


Original Article

# Application of Flexible Sheet in the Construction of Bio-Battery through Using Immobilized Bacteriorhodopsin

Enayatollah Keshavarz , Ahmad Molaeirad \* 

Department of Biophysics, Science and Research Branch, Islamic Azad University, Tehran, Iran

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## Correspondence

Molaeirad Ahmad

Email: a.molaeirad@gmail.com

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## Abstract

**Introduction:** Biophotovoltaic cells have often been studied due to their properties and their potential applications in micro and nano equipments. In order to enhance the quality and versatility of these bio-photocells, flexible sheets such as polyethylene terephthalate (PET) have been widely used. In this study, ZnO nanoporous films were used for immobilization of bacteriorhodopsin (bR) due to its great surface area, measured against titanium dioxide ( $TiO_2$ ). In addition to good conductivity, its superiority was proved by the arrangement of zinc oxide atoms at a suitable temperature.

**Materials and Methods:** In the present study, bacteriorhodopsin was immobilized on ZnO-PET surface through modifying the PET as a photoanode in (Dye-Sensitive Solar Cell) DSSCs. Furthermore, a non-toxicity protein, bR, was substituted for sensitizing ZnO-PET nanoparticles in DSSCs instead of the common expensive chemical-based dyes such as ruthenium-based or organic dyes. Atomic Force Microscopy technique was used to study the morphology of modified PET-ZnO & PET- $TiO_2$  surfaces before and after immobilization of bR

**Results:** AFM images show signs of excellence in zinc oxide in the atomic arrangement. Finally, the typical I-V curves of the biomolecule-sensitized biosolar cell were obtained. The results indicated that the overall conversion efficiency of the photocell is about 0.16 %, a solar cell flux ( $J_{sc}$ ) of 0.45 mA  $cm^{-2}$ , an open-circuit voltage ( $V_{oc}$ ) of 0.57 V, and a fill factor of 0.62.

**Conclusion:** Atomic composition of nanoparticles of zinc oxide at a suitable temperature is better than titanium dioxide. This makes the cell more efficient in transporting electrons. The efficiency of the cell produced on the PET bed is appropriate but requires more scientific research.

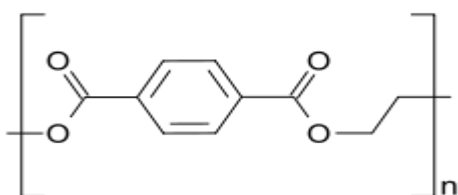
**Keywords:** Bio photovoltaic, Bacteriorhodopsin, Titanium dioxide, Atomic force microscopy, PET

## 1. Introduction

In recent years, biophotovoltaic cells have been studied because of their properties and future application of their micro and nano equipment. In all these studies, size and flexibility of implicated sheets and equipment are quite challenging; therefore, it appears that using immobilized bio macromolecules immobilized on the

flexible sheets are suitable approaches of prevalence on these challenges. Among a number of proteins used for bioelectronics applications, the photoactive membrane protein, bacteriorhodopsin (bR), is the most interesting one [1-4]. This protein is located in the purple membrane (PM) of *Halobacterium salinarum*. According to studies, manufacture of the bR film on a

transparent indium tin oxide (ITO) electrode has been reported. Nowadays, flexible sheet such as polyethylene terephthalate (PET) is prevalently used [5]. PET is a flexible polymer, generally used in photocells and in micro equipments. Polyethylene terephthalate is the most common thermoplastic polymer resin of the polyester family thermo forming for manufacturing and in combination with glass fiber for engineering resins.



PET in its natural state is a colorless, semi-crystalline resin. Based on how it is processed, PET can be semi-rigid, and is very lightweight. It is strong and impact-resistant. The reported photocurrent produced by biophotovoltaic cell based on bR/ITO/PET electrode is at the picoampere and nanoampere level, being quite low [6]. Furthermore, researchers reported effectual dye-sensitized solar cells (DSSC) via PM immobilized on a  $TiO_2$  nano particulate film [7, 8]. However, in recent years, DSSCs have adverted tremendous attention for economical production and relatively high energy conversion efficiency [9]. Up to now, numerous kinds of nanoparticles have been used as a semiconductor in DSSCs, such as rutile  $TiO_2$ ,  $SnO_2$ ,  $In_2O_3$ ,  $Nb_2O_5$ , and  $ZnO$  [10-13], among which, ZnO has attracted much attention in DSSCs due to some of its inherent properties [8]. ZnO is one of the hardest materials in the family of II-VI semiconductors [14, 15]. Moreover, compared with other semiconductors, ZnO has some unique properties such as higher exciton binding energy (60 meV) at room temperature, higher electron mobility ( $115-155 \text{ cm}^2\text{V}^{-1}\cdot\text{s}^{-2}$ ) that is more favorable for the collection of photo-induced electrons [16], high breakdown strength, cohesion, exciton stability, and direct wide band gap (3.37 eV) [17]. In addition, because of the

great surface area and finest protein adsorption, ZnO nanoporous films are an appropriate material for proteins such as bR immobilization. ZnO has also been used and designed for optoelectronics and piezoelectric equipments such as bio battery and biofuel cells [18]. It is appropriate and sensible for transparent conductor and plasma-flashover cathode emitters [19].

In the present study, bacteriorhodopsin were immobilized on ZnO-PET surface through modifying PET surface to be used as a photoanode in DSSCs. Successful conversion of visible light into electricity through utilizing this novel nanobiohybrid electrode was achieved. The optimum level for the present study was to propose a new biocompatible and biodegradable bacterial extract including purple membrane protein and some dyes for a fabrication of low-cost and environment-friendly DSSCs. Furthermore, an inexpensive extract of bR was used for sensitizing ZnO-PET nanoparticles in DSSCs instead of the general expensive chemical-based dyes such as ruthenium-based or organic dyes.

## 2. Materials and Methods

### 2.1 Materials

PET was provided from Solaronix and ZnO,  $TiO_2$ , bR and other utilized chemical materials were purchased from Sigma-Aldrich and Merk Company.

### 2.2. Methods

#### 2.2.1. Structure and Function Study of bR

Structure and function study of bR was done by using UV-visible spectrometry (Unicam UV 300 model). bR activity assay and photon induction were done through the use of KCl (3 M) and  $MgCl_2$  (80 mM). In pH 7.1, bR containing film was added to this solution. For excitation of proton pump activity of bR, a lamp with power 200 W in a distance of 30 cm from the sample was used and pH changes were measured for 10,20, and 30 minutes.

### 2.2.2 Morphology Study with AFM

In this section, the AFM technique was used to study the morphology of modified PET-ZnO surfaces before and after immobilization of bR. Results showed AFM images of modified PET-ZnO surface in the absence and presence of the bR. AFM images indicated that bR was effectively attached to the PET-ZnO surface across the two methods.

### 2.2.3 Photo Anode and Cathode Preparation

#### 2.2.3.1. Preparation of Photo Anode

In this research, the preparation of photo anode was done by using Belding method. PET sheets were used as a counter electrode. After cutting the PET glasses into the dimension of 10\* 10 mm, two holes were drilled in, using a drill press. The perforated sheets were cleaned by ultrasound in an acetone and ethanol bath for 20 Min. In this section, PET was underneath UV-O3 beam for 18 minutes and treated with TiCl<sub>4</sub> for 30 minutes. Then, TiO<sub>2</sub> and ZnO-catalyst were deposited on the PET glass, coated with a drop and heat treatment was carried out at 100 °C (5min), 110°C (10min), 120 °C for 15 Min and 150°C for 30min. The pigment-adsorbed TiO<sub>2</sub> and ZnO electrodes and the counter electrode were assembled into a sealed sandwich solar cell with hot melt Surlyn film (30 µm thickness) as a spacer between the electrodes. A drop of the electrolyte solution was placed on the drilled hole in the counter electrode of the assembled cell and was driven into the cell via vacuum backfilling. Finally, the hole was sealed using extra Surlyn [20]. AFM was used to study thickness and softness of the prepared surface of PET. Ultimately bR solution in 1mg/ml was immobilized on modified surface of PET.

#### 2.2.3.2. Cathode Preparation

Cathode preparation of photocell is a subsequent step in solar cell designing. Therefore, the platinum catalyst

was deposited on the FTO glass, coated with drop of H<sub>2</sub>PtCl<sub>6</sub> solution (2 mg Pt in 1 mL ethanol), and heat treatment was carried out at 400°C for 15 Min. The pigment-adsorbed TiO<sub>2</sub> electrode and counter electrode were assembled into a sealed sandwich solar cell with hot melt Surlyn film (30 µm thickness) as spacer between the electrodes. A drop of the electrolyte solution was placed on the drilled hole in the counter electrode of the assembled cell and was driven into the cell via vacuum backfilling. Finally, the hole was sealed using extra Surlyn [13].

## 3. Results

### 3.1. Measurements

In this study, absorption spectra and structure modification of bR was done by the use of a Unicam UV 300 spectrophotometer in the range of 250 to 700 nm. After making the bio-solar cells via bR, the current-voltage curve was obtained by applying an external bias to the cell and measuring the generated photocurrent under simulated sunlight (Luzchem) irradiation with a microstate potentiostat the model dropsens.

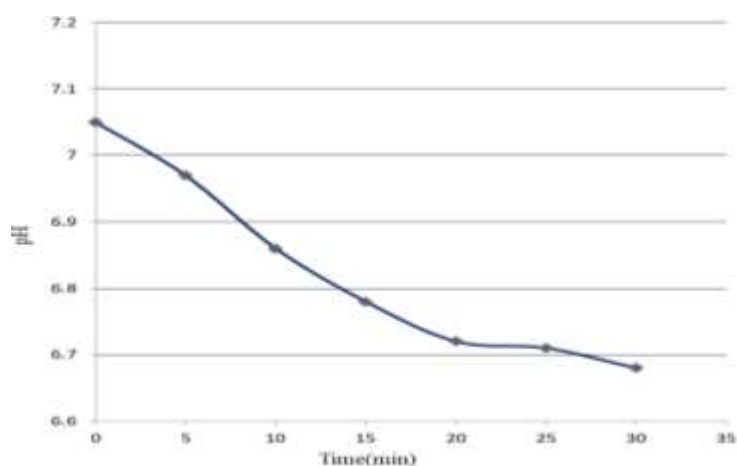
### 3.2. Study of ZnO-PET Surface Morphology

The surface morphology of ZnO-PET film was examined by using atomic force microscopy (AFM). The AFM studies could provide comprehensive evidence about the surface morphology of ZnO coated on the PET. Atomic force microscopy was used to investigate the surface of the nanocrystalline ZnO-PET morphology. The AFM images (20µm×20µm 5µm×5µm, 2µm×2µm, 5µm×5µm surface plots) of the coated PET surface by using ZnO and TiO<sub>2</sub> nanoparticles are shown in Fig. 4. The film porosity is in the range of 10 nm, which is appropriate for photovoltaic applications.

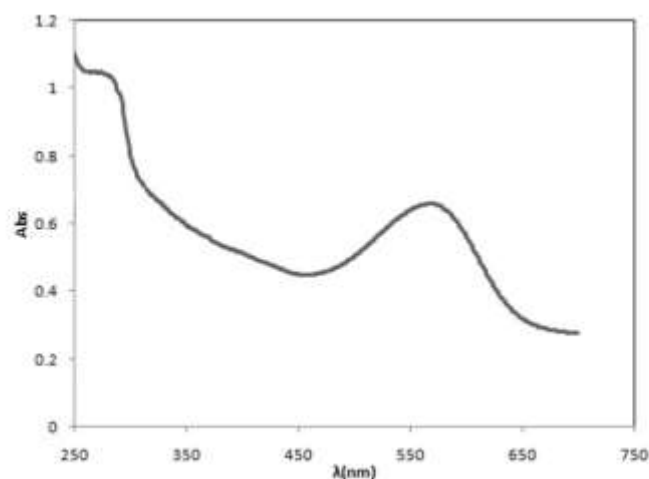
### 3.3. Photo electrochemical Properties of DSSC

The photovoltaic performance of DSSCs using bacterial pigments was investigated by measuring the current–voltage (I–V) curves under irradiation with white light AM1.5 ( $100\text{mWcm}^{-2}$ ) from a solar simulator lamp. Short circuit current ( $J_{sc}$ ), open circuit voltage ( $V_{oc}$ ), fill factor, and energy conversion efficiency were measured to investigate the performance of bR as sensitizer in DSSCs. The typical I–V

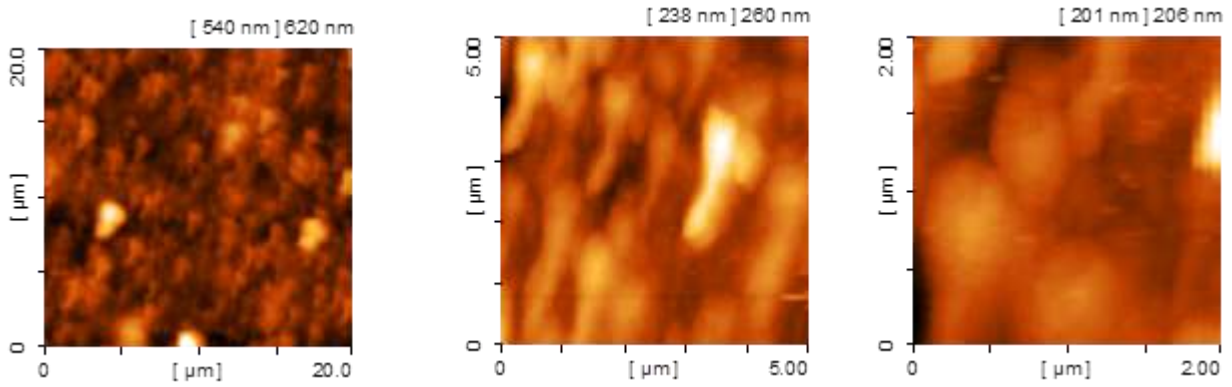
curves of the biomolecule-sensitizer solar cell using this pigment, shown in (Fig. 5). Our results show that  $J_{sc}$  of  $0.45\text{ mA cm}^{-2}$ , a  $V_{oc}$  of  $0.57\text{ V}$ , a fill factor of  $0.62$ , and an overall conversion efficiency of  $0.16\%$  when bR pigments were simultaneously used as sensitizer. A power conversion efficiency of  $0.11\%$  was obtained for DSSCs based on bR.



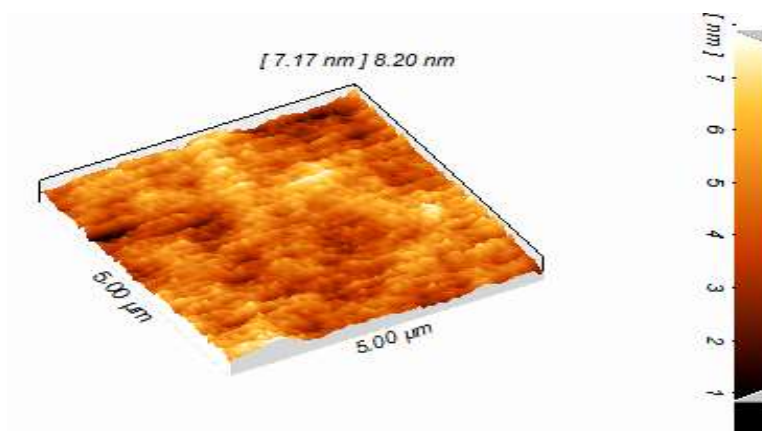
**Figure1.** pH changes as implication of activity of bR suspension under illumination by using of a tungsten lamp



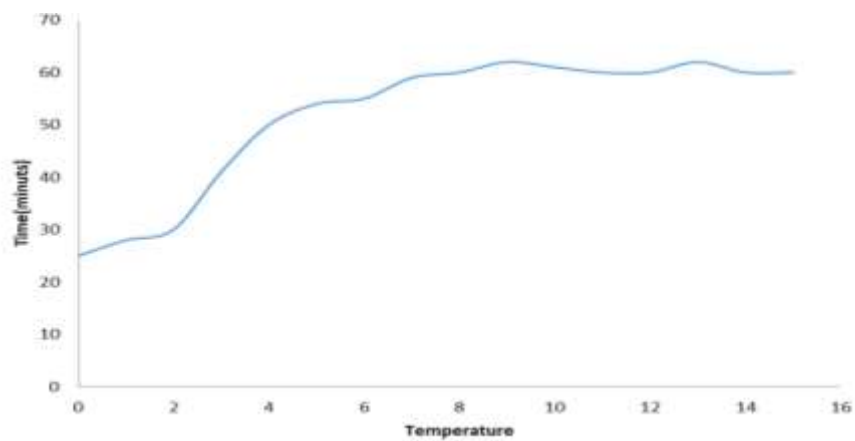
**Figure2.** UV-Vis absorption spectra of  $0.5\text{ mg/ml}$  of bR suspension  $25^{\circ}\text{C}$



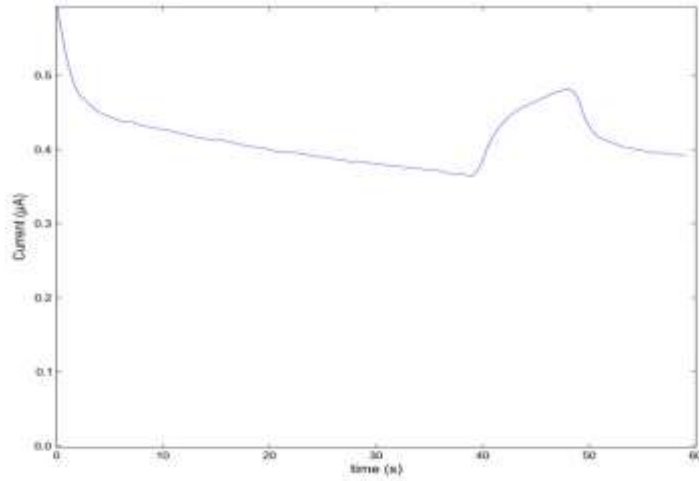
**Figure3.** AFM images of the TiO<sub>2</sub> thin film deposited on the PET glass



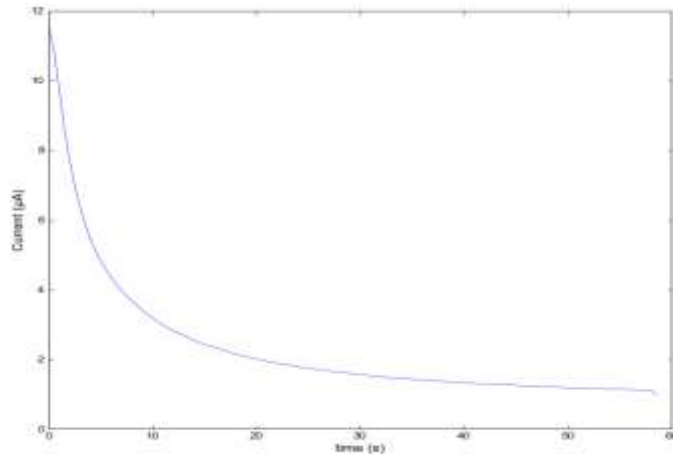
**Figure4.** Two-dimensional AFM image of the ZnO thin film deposited on the PET glass



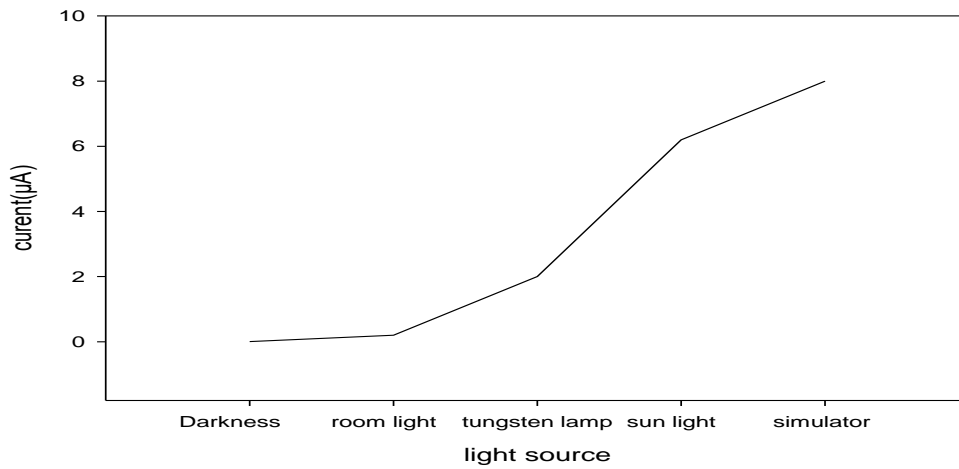
**Figure5.** Effect of enhancing of temperature on coating of ZnO on PET surface



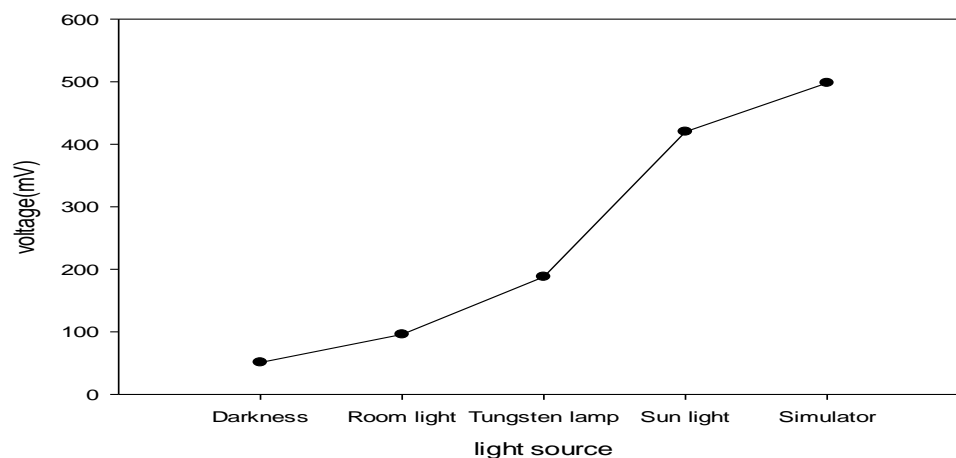
**Figure6.** Photo current generation of flexible photocell at 40-50 second by using of illumination of tungsten lamp as photon induction effect.



**Figure7.** Photocurrent generation of photovoltaic cells based on ZnO-PET/bR electrode under illumination by using of tungsten lamp in 20 cm distance from electrode and 25oC.



**Figure8.** Comparison of illumination effects on photocurrent generation of flexible photovoltaic cells by using of a: simulator, b: sun light, c: tungsten lamp, d: room light and e: darkness condition.



**Figure 9.** Comparison of illumination effects on efficiency of flexible photovoltaic cells by using of a: simulator, b: sun light, c: tungsten lamp, d: room light and e: darkness condition.

#### 4. Discussion

In according to our results, absorption spectra of the bR before and after immobilization on modified PET surface has been compared (figure 3). The maximum absorbance of bR was found at 568 nm, which is related to the absorptions of the protonated Schiff-base retinal. Any modification in maximum absorbance was related to bR photocycles. Moreover, analysis of the AFM images shows that the morphology of samples is very rough and may be advantageous to enhance the adsorption of pigments because of its immense surface roughness and high surface area (Fig. 4). These results show the increase in superior photovoltaic performance of the bR compared with that of individual DSSCs. For enhancement of sensitivity of photovoltaic cell, one effective approach is the photovoltaic performance of the DSSCs through a combination of two or more dyes with complementary absorption spectra sensitized together on the nanocrystalline titania substrates. This strategy enlarges the cell absorption by converting more photons into electrons at longer wavelengths.

#### 5. Conclusion

The present study reveals that the use of PET flexible substrate coated with ITO is

suitable for the production of flexible bio-battery light.

The ZnO nanoparticles better than TiO<sub>2</sub>, as semiconductors. The atomic alignment of zinc oxide nanoparticles is better at good temperatures than titanium dioxide. This will make the cell more efficient in electron transport and ultimately improve the quality of the photocell.

#### Conflict of Interest

The authors declare no conflict of interest.

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