

## Dynamic study of bismuth telluride quantum dot assisted titanium oxide for efficient photoelectrochemical performance

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The 3D TiO<sub>2</sub> microflowers, sensitized by Bi<sub>2</sub>Te<sub>3</sub> nanoparticles, having novel architecture were generated employing a two-step synthetic strategy, including a hydrothermal process and a potentiostatic electrodeposition technique. The design and synthesis of quantum dots (QDs) for achieving high photoelectrochemical performance is an urgent need for high technology fields

**Keywords:** Bi<sub>2</sub>Te<sub>3</sub> QDs assisted TiO<sub>2</sub>, 1D nanorods, PEC.

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### 1. Introduction

Quantum dot-sensitized solar cells (QDSCs) have received much attention because they are promising candidates for low cost and large area photovoltaic applications. Semiconductor quantum dot-sensitized solar cells (QDSSCs) have the advantages of being low cost and a simple fabrication process. The most attractive property of a semiconductor quantum dot is its ability to promote the photoconversion efficiency above Shockley-Queisser limit. The low efficiency of QDSSCs is attributed to the relatively low photovoltage in the cell compared to DSSCs and to the recombination paths induced by the electronic properties of the interfaces formed at TiO<sub>2</sub>-QD-electrolyte triple junction [1]. Secondly, it is difficult to incorporate QDs into a TiO<sub>2</sub> mesoporous matrix to obtain a well-covered QD monolayer on the inner surface of the TiO<sub>2</sub> electrode. Other possible reasons include QD-electrolyte interfaces [2], electron loss occurring through charge recombination at the TiO<sub>2</sub>-electrolyte interface [3]. To achieve higher performance photovoltaic solar cells, morphologies and structures of anode materials are also widely investigated [4]. In general, mesoporous TiO<sub>2</sub> nanoparticles are the most frequently used photoanodes in DSSCs and QDSSCs, due to their high internal surface area for sufficient sensitizer anchoring [5]. Unfortunately, mesoporous TiO<sub>2</sub> nanoparticles have some disadvantages, such as charge collection rate due to surface states and grain boundaries existing in the pathway of nanoparticles, which can lead to many unexpected trapping and de-trapping, and thus, inferior light scattering [6]. In this study, we successfully synthesized vertically aligned TiO<sub>2</sub> nanorods sensitized by Bi<sub>2</sub>Te<sub>3</sub> nanoparticles. The photoelectrochemical performance of TiO<sub>2</sub> is greatly improved by sensitization of TiO<sub>2</sub> by Bi<sub>2</sub>Te<sub>3</sub> nanoparticles [7]. The sensitization of TiO<sub>2</sub> by Bi<sub>2</sub>Te<sub>3</sub> nanoparticles leads to a separation of the charge carriers. The charge separation leads to a reduction in the overall recombination in the solar cells and the enhancement of photogenerated carrier collection.

### 2. Method

First, TiO<sub>2</sub> can be prepared by our previously-reported hydrothermal method [7]. In detail 0.04 M TTIP was added in the solution containing 3M HCl and ethylene glycol stirred for some time. The clear transparent solution then poured into a Teflon-lined stainless steel autoclave maintained at 160°C for 2 h. The electrodeposition of Bi<sub>2</sub>Te<sub>3</sub> nanoparticles on TiO<sub>2</sub> thin films was accomplished in a three electrode cell configuration containing aqueous solutions of 7 mM Bi(NO<sub>3</sub>)<sub>3</sub> and 10 mM Te in 1M HNO<sub>3</sub>. The deposition was carried out at -0.8 V vs Ag/AgCl. In this, TiO<sub>2</sub> nanorods act as working electrode, platinum as counter electrode and Ag/AgCl as reference electrode. The deposition time was fixed at 30 min. and the depositions were carried out at room temperature. In order to control the size of Bi<sub>2</sub>Te<sub>3</sub> nanoparticles and prevent large particle formation, PVA was used as structure directing agent.

### 3. Results and discussion

#### 3.1. Optical absorption spectra of Bi<sub>2</sub>Te<sub>3</sub> loaded TiO<sub>2</sub>

The light absorption properties of Bi<sub>2</sub>Te<sub>3</sub>-loaded TiO<sub>2</sub> thin was evaluated using the UV-visible spectrophotometer (Shimadzu UV-1800 Japan). Figure 1 shows the Tauc plot of Bi<sub>2</sub>Te<sub>3</sub> loaded TiO<sub>2</sub> thin films. The band gap energy of composite can be expressed by the Tauc relation. It is well known that there are fundamental optical transitions, namely directly-allowed ( $n=1/2$ ) and indirectly-allowed ( $n=2$ ) transition. It is also noteworthy that the band gap energy of Bi<sub>2</sub>Te<sub>3</sub> loaded TiO<sub>2</sub> heterostructures was found to be 2.1 eV, indicating the optical absorption of the hybrid nanostructure has been extended from the UV region to the visible region.

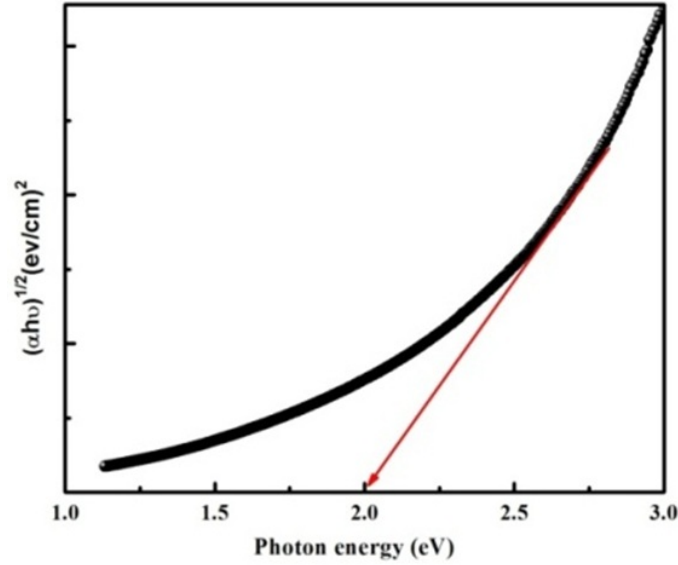


FIG. 1. Optical absorption spectra of Bi<sub>2</sub>Te<sub>3</sub> loaded TiO<sub>2</sub> thin film

#### 3.2. X-ray diffraction (XRD) pattern of Bi<sub>2</sub>Te<sub>3</sub> loaded TiO<sub>2</sub> thin film

The strong characteristic diffraction peak appeared at around 27.70° corresponds to (110) peak associated with rutile phase of TiO<sub>2</sub> (Space Group: P4<sub>2</sub>/mm, JCPDS: 00-001-0562) (Rigaku, D/MAX Ultima III XRD spectrometer (Japan)). Furthermore, it should be noted that diffraction peak appearing at 27.67° corresponds to the (015) plane of Rhombohedral Bi<sub>2</sub>Te<sub>3</sub> (JCPDS: 15-0863 space group R-3m) shown in Fig. 2. Due to overlap between (110) plane of TiO<sub>2</sub> and (015) plane of Bi<sub>2</sub>Te<sub>3</sub>, it is difficult to distinguish these two peaks in the XRD pattern. While the other peaks appeared at  $2\theta$  27.70°, 36.22°, 41.35°, 54.58°, 56.97° and 65.54°, corresponding to the (110), (101), (111), (211), (220) and (221) crystal plane of tetragonal TiO<sub>2</sub> and 27.67°, 37.86°, 62.91° and 69.91° corresponding to the (015), (1010), (0213) and (0216) crystal planes of rhombohedral Bi<sub>2</sub>Te<sub>3</sub>.

It was found that the diffraction peak of the resulting deposit confirms the successful loading of Bi<sub>2</sub>Te<sub>3</sub> nanoparticles on TiO<sub>2</sub>. The crystallite size of the material was calculated by using Debye Scherrer formula, given in equation 1:

$$D = \frac{0.94\lambda}{\beta \cos \theta}, \quad (1)$$

where  $D$  is crystallite size,  $\theta$  is Peak position of X-ray diffraction,  $\beta$  is Full Width at Half Maxima (FWHM) in radian,  $\lambda$  is Wavelength of X-ray used (0.154 nm). The XRD parameters are summarized in Table 1.

TABLE 1. XRD parameters.

Sample	Crystallite Size (D) (nm)	Microstrain( $\epsilon$ ) $10^{-3}$ (lines $m^{-2}$ )	Dislocation density ( $\delta$ ) $\times 10^{-3}$ (lines <sup>-2</sup> $m^{-4}$ )
Bi <sub>2</sub> Te <sub>3</sub> loaded TiO <sub>2</sub>	16.78	20156	3.5515

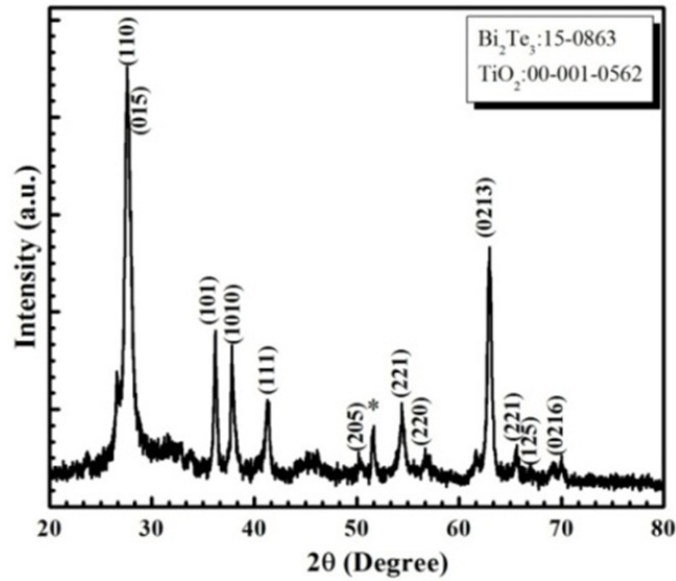


FIG. 2. X-ray diffraction pattern of  $\text{Bi}_2\text{Te}_3$  loaded  $\text{TiO}_2$  thin film

### 3.3. Field Emission Scanning Electron Microscopy (FESEM) of $\text{Bi}_2\text{Te}_3$ loaded $\text{TiO}_2$ thin film

The morphological analysis of the synthesized material was carried out using field emission scanning electron microscopy (FESEM) (Hitachi, S-4700). Fig. 3 shows the low and high magnification field emission scanning electron microscopy (FESEM) images. The FESEM image shows that entire surface of FTO substrate is covered with well-aligned  $\text{TiO}_2$  nanorods coated with  $\text{Bi}_2\text{Te}_3$  nanoparticles. From the higher magnification of such nanorod arrays, the average diameter of the  $\text{TiO}_2$  nanorod is 95–110 nm.

After  $\text{Bi}_2\text{Te}_3$  quantum dot loading, the  $\text{TiO}_2$  nanorods become rough, which means that the QDs have been successfully deposited on the surface of the  $\text{TiO}_2$  nanorods after potentiostatic electrodeposition. The vertical alignment of the  $\text{TiO}_2$  nanorods is beneficial for the improvement in the charge transfer of the solar cells. Such deep penetration of  $\text{Bi}_2\text{Te}_3$  nanoparticles into the  $\text{TiO}_2$  nanorods improves the charge separation and reduces recombination rate, which is beneficial for the photoelectrochemical performance of the solar cell.

### 3.4. Compositional analysis $\text{Bi}_2\text{Te}_3$ loaded $\text{TiO}_2$ thin film

Qualitative and quantitative analysis of the prepared  $\text{Bi}_2\text{Te}_3$  loaded  $\text{TiO}_2$  was carried out using energy dispersive X-ray spectroscopy (EDS).

The EDS spectrum confirms the presence of titanium, oxygen, bismuth and tellurium in prepared  $\text{Bi}_2\text{Te}_3$  loaded  $\text{TiO}_2$  thin film. From Figure 4, it is readily seen that the peaks at 4.5, 0.5, 2.4 and 3.7 keV confirm the presence of Ti, O, Bi and Te respectively in the  $\text{Bi}_2\text{Te}_3$ -loaded  $\text{TiO}_2$  film.

### 3.5. Photoelectrochemical performance (PEC)

The typical J-V characteristic curve of  $\text{Bi}_2\text{Te}_3$ -loaded  $\text{TiO}_2$  thin film was determined. The photoelectrochemical performance of the  $\text{Bi}_2\text{Te}_3$ -loaded  $\text{TiO}_2$  thin film was carried out using a two electrode cell configuration (AUTOLAB PGSTAT100 FRA 32 potentiostat). In order to evaluate the photoelectrochemical performance, the  $\text{Bi}_2\text{Te}_3$ -loaded  $\text{TiO}_2$  thin film acts as a photoanode, graphite as counter electrode with 0.5 polysulfide electrolyte. The cell configuration is as follows: Glass/ FTO/  $\text{Bi}_2\text{Te}_3$  loaded  $\text{TiO}_2$ / 0.5M Polysulfide/G .

The photoelectrochemical performance i.e. fill factor (FF) and overall light to electric energy conversion efficiency (%) was calculated by equation (2) and (3):

$$FF = \frac{V_{max} J_{max}}{V_{oc} J_{sc}} \quad (2)$$

$$\eta\% = \frac{V_{oc} J_{sc}}{P_{in} \times FF \times 100}, \quad (3)$$

where  $V_{oc}$  is open circuit voltage,  $J_{sc}$  is short circuit current,  $V_{max}$  is maximum voltage,  $J_{max}$  is maximum current, FF is the fill factor and  $P_{in}$  is the intensity of the incident light.

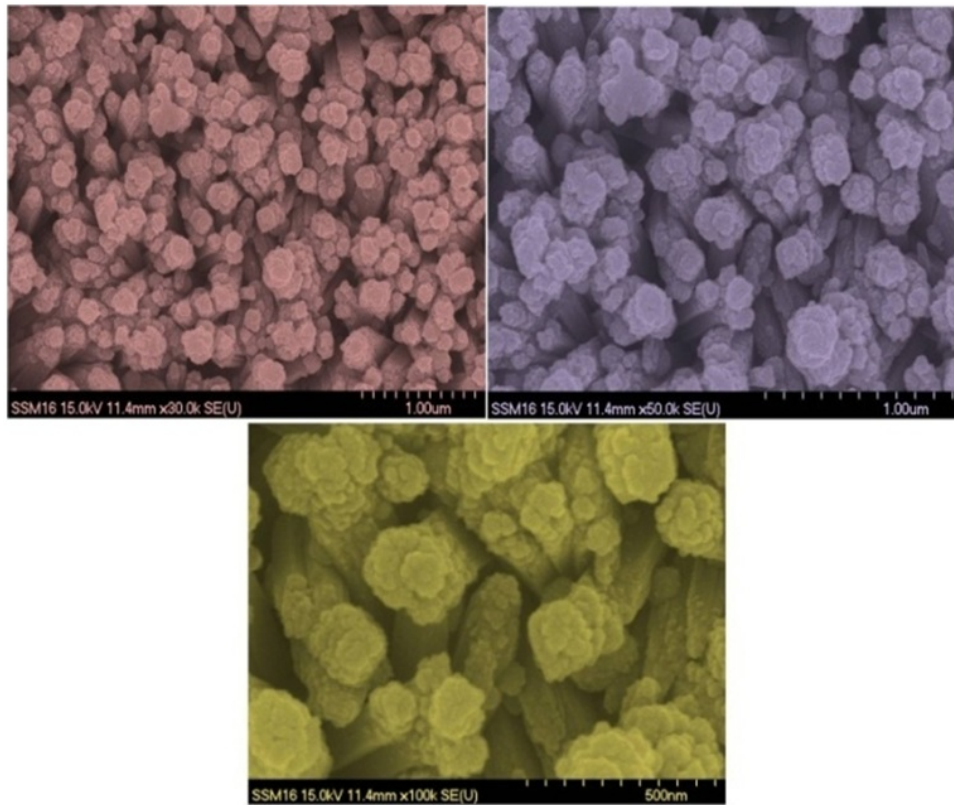


FIG. 3. Field emission scanning electron microscopy images of  $\text{Bi}_2\text{Te}_3$  loaded  $\text{TiO}_2$  thin film

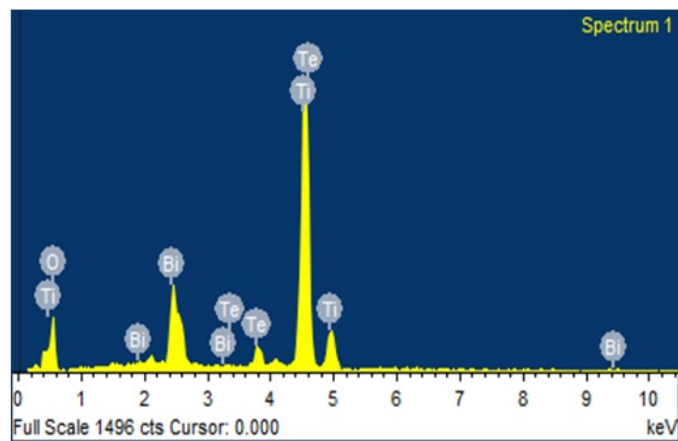


FIG. 4. EDS spectrum of  $\text{Bi}_2\text{Te}_3$  loaded  $\text{TiO}_2$  thin film

The detailed photovoltaic parameters are summarized in Table 2. The  $\text{Bi}_2\text{Te}_3$ -loaded  $\text{TiO}_2$  thin film shows 0.026% photoconversion efficiency.

TABLE 2. Photoelectrochemical solar cell parameters of  $\text{Bi}_2\text{Te}_3$  loaded  $\text{TiO}_2$  thin film

Electrode	$V_{oc}$ (mV)	$J_{sc}$ ( $\mu\text{A}/\text{cm}^2$ )	$R_s$ ( $\Omega$ )	$R_{sh}$ ( $\Omega$ )	$\eta\%$
$\text{Bi}_2\text{Te}_3$ loaded $\text{TiO}_2$	397.03	61	2660	4762	0.026

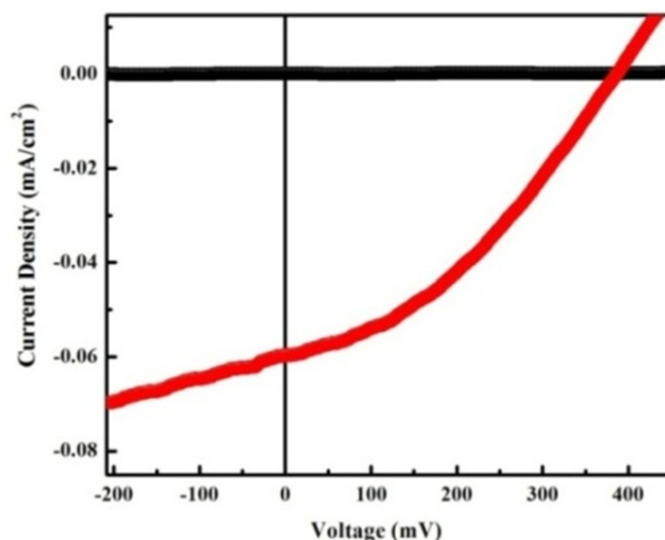


FIG. 5. J-V characteristic curve of  $\text{Bi}_2\text{Te}_3$  loaded  $\text{TiO}_2$  thin film

#### 4. Conclusion

In summary, a  $\text{Bi}_2\text{Te}_3$ -loaded  $\text{TiO}_2$  thin film was successfully prepared by a two-step synthetic strategy. 1D nanorods provided a unidirectional transport path for efficient charge, leading to high photoelectrochemical performance. Therefore, this novel combinatorial  $\text{Bi}_2\text{Te}_3$  loaded  $\text{TiO}_2$  thin film shows 0.026% photoconversion efficiency.

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