



## Short communication

Effect of surface modification of TiO<sub>2</sub> on the photovoltaic performance of the quasi solid state dye sensitized solar cells using a benzothiadiazole-based dyeG.D. Sharma<sup>a,b,\*</sup>, P. Suresh<sup>a</sup>, M.S. Roy<sup>c</sup>, John A. Mikroyannidis<sup>d,\*\*</sup><sup>a</sup> Physics Department, Molecular Electronic and Optoelectronic Device Laboratory, JNV University, Jodhpur (Raj.) 342005, India<sup>b</sup> Jaipur Engineering College, Kukas, Jaipur (Raj.), India<sup>c</sup> Defence Laboratory, Jodhpur (Raj.) 342011, India<sup>d</sup> Chemical Technology Laboratory, Department of Chemistry, University of Patras, GR-26500 Patras, Greece

## ARTICLE INFO

## Article history:

Received 17 August 2009

Received in revised form 21 October 2009

Accepted 26 October 2009

Available online 13 November 2009

## Keywords:

Dye sensitized solar cells (DSSCs)

Benzothiadiazole-based dye

BaCO<sub>3</sub> modified TiO<sub>2</sub> electrode

Polymer gel electrolyte

Electron lifetime

## ABSTRACT

We report the preparation of nanoporous TiO<sub>2</sub> electrode modified with an insulating material—BaCO<sub>3</sub> and used as electrode for quasi solid state dye sensitized solar cells (DSSCs), with a benzothiadiazole-based dye (BTDR2) as sensitizer and PEDOT:PSS coated FTO as counter electrode. We found that the BaCO<sub>3</sub> modification significantly increases the dye adsorption, resulting from the fact that the surface of BaCO<sub>3</sub> is more basic than TiO<sub>2</sub>. The performance of the DSSCs with and without BaCO<sub>3</sub> modified TiO<sub>2</sub> electrodes were analyzed by cyclic voltammograms, optical absorption spectra, current–voltage characteristics in dark and under illumination and electrochemical impedance spectra. The photovoltaic performance has been significantly improved for the BaCO<sub>3</sub> modified electrode as compared to bare TiO<sub>2</sub> electrode having the same other components in the DSSCs. The value of the overall power conversion efficiency ( $\eta$ ) improves from 2.42% to 4.38% under illumination intensity, when BaCO<sub>3</sub> modified electrode is used instead of bare TiO<sub>2</sub> electrode. The improvement in  $\eta$  has been attributed to the increased dye adsorption, reduction in recombination rate and enhancement in the electron lifetime when the modified TiO<sub>2</sub> electrode is used.

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## 1. Introduction

The dye sensitized solar cells (DSSCs) based on nanoporous TiO<sub>2</sub> films have been intensively studied as prospective alternatives of the conventional solar cells, largely because of their simple fabrication process, high power conversion efficiency (PCE) and low cost materials [1–6]. A DSSC is mainly composed of a dye adsorbed nanocrystalline film deposited on transparent conducting oxide substrate, a counter electrode and an electrolyte. The performance of DSSCs is mainly affected by the constituent's properties, i.e. sensitizers [7–11], anodic materials [12–19], electrolytes [20–22] and modification of anodic materials especially TiO<sub>2</sub> [23–26]. TiO<sub>2</sub> has been most frequently used as a photoanodic material in DSSCs due to its chemical stability and moderate charge transport capability. However, the electrons injected into TiO<sub>2</sub> layer are some times able to return to sensitizer or electrolyte, due to electron recom-

bination phenomena and cause a reduction in PCE. It has been reported that the surface modification of TiO<sub>2</sub> with oxides [27–32], or organic molecules [33] could separate the injected electrons and redox couples and thereby suppressing the charge recombination reaction.

The photosensitizers play a crucial role for the DSSCs getting higher PCE ( $\eta$ ). Up to now, DSSCs based on Ru-complex photosensitizer have exhibited the highest  $\eta$  and long term stability [34]. Since the cost of these dyes is very high, interest on metal free dyes as an alternative to these noble metal complexes has increased in recent years, due to many advantages, such as diversity of molecular structure, high molar extinction coefficient, simple synthesis as well as low cost [35–42]. Generally, organic dyes for efficient DSSCs are required to possess broad and intense spectral absorption in the visible region and proper match of its excited state redox potential with energy of the conduction band edge of nanocrystalline semiconductor. The major factors for low PCE of DSSCs based on metal free organic dyes are the formation of dye aggregation on the semiconductor surface and recombination of conduction band electrons with triiodide in the electrolyte [43].

Despite of high PCEs for the DSSCs with liquid electrolytes, problems are mainly caused by liquid electrolytes such as leakage and volatilization of liquid, possible desorption and photodegradation of the attached dyes. Moreover the corrosion of the counter elec-

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trode, have brought difficulties in device fabrication and limited the long term performance and potential use of these DSSCs [44]. To prevent or reduce electrolyte leakage of other type electrolytes, i.e. polymer/redox couple blends [45], polymer gel [46,47] and solid state or quasi solid state materials [48,49] have been introduced to replace the organic liquid electrolytes. Among them, polymer gel quasi solid state electrolytes have excellent properties such as easy fabrication, low cost and good stability so that they have obtained growing interest from the point of practical applications.

In this paper we report on the fabrication and characterization of quasi solid state DSSCs based on BaCO<sub>3</sub> modified nanoporous TiO<sub>2</sub> electrodes, metal free benzothiadiazole-based (BTDR2) dye as photosensitizer and PEDOT:PSS as counter electrode. The results show that BaCO<sub>3</sub> modification on the surface of TiO<sub>2</sub> forms an energy barrier against the electron transfer from TiO<sub>2</sub> to I<sub>3</sub><sup>-</sup>, resulting in an increase in the  $J_{sc}$  and  $V_{oc}$  due to the increased electron lifetime.

## 2. Experimental details

### 2.1. Preparation of dye sensitized photoelectrodes

Scheme 1 outlines the synthesis of the benzothiadiazole-based dye BTDR2. This dye is a linear molecule with two terminal cyanoacrylic acid anchoring moieties. A thiophene ring, which acts as  $\pi$ -conjugated segment, connects each side of the benzothiadiazole central unit with the terminal cyanoacrylic acid moieties. BTDR2 has been fully characterized by FT-IR and <sup>1</sup>H NMR spectroscopy. The detailed synthesis and characterization of BTDR2 has been described in our previous communication [50].

Fluorine doped tin oxide (FTO) glass plates were cleaned in detergent solution and then rinsed with de-ionized water and acetone. Then the plates were immersed in 40 mM TiCl<sub>4</sub> (aqueous) at 60 °C for 30 min and washed with de-ionized water and acetone. A transparent nanocrystalline layer was prepared on FTO glass plates by using the doctor blade printing employing a viscous paste of P25 TiO<sub>2</sub> (degussa) in ethanol, which was then dried for 3 h at room temperature. The TiO<sub>2</sub> electrode was sintered at 450 °C for 30 min. The modification of BaCO<sub>3</sub> on TiO<sub>2</sub> surface was performed by following steps. First the sintered TiO<sub>2</sub> thin film was dipped on a aqueous solution of saturated Ba(OH)<sub>2</sub> for 1 min, then washed thoroughly with de-ionized water followed by sintering at 500 °C for 30 min in air. The sensitization of BaCO<sub>3</sub> modified TiO<sub>2</sub> and bare TiO<sub>2</sub> electrodes were performed by overnight immersion in DMF solution containing  $5 \times 10^{-4}$  M of BTDR2. UV-visible absorption spectra of dye loaded films were measured by UV-visible spectrophotometer. The amount of dye adsorbed on the electrodes was estimated by measuring the absorption of dye solution after desorption using 0.1 M NaOH aqueous solution.

### 2.2. Fabrication of dye sensitized solar cells and their characterization

The FTO plates for counter electrodes were cleaned according to the method as described earlier for the preparation of photoelectrodes. The counter electrode was made by developing a thin film of PEDOT:PSS through spin coating, on the FTO glass substrate and then dried at 70 °C in air. After the sensitization, a quasi solid state polymer electrolyte consisting of: LiI (0.1 g), I<sub>2</sub> (0.019 g), propylene carbonate (5 mL), P25 TiO<sub>2</sub> (0.0383 g), PEO (0.2648 g), and 4-*tert*-butylpyridine (0.044 mL) into acetonitrile (5 mL) solvent, was spread over the dye sensitized photoelectrode by spin coating to form the hole transporting layer. The DSSCs were made by clamping the photoelectrode consisting of polymer electrolyte with counter electrode. We have fabricated the following quasi solid state DSSCs: FTO/TiO<sub>2</sub>-BTDR2/polymer electrolyte/PEDOT:PSS coated

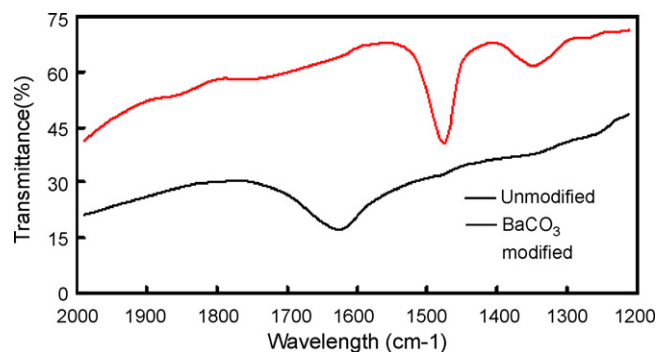


Fig. 1. FTIR spectra for BaCO<sub>3</sub> modified and unmodified TiO<sub>2</sub> films.

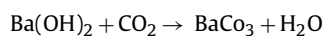
FTO (device A) and FTO/BaTiO<sub>3</sub> modified TiO<sub>2</sub> –BTDR2/polymer electrolyte/PEDOT:PSS coated FTO (device B).

The current–voltage ( $J$ – $V$ ) characteristics in dark and under illumination were obtained by a Keithley electrometer with built in power supply. A 100 W halogen lamp was used as light source and the intensity of the light is approximately 100 mw cm<sup>-2</sup> measured with the lux meter equipped with silicon detector. The electrochemical impedance spectra (EIS) measurements were carried out by applying bias of the open circuit voltage ( $V_{oc}$ ) and recorded over a frequency range of 1 mHz to 10<sup>5</sup> Hz with ac amplitude of 10 mV. The above measurements were recorded with an Autolab Potentiostat PGSTAT-30 equipped with frequency response analyzer (FRA).

## 3. Results and discussions

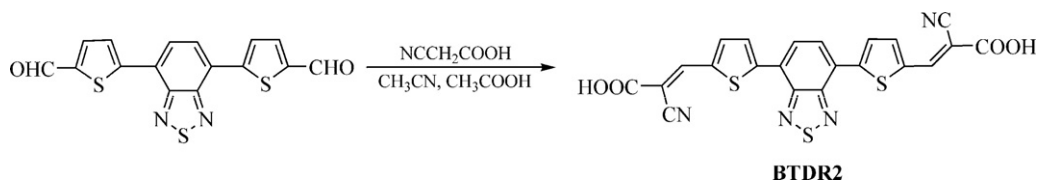
### 3.1. Characterization of electrodes

When a TiO<sub>2</sub> film is dipped into the aqueous solution of Ba(OH)<sub>2</sub>, the barium solution penetrates the porous TiO<sub>2</sub> film and barium ions are adsorbed onto the surfaces of TiO<sub>2</sub>. After exposure to air, Ba(OH)<sub>2</sub> reacts with carbon dioxide to yield the BaCO<sub>3</sub>, resulting in the formation of a layer BaTiO<sub>3</sub> on the TiO<sub>2</sub> surface:



Sintering at 450 °C does not lead to the decomposition of BaCO<sub>3</sub>, since the thermodynamic equilibrium temperature necessary for the direct decomposition of BaCO<sub>3</sub> in air is more than 800 °C [51]. We have recorded the FTIR spectra of both BaCO<sub>3</sub> modified and unmodified TiO<sub>2</sub> films to confirm the formation of BaCO<sub>3</sub> as shown in Fig. 1. The broad peak at 1633 cm<sup>-1</sup> in bare TiO<sub>2</sub> film can be attributed to bending mode of the O–H groups of the adsorbed water. However, the two peaks observed at 1473 cm<sup>-1</sup> and 1347 cm<sup>-1</sup> in modified TiO<sub>2</sub> film strongly support the formation of carbonate [52]. The sharp peak at 1473 cm<sup>-1</sup> is attributable to the asymmetric O–C–O stretch vibration and the broad peak at 1347 cm<sup>-1</sup> to the symmetric stretch vibration. These two peaks indicate the formation of coordination bonds between CO<sub>3</sub><sup>2-</sup> moiety and Ti(IV).

Fig. 2 shows the UV–visible spectra of BTDR2 dye loaded unmodified and BaCO<sub>3</sub> modified TiO<sub>2</sub> films. In comparison to the spectrum in THF solution, the absorption spectrum in TiO<sub>2</sub> film was broader which is due to an interaction between the dye and TiO<sub>2</sub> [53] indicating that the BTDR2 molecules are assembled on the TiO<sub>2</sub> film in a monolayer state with very little aggregation due to its dimensional structure. It can be seen from the Fig. 2 that with the BaCO<sub>3</sub> modification the maximum absorbing peak at 470 nm blue shifted by 15 nm and was further broadened. It also reveals that the modification of BaCO<sub>3</sub> apparently increases the amount of adsorbed dye molecules. We have measured the absorption spectra of the dye desorbed from the TiO<sub>2</sub> surfaces into 0.05 M NaOH solution



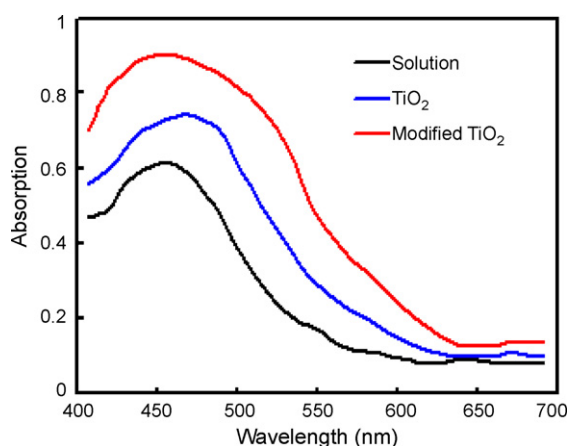
**Scheme 1.** Synthesis of the benzothiadiazole-based dye BTDR2.

to estimate the surface concentration of dye. The surface concentration of dye increased to  $8.50 \times 10^{-8}$  from  $4.5 \times 10^{-8}$  mol cm<sup>-2</sup> after the surface modification of TiO<sub>2</sub>. This can be attributed to the higher basicity of TiO<sub>2</sub> surface upon BaCO<sub>3</sub> modification. The carboxyl groups in BTDR2 dye molecule are more easily adsorbed to the surface of the basic coating layer [31,54]. The better dye adsorption on the surface having more basic nature favors the attachment of the dye with carboxyl groups [28].

### 3.2. Current–voltage characteristics

Fig. 3(a) shows the *J*–*V* characteristics of the quasi solid state DSSCs under illumination intensity of 100 mW cm<sup>-2</sup>. The bare TiO<sub>2</sub> electrode showed a  $V_{oc} = 0.65$  V,  $J_{sc} = 7.72$  mA cm<sup>-2</sup>, fill factor (FF) = 0.45 and PCE ( $\eta$ ) = 2.42%. On the other hand, the BaCO<sub>3</sub> modified TiO<sub>2</sub> electrode showed  $V_{oc} = 0.72$  V,  $J_{sc} = 11.5$  mA cm<sup>-2</sup>, FF = 0.53 and  $\eta = 4.38\%$ . The BaCO<sub>3</sub> modified electrode enhances the PCE. The increase in  $V_{oc}$  might be due to the movement of the TiO<sub>2</sub> conduction band to negative direction, which is related to the formation of a barrier layer at the TiO<sub>2</sub> surface. Moreover, in the BaCO<sub>3</sub> modified electrode the suppression of charge carrier recombination between the photoinjected electrons of TiO<sub>2</sub> and the triiodide ions of the redox electrolyte takes place, resulting in an improvement in the  $V_{oc}$  of the DSSC.

The improvement in photocurrent can be attributed to the decrease in the electron loss at the electron transfer in the interface of TiO<sub>2</sub> electrode/electrolyte. The improvement in photocurrent may also correspond to the increase in the amount of dye adsorbed (Fig. 2). The increased dye adsorption by the BaCO<sub>3</sub> modified TiO<sub>2</sub> as compared to the bare TiO<sub>2</sub> film, indicates an increased surface area of the modified TiO<sub>2</sub> film. This increased surface area provides additional adsorption sites for the dye, which contributes to the increase in  $J_{sc}$ . The increase in the  $J_{sc}$  may also arise from the enhanced light scattering by the modified TiO<sub>2</sub> film relative to that by the bare TiO<sub>2</sub> film, because the former apparently has larger and clustered particles than the latter.



**Fig. 2.** Optical absorption spectra of BTDR2 in solution and loaded with TiO<sub>2</sub> and modified TiO<sub>2</sub>.

The effect of BaCO<sub>3</sub> modification is further confirmed by the *J*–*V* characteristics in dark as shown in Fig. 3(b). The origin of dark current in DSSC is due to the porous nature of TiO<sub>2</sub> structure, which provides pathways for liquid redox electrolyte (i.e. I<sub>3</sub><sup>-</sup> species) to penetrate through the porous film and contact the FTO surface. During the penetration, electron recombination takes place and results in a loss of photocurrent. It can be seen from this figure that the dark current corresponding to DSSC with modified TiO<sub>2</sub> decreases, relative to the DSSC with bare TiO<sub>2</sub>. It is also observed that the BaCO<sub>3</sub> modification shifts the onset potential towards higher potential (from 0.38 V to 0.60 V). The observed decrease in dark current is a result of the suppression of I<sub>3</sub><sup>-</sup> reduction at the dye sensitized TiO<sub>2</sub> electrode. This favors reduction of back electron transfer and consequently increases the  $V_{oc}$ . One explanation of the decrease in the dark current in the DSSC with BaCO<sub>3</sub> modified TiO<sub>2</sub> film electrode relates to the increased energy barrier at TiO<sub>2</sub> electrolyte interface enable by the BaCO<sub>3</sub> deposition. BaCO<sub>3</sub> can form a barrier at the TiO<sub>2</sub> electrode interface, owing to the fact that its conduction band edge shifts more negative than that of TiO<sub>2</sub>. This energy barrier reduces the back electron transfer from the conduction band of TiO<sub>2</sub> to I<sub>3</sub><sup>-</sup> in the electrolyte, which in turn increases the  $V_{oc}$ .

Since the amount of the photogenerated electrons is directly proportional to the incident illumination intensity, the variation of short circuit photocurrent ( $J_{sc}$ ) with the illumination intensity ( $P_{in}$ ) can be used to get information about the amount of photogenerated electrons contributing to the photocurrent and also electron transfer kinetics. Fig. 4(a) shows that  $J_{sc}$  of the DSSCs with bare TiO<sub>2</sub> and modified TiO<sub>2</sub> were direct proportional with  $P_{in}$ . This indicates that the current density for both DSSC's was limited by the  $P_{in}$ , rather than electron transfer processes such as mass transport of I<sub>3</sub><sup>-</sup> or electron transfer at counter electrode [55]. The slope for the modified TiO<sub>2</sub> (i.e. 0.112) is 30% higher than that for bare TiO<sub>2</sub> (0.086) electrode, which indicates that 30% more electrons are collected from the same amount of photogenerated electrons at FTO surface. This confirms that the use of modified TiO<sub>2</sub> electrode in DSSCs facilitates the electron transfer at the porous TiO<sub>2</sub>/FTO interface, resulting in an increase in collection efficiency.

Open circuit voltage decay (OCVD) technique has been employed as a powerful tool to study the electron lifetime in DSSC's and also provide some quantitative information on the electron recombination rates in DSSCs [28,55–57]. In order to conduct the OCVD measurement, the device is illuminated with white light and a steady state voltage was obtained and then the decay of voltage was monitored after interrupting the illumination. The decay of the photovoltage reflects the decrease of the electron concentration at the FTO surface, which is mainly caused by the charge recombination. Fig. 4(b) shows the OCV decay curves of DSSCs with and without modified TiO<sub>2</sub> electrodes. It can be seen from these curves that the OCVD response of the DSSC with modified TiO<sub>2</sub> is much slower than that bare TiO<sub>2</sub> electrode. From the OCVD measurement, the electron lifetime ( $\tau_n$ ) is determined by the reciprocal of the derivatives  $(dV_{oc}/dt)^{-1}$  of the decay curves normalized by the thermal voltage ( $kT/q$ ), using the following expression:

$$\tau_n = \frac{kT}{q} \left( \frac{dV_{oc}}{dt} \right)^{-1}$$

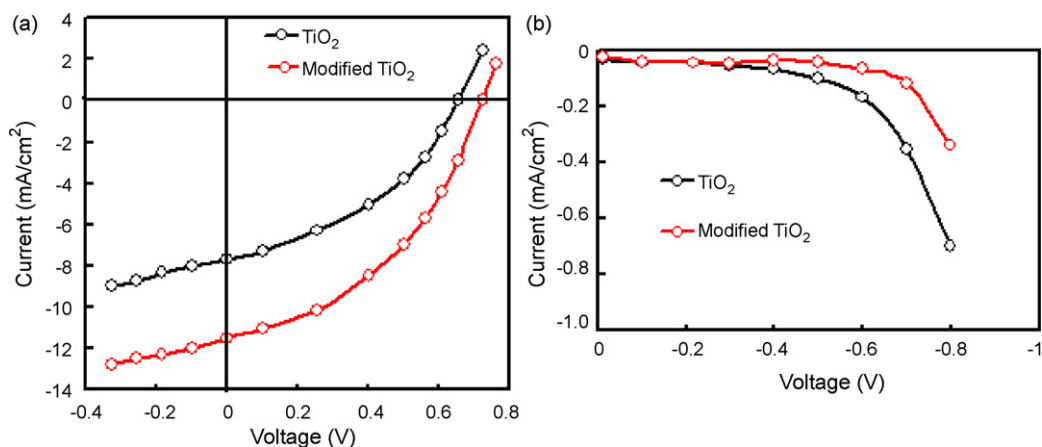


Fig. 3. Current–voltage characteristics of the DSSCs with  $\text{TiO}_2$  and  $\text{BaCO}_3$  modified electrodes (a) under illumination intensity  $100 \text{ mW cm}^{-2}$  (a) in dark.

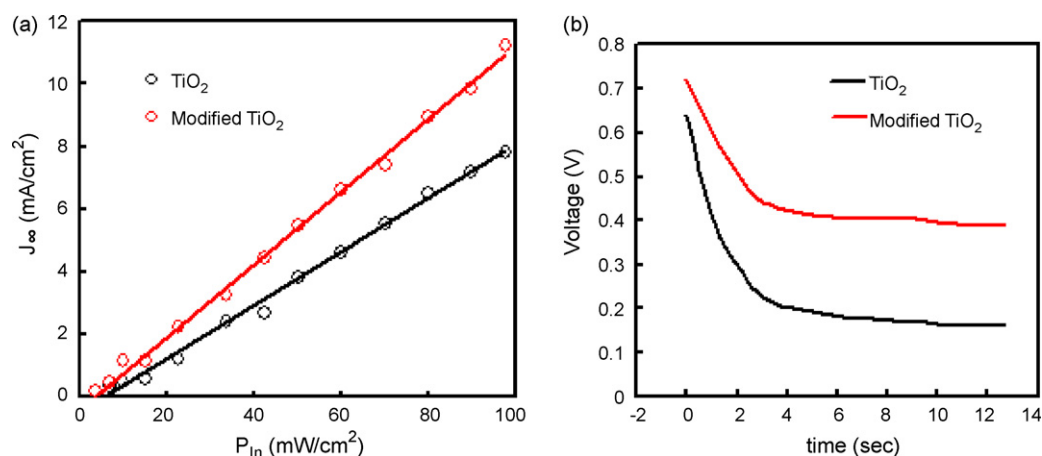


Fig. 4. (a) Variation of  $J_{sc}$  with  $P_{in}$  (b) open circuit voltage decay curves for DSSC's with  $\text{TiO}_2$  and  $\text{BaCO}_3$  modified electrodes.

The value of  $\tau_n$  for the DSSC with modified  $\text{TiO}_2$  film is longer than that for bare  $\text{TiO}_2$  film suggesting that the electron injected from the excited dye can survive for a longer time and hence facilitate electron transport without undergoing losses at FTO surface. Therefore, OCVD measurements demonstrate that the modified  $\text{TiO}_2$  film, are able to reduce the photoelectron recombination rate effectively due to the longer electron lifetime.

### 3.3. Incident photon to conversion efficiency (IPCE)

Fig. 5 shows the incident photon to current conversion efficiency (IPCE) of quasi solid state DSSCs based on bare  $\text{TiO}_2$  and  $\text{BaCO}_3$  modified  $\text{TiO}_2$  electrodes, as a function of the illumination wavelength. The DSSC with  $\text{TiO}_2$  electrode shows values in the range 32–38% in the wavelength region of 440–532 nm, while the DSSC based  $\text{BaCO}_3$  modified  $\text{TiO}_2$  electrode shows values of 50–56% in same wavelength region. Since the IPCE is defined as the ratio of the number of electrons in the external circuit produced by an incident photon at a given wavelength and can be expressed by following expression [58].

$$\text{IPCE}(\lambda) = \text{LHE}(\lambda)\phi_{inj}\eta_c$$

where  $\text{LHE}(\lambda)$  is the light harvesting efficiency,  $\phi_{inj}$  is the quantum yield of the charge injection and  $\eta_c$  is the collection efficiency of the photoinjected electrons at the back contact. The factor,  $\text{LHE}(\lambda)$  is mainly related to the adsorbed dye molecules  $\text{cm}^{-2}$ . Since the surface concentration of dye adsorbed by the  $\text{BaCO}_3$  modified  $\text{TiO}_2$

electrode is higher than that for bare  $\text{TiO}_2$  electrode, the increased value of LHE may be one of the reasons for the enhancement in the IPCE.

Since the factor  $\phi_{inj}$  is related to the energetic discrepancy between the conduction band of  $\text{TiO}_2$  and the LUMO level of the dye, the large energetic difference creates a driving force, which facilitates charge transfer from the LUMO of the dye molecules to the conduction band of  $\text{TiO}_2$  [59], resulting in an increase in  $J_{sc}$  and consequently the IPCE.

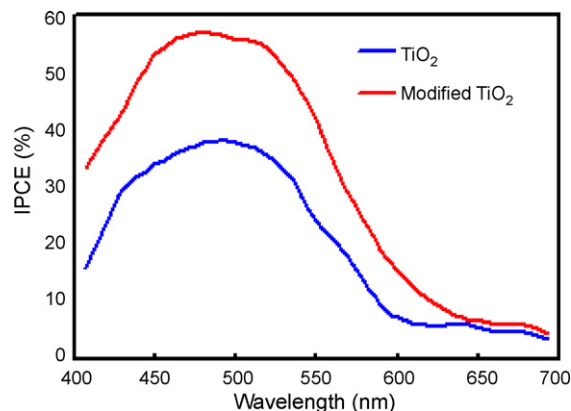


Fig. 5. IPCE action spectra of quasi solid state DSSCs with bare  $\text{TiO}_2$  and  $\text{BaCO}_3$  modified  $\text{TiO}_2$  electrodes.

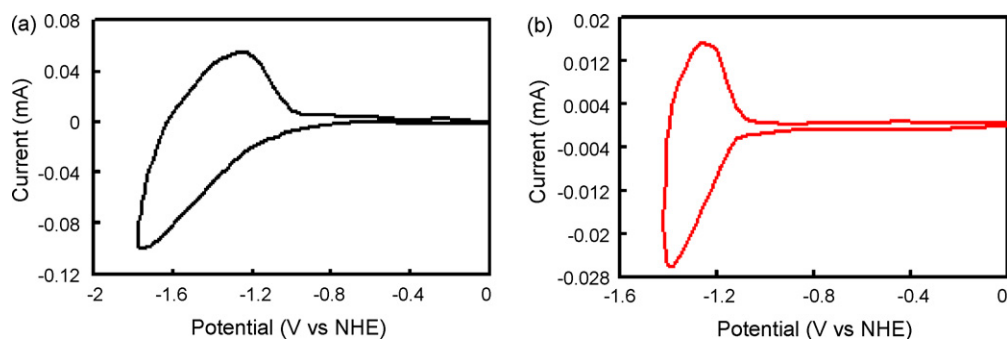


Fig. 6. Cyclic voltammograms of (a) TiO<sub>2</sub> electrode and (b) BaCO<sub>3</sub> modified TiO<sub>2</sub> electrode.

The  $\eta_c$  is a critical factor for the enhanced PCE after the BaCO<sub>3</sub> modification. Since the charge recombination in the electrode/electrolyte interface cause a loss of electron collection along the TiO<sub>2</sub> layer, the modification of BaCO<sub>3</sub> forms a thin barrier layer that delays the recombination reaction. The thin layer of BaCO<sub>3</sub> in modified TiO<sub>2</sub> blocks the back flow in the back reaction (triiodides of redox electrolyte and cations of dye), which contribute to the increase in  $V_{oc}$  of the DSSCs.

#### 3.4. Interfacial reaction obtained from the cyclic voltammetry and electrochemical impedance spectra

The cyclic voltammetry is a useful method for detecting interfacial electron flow in the TiO<sub>2</sub> electrolyte. Fig. 6 shows the cyclic voltammograms curves of the bare and BaCO<sub>3</sub> modified TiO<sub>2</sub> electrode in lithium perchlorate in acetonitrile solution as electrolyte. Both voltammograms show hysteresis shape characteristics which suggest that electron charging/discharge occurs in the anodic TiO<sub>2</sub> film electrolyte interface, indicating capacitive currents in the electrolyte. From Fig. 6, it can be seen that a gradual onset of the capacitive current forward scan due to the injection of the surface trap state electrons below the bulk conduction band edge [33]. However, a much lower capacitance is found for the BaCO<sub>3</sub> modified electrode compared to the bare TiO<sub>2</sub> electrode, implying that the number of deep trap state electrons existing in the surface of TiO<sub>2</sub> [60], decreases upon the modification with BaCO<sub>3</sub>. As it can be seen from Fig. 6, the onset potentials are around -0.9 V and -1.2 V (vs NHE) for the TiO<sub>2</sub> and the modified TiO<sub>2</sub> electrodes, respectively. This demonstrates that BaCO<sub>3</sub> modification forms an energy barrier, which plays the role of blocking layer that suppresses back electron flow to the electrolyte, improving the PCE of the DSSC. In addition, the BaCO<sub>3</sub> modification appears to passivate the surface state or trap sites on the surface of the anodic TiO<sub>2</sub> electrode [61]. This is because the current in the positive potential, originates from the charge transfer through the trap surface states in the

band gap of TiO<sub>2</sub>. At this point, the Ti<sup>3+</sup> states leaving the surface region participate in electron transfer that influences the electron lifetime of the photoinduced electrons in the interfacial electron transfer.

Electrochemical impedance spectroscopy has been widely used to investigate the kinetics and energetics of transport and recombination in DSSCs [62–66]. Fig. 7 shows the electrochemical impedance spectra of DSSCs with and without BaCO<sub>3</sub> modified TiO<sub>2</sub> measured at 0.7 V. The Nyquist Plots (Fig. 7(a)) consists of two semicircles. The semicircle in high frequency region is assigned to the impedance related to charge transport at PEDOT:PSS counter electrode, while the larger semicircle in low frequency region represents the electron transfer at the TiO<sub>2</sub>/electrolyte interface and ion diffusion of redox species, in the electrolyte. Fitting the low frequency semicircle with the equivalent circuit as shown in Fig. 7, gives charge transfer resistance ( $R_{ct}$ ) and chemical capacitance ( $C_{\mu}$ ) [67,68]. It is found that the DSSC with BaCO<sub>3</sub> modified TiO<sub>2</sub> exhibits higher value of  $R_{ct}$  (255  $\Omega$ ) and lower value for  $C_{\mu}$  (98  $\mu$ F) than that of bare TiO<sub>2</sub> DSSC with 96  $\Omega$  for  $R_{ct}$  and 110  $\mu$ F for  $C_{\mu}$ .

We have estimated the values of electron life time ( $\tau_n$ ) from the product of  $R_{ct}$  and  $C_{\mu}$  and the values are 9 ms and 25 ms for DSSC employing bare TiO<sub>2</sub> and BaCO<sub>3</sub> modified TiO<sub>2</sub> electrodes, respectively. The Bode plots of EIS Spectra (mid frequency range) are shown in Fig. 7(b). The frequency peak related to the BaCO<sub>3</sub> modified TiO<sub>2</sub> electrode shifted towards the lower frequency side relative to bare TiO<sub>2</sub> electrode. The electron lifetime have been estimated from the expression  $\tau_n = 1/2\pi f_{max}$ , where  $f_{max}$  is the peak frequency and found to be 10 ms and 23 ms for DSSCs with modified TiO<sub>2</sub> and bare TiO<sub>2</sub> respectively. These values are in good agreement estimated from the Nyquist plots of EIS spectra. The increase in  $\tau_n$  indicates that using BaCO<sub>3</sub> modified TiO<sub>2</sub> electrode, decreases the interfacial recombination rate for electrons with triiodide ions. This may be one of the reasons for the improvement in the PCE of the DSSCs with BaCO<sub>3</sub> modified TiO<sub>2</sub> electrode.

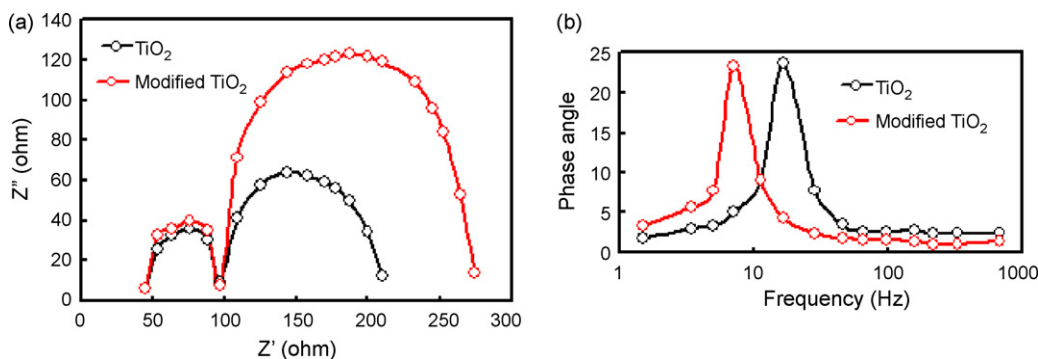


Fig. 7. EIS spectra (a) Nyquist plots (b) Bode plots for DSSCs based on TiO<sub>2</sub> and BaCO<sub>3</sub> modified electrodes.

#### 4. Conclusions

In conclusion, we have prepared the BaCO<sub>3</sub> modified TiO<sub>2</sub> electrode and applied it for the fabrication of quasi solid state dye sensitized solar cell (DSSC) using a benzothiadiazole-based dye (BTDR2) as sensitizer and PEDOT:PSS coated FTO as counter electrode. The performance of the DSSC with modified TiO<sub>2</sub> was investigated systematically employing *J*–*V* characteristics in dark and under illumination, incident photon to current efficiency (IPCE) and electrochemical impedance spectra measurements. It was found that the PCE significantly improves as compared to bare TiO<sub>2</sub> electrode. This improvement in PCE is due to the increase dye adsorption, formation of an energy barrier against the electron transfer from TiO<sub>2</sub> to electrolyte and increased electron density to external circuit due to the longer electron lifetime as compared to bare TiO<sub>2</sub> electrode.

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