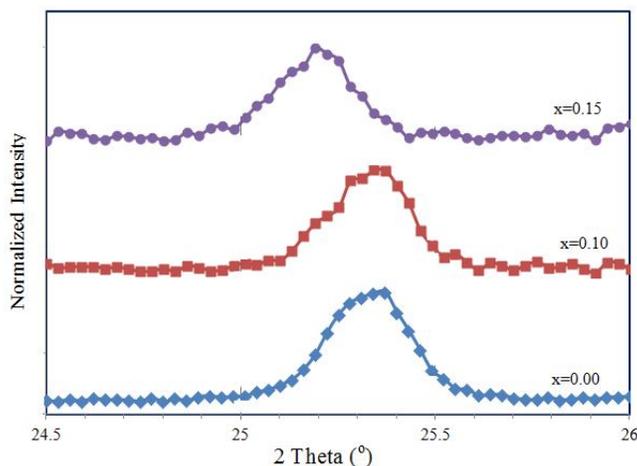


**Fig. 1:** XRD pattern spectra of  $(\text{Bi}_2\text{O}_3)_x\text{-(TiO}_2)_{1-x}$  photoanodes for  $x = 0.0, 0.10$  and  $0.15$  and powder  $\text{Bi}_2\text{O}_3$ . Standard diffraction patterns of  $\text{SnO}_2$ , rutile and anatase phases of  $\text{TiO}_2$  were given.

superior to both liquid phase processes and solid state reaction as it gives finer particle sizes by using low cost raw materials and without the need to high sintering temperatures<sup>26</sup>. Ohara et al.<sup>27</sup> prepared  $\text{BiTiO}_3$  with particle size of 22 nm by using mechanochemical procedure by ball-milling  $\text{TiO}_2$  and  $\text{BaCO}_3$  powders for 10 min. The reported XRD chart showed the absence of  $\text{TiO}_2$  and  $\text{BaCO}_3$  peaks and only  $\text{BiTiO}_3$  peaks were observed. Now, the fact that our XRD chart for  $x = 0.0$  represents pure  $\text{TiO}_2$  (anatase phase) photoanode is confirmed by the absence of all  $\text{Bi}_2\text{O}_3$  and rutile peaks; especially major diffractions. This argument is actually applied for Bi-doped photoanodes ( $x = 0.15$  and  $x = 0.15$ ) as well, where neither  $\text{Bi}_2\text{O}_3$  nor rutile peaks were observed. The effects of Bi-doping were observed in the shift of peaks toward lower  $2\theta$  angle and the gradual decrease of  $\text{TiO}_2$  (200) diffraction intensities with the increase of  $x$ . Figure 2 showed the observed shift of the major  $\text{TiO}_2$  (101) diffraction peak where it shifted from  $2\theta = 25.37^\circ$  for undoped sample to  $2\theta = 25.19^\circ$  for  $x = 0.15$ . This shift suggested an increase in the unit cell volume with increasing of  $x$ . Table 1 listed the calculated distortion,  $\delta(a/c)\%$ , of  $\text{TiO}_2$  lattice for Bi-doped samples, whereas:

$$\delta(a/c) = (a/c) - (a_0/c_0)$$

where  $(a/c)$  and  $(a_0/c_0)$  are the ratios between lattice parameters of Bi-doped and undoped samples, respectively. As observed, the calculated distortion increased with increasing of Bi-doping. On the other hand, we should take in account that there is no evidence of  $\text{Bi}_2\text{O}_3$  phase in Bi-doped samples, as mentioned above, and the fact that the ionic radius of  $\text{Bi}^{3+}$  (0.103 nm) is greater than that of  $\text{Ti}^{4+}$  (0.061 nm)<sup>28</sup>. These facts imply that  $\text{Bi}^{3+}$  ions substituted  $\text{Ti}^{4+}$  sites leading to an



**Fig. 2: XRD major  $\text{TiO}_2$  (101) diffraction peak of photoanodes for  $x = 0.0, 0.10$  and  $0.15$ .**

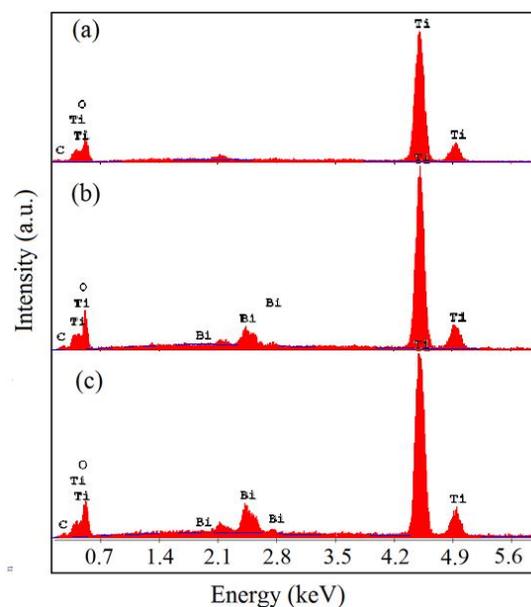
increase in unit cell volume and absence of any Bi-based phases. Furthermore, the size of the crystallites ( $D$ ) for different values of  $x$  was calculated by using Scherrer formula for the major (101) diffraction peak, as given in Table 1. The reported minute decrease in the average crystallite size with increasing of  $x$  could be attributed to growth suppression of similar  $\text{TiO}_2$  crystallites due to  $\text{Bi}^{3+}$  ions doping. In other words, the mismatch between  $\text{Bi}^{3+}$ -free unit cells and bigger cells with  $\text{Bi}^{3+}$  ions substituted  $\text{Ti}^{4+}$  sites decrease the possibility of crystallite growth, i.e. the more the Bi-doping the smaller the crystallite size. Moreover, let us study the effect of Bi-doping on the crystallinity of  $\text{TiO}_2$  by considering the peak at about  $2\theta = 48.1^\circ$  with (200) diffraction plane. As seen, this peak undoubtedly refers to  $\text{TiO}_2$  (anatase phase) and its intensity decreased with the increasing of Bi-content,  $x$ . Therefore, Bi-doping resulted in a decrease in crystallinity of  $\text{TiO}_2$  as confirmed by the observed gradual decrease in the intensity of this peak with increasing of  $x$ .

Energy-Dispersive X-ray (EDX) spectroscopy was employed to elementally analyze the composition of  $(\text{Bi}_2\text{O}_3)_x - (\text{TiO}_2)_{1-x}$  photoanodes. Figure 3 showed peaks corresponding to titanium, bismuth, oxygen and carbon indicating the absence of impurities in the prepared photoanodes. The presence of carbon is due to coating of samples with such conducting element. The calculated

content of bismuth in Bi-doped samples were tabulated in Table 1 and agrees fairly well with the starting stoichiometry, x, of  $(\text{Bi}_2\text{O}_3)_x\text{-(TiO}_2)_{1-x}$  photoanodes.

**Table No. 1: “Crystallite size (D), lattice parameters, lattice distortion and EDX analysis of photoanodes”**

x	D (nm)	a (Å)	c (Å)	δ (%)	x (EDX)
0.0	33	3.7739	9.5069	0	0.0
0.10	31	3.7794	9.4996	0.0879	0.09
0.15	30	3.8019	9.5505	0.1112	0.14



**Fig. 3: SEM-EDX analysis of  $(\text{TiO}_2)_{1-x}\text{-(Bi}_2\text{O}_3)_x$  photoanodes for (a) x= 0.0, (b) x= 0.10 and (c) x= 0.15.**

The photocurrent density-voltage curves (J-V) of DSSCs with different Bi-doping concentrations of  $\text{TiO}_2$  photoanodes are shown in Figure. 4. The photovoltaic parameters were calculated and tabulated in Table 2. The values of the fill factor (FF) for DSSCs with different concentrations of the dopant were calculated and indicated in Table 1. This parameter is a measure of the ideality of a solar cell and is given as:

$$FF = J_{max} V_{max} / J_{sc} V_{oc}$$

where  $J_{max}$  and  $V_{max}$  are the current density and voltage corresponding to the maximum output power ( $P_{max}$ ) of the P-V curves and given in Table 2. As observed, both short-circuit current density ( $J_{sc}$ ) and open-circuit voltage ( $V_{oc}$ ) were decreased with increasing of Bi-doping, x.

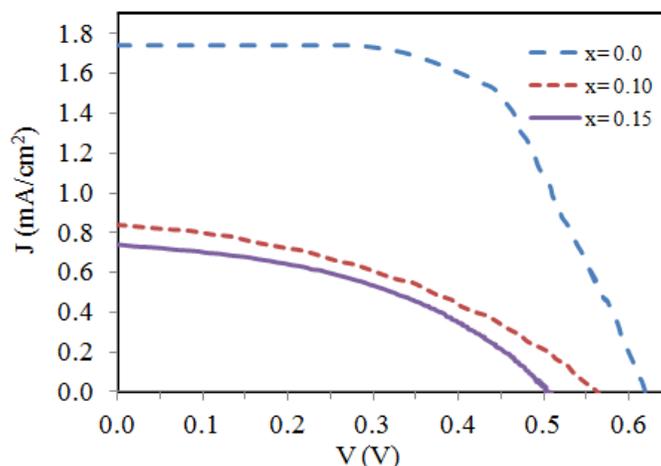


Fig. 4: Current density-voltage curves of  $(\text{Bi}_2\text{O}_3)_x\text{-(TiO}_2)_{1-x}$  DSSCs for  $x=0.0, 0.10$  and,  $0.15$ .

Table No. 2: “Parameters of DSSCs with  $(\text{Bi}_2\text{O}_3)_x\text{-(TiO}_2)_{1-x}$  photoanodes for  $x=0.0, 0.10$  and  $0.15$ ”

$x$	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA}/\text{cm}^2$ )	$P_{max}$ (mW)	$FF$ (%)	$\eta$
0.00	0.62	1.75	0.236	62.3	1.23
0.10	0.56	0.84	0.067	40.6	0.35
0.15	0.51	0.74	0.057	43.0	0.30

Consequently, the light-to-electrical energy conversion efficiency ( $\eta$ ) of doped DSSC devices is lower than that of undoped cells, see Table 1. The efficiency ( $\eta$ ) was calculated according to the following equation:

$$\eta = P_{max} / P_{in} = J_{sc} V_{oc} FF / P_{in}$$

where  $P_{in}$  is the input power of the incident light on the active area of the cell. The observed decrease in  $J_{sc}$  with Bi-doping could be attributed to reduction in  $\text{TiO}_2$  crystallinity, as discussed above. This decrease in crystallinity of anatase- $\text{TiO}_2$  phase causes an increase in electron-hole recombination due to reduction in the speed of electrons<sup>22</sup>. Therefore, the observed gradual decrease in current density with increasing of  $x$  (Fig. 4) could be attributed to loss of photo-generated electrons by electron-hole recombination processes. To clarify the reduction in  $V_{oc}$  with Bi-doping (Fig. 4), let us recall that the measured  $V_{oc}$  is the difference between two potentials, namely, the Nernstian potential of the electrolyte and the quasi-Fermi level of  $\text{TiO}_2$ <sup>29</sup>. Since conduction bands of  $\text{TiO}_2$  and  $\text{Bi}_2\text{O}_3$  with respect to the absolute vacuum scale are  $-4.21$  eV and  $-4.83$  eV<sup>30</sup>, respectively, then the former conduction band is higher than the later. Moreover, the substitution of  $\text{Ti}^{4+}$  by  $\text{Bi}^{3+}$  is expected to shift-down the quasi-Fermi level of  $\text{TiO}_2$ . Consequently,

the effect of increasing Bi-doping of TiO<sub>2</sub> photoanodes is expected to gradually shift-down its conduction band edge and accordingly  $V_{oc}$  decreases.

## CONCLUSION

We employed powder bismuth oxide to prepare (Bi<sub>2</sub>O<sub>3</sub>)<sub>x</sub>-(TiO<sub>2</sub>)<sub>1-x</sub> photoanodes with  $x = 0.0, 0.10$  and  $0.15$ . XRD analysis showed that the prepared titanium oxide nanoparticles have a size of 33 nm with a pure anatase phase. Also, Bi-doping caused distortion in TiO<sub>2</sub> lattice and a reduction in both crystallite size and crystallinity as Bi<sup>3+</sup> ions substituted Ti<sup>4+</sup>. The photocurrent density-voltage curves of DSSCs revealed that both short-circuit current density and open-circuit voltage were decreased with increasing of  $x$ . The decrease in current density was attributed to an increase in electron-hole recombination associated with the observed reduction in TiO<sub>2</sub> crystallinity. Finally, the observed decrease in open-circuit voltage with increasing Bi-doping was explained in terms of a shift-down of the conduction band edge of titanium oxide.

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