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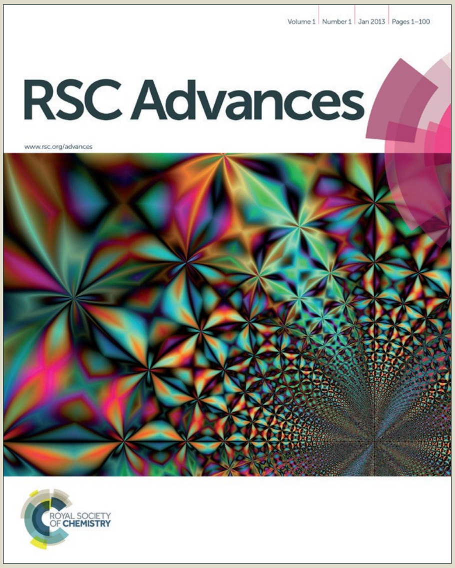

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FULL PAPER

Visible-Switchable bR/TiO$_2$ Nanostructured Photoanodes for Bio-inspired Solar Energy Conversion

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Today, regarding limitation and environmental side effects of fossil fuel resources, solar hydrogen production is one of the main interests in the energy research area. Visible sensitizing semiconductors based on non toxic, low cost and available bio-species is an ongoing approach for H_2 generation based on water splitting reactions. Here, two different morphology of TiO_2 photoanodes, nanoparticulated and nanotubular, have been modified with simply extracted bacteriorhodopsin (bR) without any linker. Achieving a significant enhancement in photoconversion efficiency of TiO_2 photoanodes, η% was increased from 2.9 to 16.5 by bR addition to TiO_2 nanoparticulate electrode while it increased from 0.5 to 1.9 for nanotubular system. This result revealed that because of large size of the extracted purple membranes, nanoparticles showed higher explosion sites for bR attachment and they were more efficient than nanotubes. Moreover, comparing these values with ones reported for bR/TiO_2 photoanodes before, the simple proposed decoration method obtained remarkable improvement in the visible response of the TiO_2 based photoanodes. This approach can be beneficial for the area of solar water splitting, photoelechemical sensing, and any other photoresponsive systems.

1. Introduction

Today, substituting fossil fuels with renewable ones is one of the main human challenges. Considering solar energy as a free, available and clean energy resource and also water as a byproduct of hydrogen combustion/conversion, it seems that using solar produced H_2 as a future energy carrier is the best solution [1]. In this regard; two separate scenarios were developed to generate solar assisted hydrogen based on water splitting reaction. In the first method, the required energy for a conventional electrolyser system is provided by photovoltaic systems [2] while in the second one, water splits directly to H_2 and O_2 on the surface of photoexcited semiconductor material in a photoelectrochemical (PEC) process [3]. Photoelectrochemical water splitting is more promising approach because small required current density on the surface of semiconducting electrode leads to lower over potentials and also PEC system can be installed as a single monolithic device [1].

From the first report about PEC water splitting using TiO_2 photoanode by Fujishima and Honda [4], a huge number of researches have been published reflecting scientist's attempts to overcome the challenges in this field [5-7]. One of the important difficulties is the large band gap of the low cost stable semiconductors which does not match with the main part of solar spectrum (400 nm < λ < 700 nm). Addition of visible responsive quantum dots [8], dye and low band gap semiconductors [9] to the main photoelectrode and also doping with various anions/cations [10-14] are ongoing procedures. In this context, finding visible sensitizing materials which are non toxic and also highly abundant to fabricate bio-conjugated hybrid photoanodes is important. Gratzel has developed chlorophyll based solar cells in which by visible light irradiation, the photoexcited electrons were injected from chlorophyll to TiO_2 and entered to external circuit. [15,16] Similar to this idea can be used for photoelectrochemical water splitting systems.

Bacteriorhodopsin (bR) is a protein in the purple membrane (PM) of *Halobacteriumsalinarium* including seven helices and one interior retinal chromophore [17]. It can act as visible activating building block in photoanodes and also proton pump for hydrogen generation [18]. Recently, N.K. Allam et al have attached bRs to TiO_2 nanotubes surface using a specific chemical linker (3- Mercaptopropionic acid) and observed 50% increase in photocurrent densities [19]. A nearly similar enhancement was reported by S. Balasubramanian for Pt/TiO_2 nanoparticles modified with bR using a long time process based on immersion of the samples in bR solution over a night [20]. Despite of these published reports, the obtained photocurrent improvement for bR modified systems are still low and effect of supporting semiconductor (TiO_2) morphology on the bR leading and performance is also obscure.

Here, we have proposed a simple and fast one step method for decoration of different TiO_2 nanostructures with bR species which increased photocurrent density of the systems to several times more. On the other hand, a comparison between TiO_2 nanotubular and TiO_2 nanoparticlate films in PEC performance of bR/TiO_2 photoanodes has been reported.

2. Experimental Details

2.1. Preparation of TiO$_2$ photoanodes

To compare the effect of TiO_2 film morphology on the photoelectrochemical performance of bR decorated photoanodes, two different nanostructure of TiO_2 were grown: nanoparticulate and nanotubular films.

Self organized TiO_2 nanotubes arrays (TNA) were synthesized using anodization method which is reported before [21,22]. Briefly, titanium sheets (99.5% purity, 0.5 mm thickness) have anodized in electrolyte solution contained deionized (DI) water and ethylene glycol with ratio 10:90 with 0.1 M NH_4F and small amount of 1 M H_3PO_4 (for reducing the pH to 5.6). The anodization was carried out at 60 V for 120 min. After the anodization, samples were sonicated for about 30 min in pure ethanol to eliminate depress surface layer and opening the nanotube's mouth. To crystallize TNAs in anatase phase, the prepared samples were annealing in air at 520˚C for 6 hours with heating rate of 90˚C per hour.

TiO_2 nanoparticulate (TNP) films were fabricated using a commercial paste of well crystallized TiO_2 nanoparticles in anatase phase with an average size of 40 nm (Sharif Solar Co.). The paste was spread on Ti sheet using Doctor Blade method and then, the obtained layers was heated in 450 ^{o}C for an hour to evaporated the solvent and decompose binders.

2.2. Decoration of TiO_2 photoanodes with bacteriorhodopsin

Purple membrane was isolated by the well known method of Oesterhelt and Stoeckenius [23]. To attach the extracted bR on the TiO_2 surface, the fresh annealed TNA and TNP films were immersed in bR solution as soon as the heat treatment step finished. Afterwards, the bR grafted layers were dried in the room temperature.

2.3. Characterizations

The optical absorption of the extracted bR solution was studied using a UV-vis spectrophotometer (StellarNet Model EPP2000) with 1 nm wavelength resolution. Surface morphology of the fabricated TNA and TNP films was investigated by scanning electron microscopy (SEM) (TESCAN-VEGA3-SB).

Photoelectrochemical response of the bR/TiO_2 photoanodes was studied in a three electrode glassy reactor using Ag/AgCl, Pt wire and phosphate buffer solution (pH = 8) as a reference electrode, counter electrode, and electrolyte, respectively. The reactor was equipped with a quartz window putting the photoanodes as working electrodes behind it and illuminating the layer. The light source was a xenon lamp (YUSHIO, 110 W) with a solar like spectrum. To check the photoactivity of deposited bR, the whole spectrum was eliminated except green part (λ = 532 nm) by an optical cut off filter. Current-voltage measurements were performed using a galvanostat/potentiostat system (SAMA-500) in a linear sweep voltammetry mode with the scan rate of 100 mV/s. All reported potentials are versus Ag/AgCl reference electrode.

3. Results and Discussions

3.1. Optical measurements

The main characteristic for successfully extracted bacteriorhodopsin is its optical spectrum which is presented in Fig. 1(a) for the fresh prepared bR solution. The observed absorption peak at λ = 568 nm revealed the visible activity of the extracted protein as also reported by others [19, 24]. In this figure, the absorption spectra of bare TNP and bR decorated TNP photoanodes have been also presented. As can be seen, the characteristic peak of bR was also present for the bR/TNP photoanodes at 568 nm with lower intensity while it disappeared for bare TNP sample.

Moreover, Fig.1(b) shows the photograph of the TiO_2 photoanodes before and after functionalizing with bRs representing purple appearance for bR decorated TiO_2 samples, even after washing with DI water for several times. This evidence confirmed efficient attachment of photoactive species on the TiO_2 surface by a simple immersion process and in the absence of any linker.

3.2. Surface morphology

Fig. 2 represents the SEM images of the prepared TiO_2 nanostructured photoanodes. According to Fig. 2(a), the vertically oriented TiO_2 nanotube arrays were self organized with an average wall thickness of 20 nm and 150 nm in diameter. Furthermore, based on Fig. 2(b), the all nanotubes are exposed to the electrolyte which reveals that sonication step opened the tube's mouth effectively. As can be seen in the cross section image of the grown structure in Fig. 2(c), the thickness of the nanotubular film was about 5 μm after 2 hours anodizing the Ti sheet. In the case of nanoparticulate film, SEM image in Fig. 2(d) represents formation of TiO_2 nanoparticles with size variation in the range of 30 to 50 nm. In addition, formation of anatase phase in such an annealing procedure has been approved in our previous reports [21, 22].

3.3. Photocurrent measurements

To study electrochemical behavior of TNA and TNP electrodes, linear sweep technique was used in phosphate buffer electrolyte (pH = 8) under dark condition. The recorded I-V curves in Fig. 3(a) cleared that no oxidation/reduction peak was observed for both electrodes revealing they are chemically inert in the selected potential range. The observed increase in anodic current was related to water oxidation on the TiO_2 surface. On the other hand, it can be seen that dark anodic response of the TNP electrode was significantly higher than one recorded for TNA sample. In the potential of + 0.5 V, current density of TNP layer was 0.06 mA/cm^2 which was nearly ten times more than one for TNA electrode. This result was attributed to higher film/electrolyte interface in nanoparticulate system in comparison with nanotubular TiO_2 structure.

The photoresponse of the bare and bR decorated TiO_2 photoanodes was measured illuminating white light (380 nm < λ < 700 nm) and the results are shown in Fig. 3(b). In the case of TNP photoanodes, loading bR on the system caused a remarkable increase in photocurrent density from 0.09 mA/cm^2 for bare TNP to 0.64 mA/cm^2 for bR/TNP electrode in the bias of +0.5 V. The lower enhancement was also observed for nanotubes in which the photocurrent increased from 0.07 mA/cm^2 to 0.12 mA/cm^2 by decorating TNAs with bacteriorhodopsin. It is clear that the photoactivity improvement made by bR species is significantly higher for TNP system than TNA one which is attributed to higher effective sites in nanoparticulate film for grafting bR on it. After PM extraction, the size of the obtained bR included membrane was several hundred nanometers. On the other hand, the tubes were 100 nm in diameter. Hence, bR attached just on the top surface of the nanotubular TiO_2 film which led to covering the tube's mouths and lower effective bR loading in these systems. However, in both TNP and TNA based photoanodes, addition of bR caused a negative shift in onset potential which is beneficial for separating charge carriers and preventing photoexcited electron/hole recombination [1]. All photoelectrochemical parameters are listed in Table 1.

Table 1. Photoelectrochmical characteristics of bR modified TiO_2 photoanodes

Photoanode	J (mA/cm^2) (1)	V_{on} (mV) (1)	J (mA/cm^2) (2)	η (%) (2)
TNP	0.09	-510	0.06	2.9
bR/TNP	0.64	-590	0.34	16.5

TNA	0.07	-523	0.01	0.5
bR/TNA	0.12	-580	0.04	1.9

(1) Illuminated with white light at fixed V = +0.5 V
(2) Illuminated with λ = 530 nm at fixed V = +0.5 V

It is important to understand this improvement is related to visible activity of attached bR or any other changes in the TiO_2/electrolyte interface after decoration with bR. In this regard, all prepared photoanodes are also studied by illuminating the samples with single special wavelength, λ = 532 nm which eliminated all possible excitations in titanium dioxide layer (Fig. 3(c)). However, as can be followed in table 1, the significant photocurrent enhancement was still observable for bR attached photoanodes representing the main mechanism for photoactivation of samples was attributed to injection of electrons from protein-retinal complex to semiconducting nanostructures and also H^+ pumping by bR. In fact, absorption of green light photo by bR caused excitation of electrons from HUMO to LUMO and because the CB of TiO_2 located in lower energy level, injection of the photoelectrons from bR to TiO_2 is energetically favorable [24]. These electrons finally transferred to the external circuit and reduced H^+ on the Pt (counter electrode) surface while water oxidized on the photoanode surface. Schematic of this process is shown in Fig. 4. The photoelectrochemical efficiency of the prepared photoanodes was also estimated based on photo-conversion efficiency which is defined as the following equation:

$$\eta = \frac{J\ (E - V_{app})}{P} \qquad (1)$$

Where J, E, V_{app} and P are photocurrent density of the system (mA/cm^2), fundamental required voltage for water splitting (1.23 V), applied potential (V) and the intensity of incident photons (mW/cm^2). These values were calculated for the systems excited with green light (λ = 532 nm) applying an anodic potential of + 0.5 V which were also listed in Table 1. The efficiency was estimated 16.6, 3.0, 1.6 and 0.3 % for bR/TNP, TNP, bR/TNA and TNA photoanodes, respectively. These obtained values are significantly higher than ones reported for bR modified TiO_2 photoanodes elsewhere.

N. Allam et al. reported decoration of TiO_2 nanotubes with bR using 3-Mercaptopropionin as a linker and observed 50% increase in the photocurrent density of the systems.[19] S. Balasubramanian et al. also modified TiO_2 nanoparticles with bR by immersion of particles in the bR solution over night leading to ~ 50 % enhancement in their photoresponce [20]. Despite of these reports, the main advantage of the present system is the remarkable increase in the measured photocurrent was obtained in the absence of any chemical ligand as a linker. This may be due to better performance of bR in buffer based electrolyte (pH=8) than citrate based (pH=7) or eliminating sonication step which ma denature the proteins. Hence, bR species attached to the TiO_2 surface by a simple, low cost approach effectively leading to much more increase in the photoresponse of the samples (1.7 and 7 times for TNA and TNP based systems, respectively).

As mentioned before, for better mechanical and electrical connection between bR and TiO_2 nanostructures, the fresh annealed TiO_2 was immersed in prepared bR solution as soon as it cooled to a suitable temperature (~ 80 °C) to avoid absorption of any pollution on it. Another usual method for improving such as this self organized attachments is UV treatment of the substrate and /or heating the sample after immersion in additive solution. To compare these tricks with each other for the bR/TiO_2 nanoparticulate system, three different strategies were selected. In first sample, the hot (~80°C) TNP electrode just after annealing was immersed in bR solution (S1). In second one, the surface of TNP electrode which was annealed a day before was exposed to UV irradiation for an hour and then immersed in bR solution (S2). In the third, annealed TNA decorated with bR and then heated in 80 °C for about 30 min (S3). Photocurrent measurements illustrated that current density of these bR-modified TNP photanodes were 0.34, 0.11 and 0.28 mA/cm^2 for the S1, S2 and S3 samples, respectively. This result suggest that heating samples after modification led to less enhancement in photoactivity of the samples due to deactivation or denaturing some of grafted bR on the surface during heating step. Moreover, UV treatment was not as efficient as other two approaches.

4. Conclusions

Two different TiO_2 morphology (nanoparticulate and nanotubular films) were modified with bacteriorhodopsin as a visible sensitizer using a simple linker free approach. Studying I-V characteristics of the modified photoanodes revealed that decoration of TiO_2 nanoparticles with bR led to more significant photoresponse enhancement (~ 7 times) as compared with nanotubular film (~1.7 times) due to more surface sites for attachment of submicron bR species. Moreover, the observed photocurrent improvement made by bR decoration for the both TNP and TNA photoanodes were much more than reported values for similar bR decorated photoanodes before. Base on this result, tuning cleanness of adsorbing surface by simple methods to void using chemical linkers can lean to efficiencies even higher than complicated linker based approaches which is useful strategy to develop bio-inspired systems in optobioelectronic applications. Coupling these systems with two dimensional nanostructures (such as graphene [25] or metal dichalcogenides), tuning the size of extracted bR and/or investigating a variety of TiO_2 morphologies can obtain even higher efficiencies in visible induced PEC performances in future.

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Notes and references

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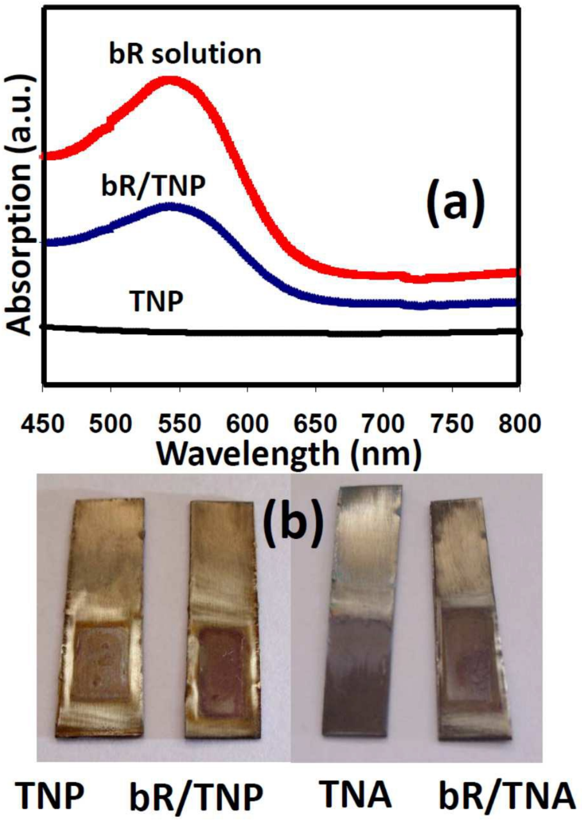


Fig. 1. (a) Optical absorption of extracted bR solution, bR/TNP and bare TNP samples and (b) photographs of TNP and TNA photoanodes before and after decoration with bR.

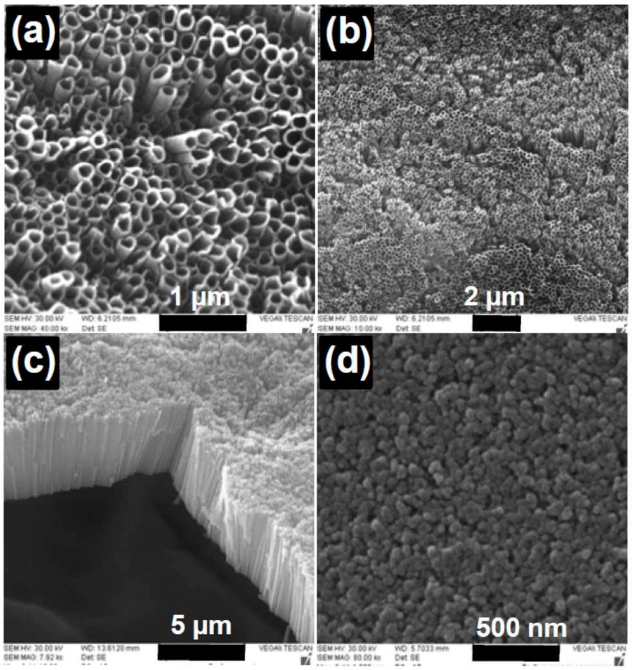


Fig. 2. SEM images of (a-c) nanotubular and (d) nanoparticulate TiO_2 photoanodes before bR decoration.

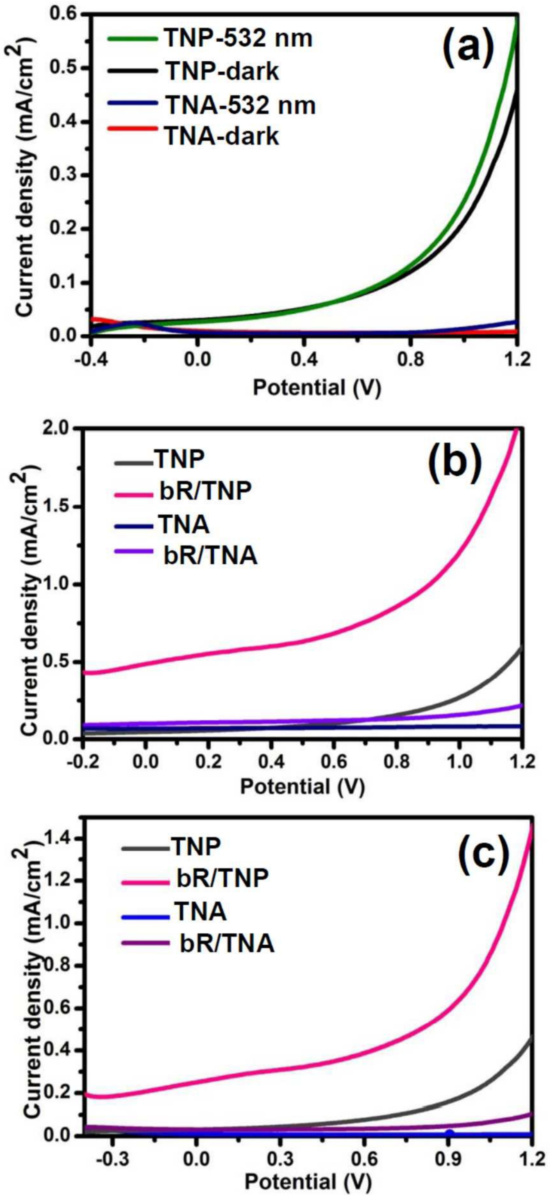


Fig. 3. I-V characteristics of (a) TNP and TNA systems without bR decoration in dark and irradiating green light, TNP and TNA systems decorated with bR under illumination with white (b) and green (c) light.

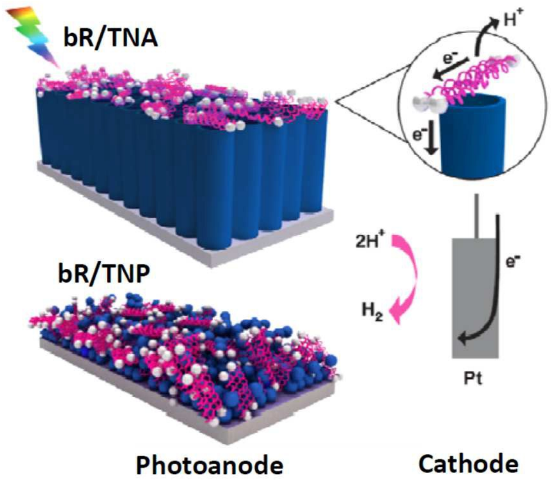
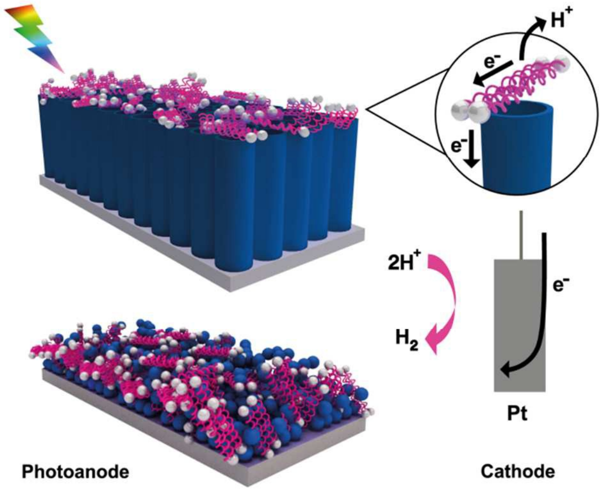


Fig. 4. Schematic of the synthesized bR decorated TNA and TNP photoanodes for water splitting reaction.



Bacteriorhodopsin, a visible sensitizer for water splitting reaction, adsorbed on TiO_2 nanoparticulate photoanode without any linker and caused a significant PEC enhancement.