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# Efficient Nanostructured Biophotovoltaic Cell Based on Bacteriorhodopsin as Biophotosensitizer

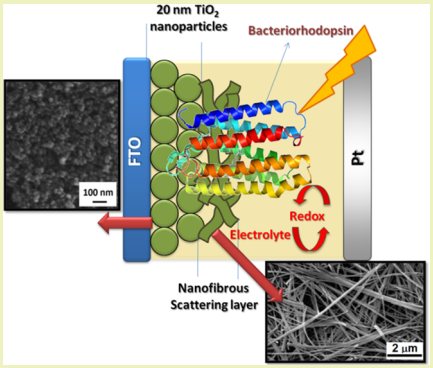
Raheleh Mohammadpour*[,†] and Sajad Janfaza[‡,§]

[†]Institute for Nanoscience and Nanotechnology, Sharif University of Technology, Azadi Avenue, Tehran 14588-89694, Iran

[‡]Young Researchers & Elite Club, Pharmaceutical Sciences Branch, Islamic Azad University, Tehran, Iran

[§]Department of Nanobiotechnology, Tarbiat Modares University, Jalal Ale Ahmad Highway, Tehran 14117, Iran

**ABSTRACT:** Here, we report on utilizing a photoactive protein, bacteriorhodopsin (bR), as a light harvester in combination with $TiO_2$ nanoparticles in biosensitized solar cell application. Experiments have been conducted to investigate the capability of surface adsorption of bR on nanoparticular $TiO_2$photoanodes. Different pretreatment processes have been done to modify the interface of $TiO_2$ nanoparticles and bR as a biophotosensitizer. Our results indicate the feasibility of efficient immobilization and photoinduced charge transfer of bR to the nanostructured $TiO_2$ photoelectrode. Under illumination of simulated AM1.5 sunlight, the solar-light-to-electricity conversion efficiency of the designed solar cell, composed of nanoparticular and nanofibrous layers, reached up to 0.35%, with an open circuit voltage of 533 mV and photocurrent density of 1 mA $cm^{-2}$. This optimized design of our bR-sensitized solar cell shows superior energy conversion efficiency in comparison to previously reported studies.




**KEYWORDS:** *Bacteriorhodopsin, Biophotovoltaic cells, Titanium dioxide, Nano−bio interface, Biosensitizer*

## INTRODUCTION

Bacteriorhodopsin (bR) is a light-driven proton pump found in the purple membrane of the halophilicarchaeon, *Halobacterium salinarium* (formerly called *Halobacterium halobium*).[1] This small seven-helix, 27 kDa protein has attracted a lot of attention as a material for bioelectronics and bio-optics because of its unique properties. The main advantages of the bR molecule include high quantum efficiency of converting light into a state charge, wide range absorption of visible light, extremely large optical nonlinearities, high thermal and photochemical stability, ability to form thin films in polymers and gels, and the existence of genetic variants with enhanced spectral properties for specific device applications.[2,3]

bR can be immobilized on different solid substrates for use in a wide range of optoelectronic devices, including biosensors,[4] holographic memories,[5] photonic transistors,[6] and biosolar cells.[7] Organic photovoltaic solar cells based on bacteriorhodopsin have been widely investigated in the past decade. A large number of studies on conversion of light energy into electric energy by bR have been devoted to optoelectronic characteristics of bR on modified or bare indium tin oxide (ITO) electrode,[8] mostly concerning their photovoltage, but a few also discussed photocurrents. The reported photocurrent produced by biophotovoltaic based on bR/ITO electrodes were at pA or nA level which is quite low. Similar to what is reported for photocurrent, most reported values for photovoltage of bR based solar cells are pretty low (mV level).[9]

Most promising next-generation of biosolar cells, biomolecule-sensitized solar cells (BSSCs), have been reported with photocurrent value of $\mu$A and photovoltage value of *V* recently.[10−13] The mechanism of BSSCs is very similar to dye-sensitized solar cells (DSSCs) developed by Grätzel and co-workers.[14,15] Bacteriorhodopsin plays the role of light harvester and electron transfer agent in BSSC same as the function plays in natural purple membrane of *H. salinarum*. In contrast to conventional DSSCs that use expensive and toxic ruthenium complexes, BSSCs employ low cost, environment-friendly biomolecules as light harvesters. A typical bR based BSSC is composed of four components, including (1) bacteriorhodopsin protein as the biophotosensitizer, (2) a mesoprorous nanocrystalline semiconductor layer coated on a transparent conducting oxide substrate and the scattering layer, (3) a Pt-coated transparent conducting oxide substrate, and (4) a liquid electrolyte between the two electrodes that contains the redox couple of iodide/tri-iodide.[16,17] Figure 1 shows the schematics of these four components and the related scanning electron microscopy images bR has suitable range of light absorption in visible spectrum; Additionally, the lowest unoccupied molecular orbital (LUMO) of bR is located at −3.8 eV, which shows the favorable electron injection to the conduction band of $TiO_2$ located at −4.2 eV; on the other hand the highest occupied molecular orbital (HOMO) of bR located at −5.4 eV is suitable respect to redox potential of iodine based electrolyte at −5 eV (Figure 1c).[18]

Based on previous studies, both the extracellular and cytoplasmic sides of bR contain positively charged residues

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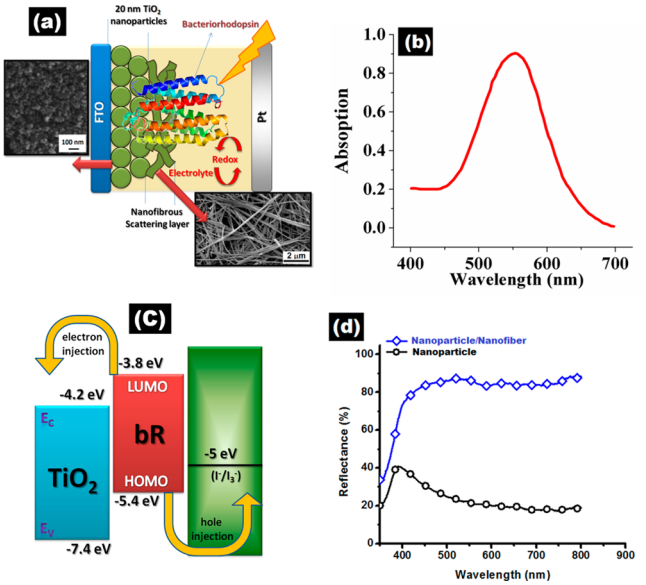


**Figure 1.** (a) Schematic of BSSC, utilizing bR as biophotosensitizer; the photoelectrode consist of nanoparticular $TiO_2$ as active medium and nanofibers as scatterers; (b) optical absorption spectrum of bR protein; (c) simple energy level diagram of BSSC; (d) diffuse reflectance spectrum of nanoparticular electrode and the electrode with nanofibers as scattering layer.

that can bind to exposed oxygen atoms on the of bR to surface of $TiO_2$; the positively charged residues from cytoplasmic side of bR are able to bind to anatase surface too. So, the exposed oxygen atoms at groove edges can electrostatically interact with positively charged bR residues. In this regard, the surface treatment of photoelectrode to get the direct interact of negatively charge points will be the crucial factor for stable attachment and effective charge transfer from bR to the ceramic metal oxide $TiO_2$ surface.[18] In the present work, studies of the performance of bR based BSSC have been carried out with optimization of the materials at the nano–bio interface and also morphology design. Our new design composed of nanoparticluar layer for bR adsorption and nanofibrous film for increasing light harvesting in active layer, offers a high efficient biophotovoltaic for solar energy conversion. In addition, to further increase the performance of solar cell, the time course of bR loading on the nanocrystalline $TiO_2$ films has been investigated.

## EXPERIMENTAL SECTION

**Materials.** The purple membrane of *Halobacterium salinarum* containing bacteriorhodopsin was isolated according to the method of Oesterhelt and Stoeckenius.[19] Titanium dioxide screen printing pastes, platinum paste (Platisol T/SP paste), and electrolyte were provided from Solaronix. Fluorine-doped tin oxide (FTO) glass was purchased from Dyesol. All other materials not specifically indicated were obtained from Sigma or other reputable sources.

**Preparation of Nanostructured Photoanodes.** To study the impact of materials at the interface of protein and nanostructures, the photoanodes were prepared by different process, as shown in Table 1. A comprehensive procedure of photoanodes preparation is described below. The 2 × 1.5 cm FTO-coated glass sheets were used as substrates after being cleaned ultrasonically by acetone and alcohol, respectively. The titania paste was spread on FTO conductive glass using "doctor blading" technique and then dried for 6 min at 125 °C. This procedure was repeated to get a thickness of 10 $\mu$m for the photoanode. After the 20 nm-sized $TiO_2$ layers were dried, in some photoelectrodes, a layer of light-scattering paste consists of micrometer-length nanofibers were deposited to enhance the light harvesting efficiency in active medium. Nanofibers fabricated thorough an electrospinning method utilizing polyvinylpyrrolidone and titanium(IV) isopropoxide as precursors. The resulting films (thickness, 15 $\mu$m, and area of 0.25 $cm^2$) were annealed at 500 °C for 1 h. Afterward, two sets of photoelectrodes were prepared. In the first one, the surface of the photoelectrode was treated with 40 mM $TiCl_4$ solution for 30 min in 70 °C and the second one kept bare. For both types, the photoelectrode was dipped into the bacteriorhodopsin solution (20 mL, 1 mg $mL^{-1}$), either at room temperature or at 80 °C and loaded for different durations from 30 min to 7 days at 4 °C.

**BSSC Assembly.** A Pt counter electrode was prepared by deposition of Pt paste on another FTO substrate. The bR-sensitized $TiO_2$ electrode and counter electrode was assembled into sealed sandwich solar cell with hot-melt Surlyn film (30 $\mu$m thickness) as a spacer between the electrodes. Redox electrolyte was introduced through small holes drilled in the counter electrode that were sealed afterward. The composition of the electrolyte was 0.1 M $I_2$, 0.1 M LiI, 0.6 M tetrabutylammonium iodide, and 0.5 M 4-tertbutylpyridine in acetonitrile.

**Characterization and Measurement.** A LEO 1550 field-emission scanning electron microscope was employed for morphological characterization of photoelectrodes. The absorption spectra of the photoelectrodes sensitized with 1 mg $mL^{-1}$ solution of bR were recorded using a PerkinElmer UV–vis-NIR Model Lambda 950 double beam spectrophotometer in the wavelength range 400–700 nm. The photocurrent–voltage ($I$–$V$) characteristics of the biophotovoltaic cells were carried out using an Iviumstat potentiostat under simulated air mass 1.5 illumination (100 mW/$cm^2$) provided by a solar simulator (Luzchem). Electron lifetime in nanostructured photoelectrodes were obtained through photovoltage-decay measurements using an Autolab potentiostat. This method consists of turning off the light source (10 W white LED) in a steady state and monitoring the subsequent decay of photovoltage.

## RESULTS AND DISCUSSION

Figure 1b shows the absorption spectrum of bR anchored to $TiO_2$ film. It shows the broad peak of optical absorbance in the visible range from 400 to 700 nm. To find out the role of surface treatment on immobilization of bR, various conditions for dye loading have been investigated. Figure 2a illustrates current–voltage characteristics of bR-sensitized photoeletrode with four different pretreatment processes. Following the sintering of nanoparticular $TiO_2$ based photoelectrode with 10 $\mu$m active layer thickness, two electrodes were treated with $TiCl_4$ solution, and the remains kept untreated. Afterward, each photoelectrode loaded in bR solution for 30 min either in room temperature or at 80 °C. Based on the results of Figure 2a and the extracted data in Table 1, it seems that pretreatment of nanostructured photoelectrode with $TiCl_4$ solution could enhance biosolar cell performance by increasing photocurrent and photovoltage greatly. This effect is very similar to sensitization of $TiO_2$ electrode with typical metal–organic dye such as N719. It addition, change of dye loading condition from room temperature to 80 °C could enhance cell performance obviously. This might be as a result of removing hydroxyl group from $TiO_2$ surface and much effective bR-binding to the $TiO_2$ surface. As it is shown, the photovoltage and photocurrents increase from 385 to 478 mV and 0.363 to 0.811 mA $cm^{-2}$ in the pretreated photoelectrode in comparison to the untreated one, respectively. The improvement in filling factor of BSSCs from 0.5 to 0.67 also indicates the better coverage, which could result in higher shunt resistance values and longer electron lifetimes.


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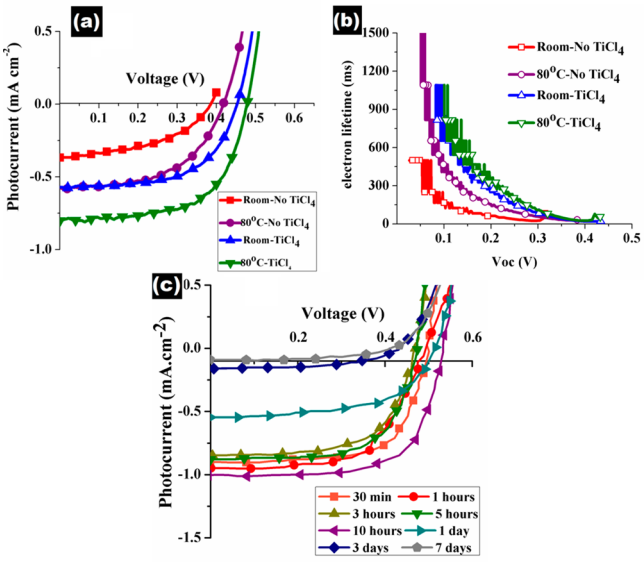


**Figure 2.** (a) Current−voltage characteristics, (b) electron lifetime measurement of BSSCs consist of photoelectrode prepared under different pretreatment conditions, and (c) current−voltage characteristics of BSSCs with different time loading of bR biophotosensitizer.

Figure 2b shows the values of electron lifetime in these four types of photoelectrodes in various quasi-Fermi level positions. As it was expected, much longer electron lifetimes have been achieved in optimized photoelectrode utilizing $TiCl_4$ pretreatment and loading temperature of 80 °C. Typically, the back-recombination of an injected photoelectron with the oxidant species in electrolyte results in a lower quasi-Fermi level in the photoelectrode; coverage of the mesoporous structure with the monolayer of the sensitizer reduces the kinetic of back-recombination extensively, so we can expect a longer electron lifetime.[20] Results showed much effective dye coverage has been achieved upon $TiCl_4$ pretreatment and loading the photoelectrode at a suitable temperature, which resulted in longer electron lifetime in optimized photoelectrodes. The longer electron lifetime achieved in photoelectrodes with $TiCl_4$ treatment and loaded with bR at 80 °C can result in larger values of quasi-Fermi level in these photoelectrodes. As it is illustrated in the diagram of current−voltage of Figure 2a, the enhancement of open-circuit voltage up to around 100 mV in this photoanode could be as a direct result of improved electron lifetime and larger values of the Fermi level.

To further enhance the performance of bR-sensitized BSSC, a fibrous scattering layer has been coated on the active layer to enhance the optical path length in the active medium. One-dimensional (1-D) $TiO_2$ nanostructures have been employed extensively in the photoelectrode of DSSCs due to enhanced light harvesting efficiency especially at the red part of the solar spectrum.[21−23] Figure 1d shows the diffuse reflectance spectra of nanoparticular electrode with and without employing nanofibers as the scattering layer. As it is obvious, utilizing nanofibers causes the enhancement in diffuse reflectance to change from 30% to more than 80% in the visible range spectrum, so we can expect improved light harvesting in this range. As it has been illustrated in Table 1, this could result in enhancement of the photocurrent from 0.811 to 0.899 mA cm$^{-2}$ in photoelectrodes with a scattering layer and loading time of 30 min in bR solution. Afterward, different loading durations have been evaluated; Figure 2c illustrates the photocurrent-photovoltage of optimized photoelectrode loaded in bR solution for different duration. As it is obvious by increasing the dye loading time to 10 h, enhanced photocurrent density up to 1 mA cm$^{-2}$ has been achieved. This is related to maximum power conversion efficiency of 0.35%. As it is apparent from current−voltage characteristics and also results indicated in Table 1, extending dye loading duration resulted in multilayer bR formation; loading the nanostructured photoelectrode with more than one layer of sensitizer cause the quenching of sensitizer because it is impossible for generated photoelectron to pass through sensitizer layer so it deteriorates the charge transfer processes from sensitizer layer to active photoelectrode.[20] Because of natural thermal robustness of bR, long-term stability has been achieved. No sensible reductions in different cells' performance have been revealed in 3 months of continuous measurements.

Comparing our results to similar studies, it appears clearly that a bR-sensitized solar cell using an appropriately designed nanostructured photoanode is more efficient compared to those fabricated using other reported photoanodes. For instance, photocurrent generation using a bacteriorhodopsin based photoelectrochemical cell has been studied by Chu et al.[9] The reported photocurrent is at the nA level, which is significantly smaller compared to the measured 1 mA cm$^{-2}$. Recently, mutant or wild-type bR sensitizers have been used as

**Table 1. Photovoltaic Characteristics of Different bR-Sensitized BSSCs[a]**

| $TiCl_4$ treatment | scattering layer | temperature of bR-loading (°C) | duration of dye loading | open-circuit voltage (mV) | short-circuit current (mA cm$^{-2}$) | efficiency (%) | filling factor |
|---|---|---|---|---|---|---|---|
| no | no | 25 | 30 min | 385 | 0.363 | 0.07 | 0.5 |
| no | no | 80 | 30 min | 420 | 0.564 | 0.13 | 0.55 |
| yes | no | 25 | 30 min | 453 | 0.577 | 0.16 | 0.61 |
| yes | no | 80 | 30 min | 478 | 0.811 | 0.3 | 0.67 |
| yes | yes | 80 | 30 min | 496 | 0.9 | 0.3 | 0.67 |
| yes | yes | 80 | 1 h | 497 | 0.95 | 0.29 | 0.61 |
| yes | yes | 80 | 3 h | 470 | 0.85 | 0.25 | 0.63 |
| yes | yes | 80 | 5 h | 473 | 0.9 | 0.27 | 0.63 |
| yes | yes | 80 | 10 h | 533 | 1 | 0.35 | 0.66 |
| yes | yes | 80 | 1 day | 516 | 0.55 | 0.17 | 0.60 |
| yes | yes | 80 | 3 days | 440 | 0.16 | 0.04 | 0.57 |
| yes | yes | 80 | 7 days | 417 | 0.09 | 0.02 | 0.53 |

[a]Values extracted from Figure 2a,c curves.



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a promising bioelectronic material for photocurrent generation. The short-circuit current of 89 $\mu$A cm$^{-2}$ and open-circuit voltage of 0.35 V have been achieved in optimum conditions, under an illumination intensity of 40 mW cm$^{-2}$.[18] Furthermore, photocurrent generation using a bR/$TiO_2$ nanotube array photoanode has been investigated by Allam et al.[24] However, they showed a remarkable photocurrent density of 0.87 mA cm$^{-2}$, which was significantly higher than previous studies, but the photocurrent can be increased up to 1 mA cm$^{-2}$ using our newly developed multilayer photoanode, composed of layers of nanoparticles and nanofibers. In addition, the fairly high $V_{oc}$ of 533 mV recorded for the bR-sensitized solar cell is well comparable with those of even DSSCs. Therefore, the newly designed nanostructured protein-sensitized solar cell, due to its improved efficiency, cost savings, and environmental friendliness, can act as promising bioelectronic devices.

## CONCLUSIONS

In conclusion, our results showed that surface treatment of $TiO_2$ nanoparticle and optimum bR loading conditions could enhance the charge transfer rate in the $TiO_2$/bR interface. By the aid of appropriate design of the photoelectrode, composed of a nanoparticular layer for effective bR loading and a nanofibrous layer for enhanced light harvesting in active medium, a maximum efficiency of 0.3% with the photocurrent reaching up to 1 mA cm$^{-2}$ has been achieved. The reported result in this work is the highest among those previously reported. This result shows that bR has the potential to be considered as an efficient biophotosensitizer with further improving in charge transfer in a biomolecule−metal oxide surface.

## AUTHOR INFORMATION

### Corresponding Author

*Raheleh Mohammadpour. Phone: +98-21-66164124. Fax: +98-21-66164119. E-mail: mohammadpour@sharif.edu.

### Present Address

S. Janfaza. Room 316, 2nd Floor, Institute for Nanoscience and Nanotechnology, Khodro Building, Sharif University of Technology, Azadi Avenue, Tehran 14588-89694, Iran

### Author Contributions

The paper was written through contributions of all authors. All authors have given approval to the final version of the paper.

### Notes

The authors declare no competing financial interest.

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