Dye-sensitized solar cells based on natural and artificial phycobiliproteins to capture low light underwater

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Article history:
Received 29 July 2018
Received in revised form 13 October 2018
Accepted 23 October 2018
Available online 5 December 2018

Keywords:
Dye-sensitized solar cells
Artificial photosynthesis
Light harvesting
Phycobiliprotein

Abstract
We developed dye-sensitized solar cells (DSSCs) based on natural and artificial phycobiliproteins (PBPs) to capture low light underwater. We assembled DSSCs with seven types of PBPs as sensitizers and studied their photoelectric properties. The results showed that the PBPs could markedly improve the photoelectrical properties of the DSSCs. The sensitization achieved by B-phycoerythrin (B-PE) from Porphyridium cruentum was superior to that of the other PBPs. The short-circuit current density, open circuit voltage, fill factor, and photoelectric conversion efficiency of the DSSC containing B-PE with a mesoporous titanium dioxide film as a photoelectrode were 3.236 mA/cm², 0.545 V, 0.569, and 1%, respectively. The DSSC based on B-PE displayed its highest photoelectric conversion efficiency between 525 and 570 nm. However, the maximum photoelectric conversion efficiencies of the DSSCs based on C-phycocyanin from Spirulina platensis and artificial PBPs were observed around 690 nm. DSSCs containing B-PE show great potential for use in underwater photovoltaic applications.

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Introduction

The underwater light environment is quite different from that on the land. When sunlight passes through the surface of water, long-wavelength light (such as red light) is completely absorbed by the surface water. Although purple light has strong penetrating power through water, it is easily scattered by water molecules and cannot be transmitted to deeper seawater. Therefore, the light present in deep water is mainly blue and green. In addition, the intensity of light in a water body decreases logarithmically with increasing water depth. For example, in pure seawater at a depth of 100 m, the light intensity is only 7% of that of the water surface. Generally,
submerged vascular plants can survive at a depth of 5–10 m, and few vascular plants grow below 10 m. Some cyanobacteria and red algae can survive underwater at depths from 20 m to over 100 m. This is because these organisms have light-harvesting antennas that can efficiently capture and transmit light energy in deep water, especially short-wavelength (blue-green) light [1,2].

The light-harvesting antennas in cyanobacteria and red algae, which are named phycobilisomes (PBSs), are one of the two major types of light-harvesting systems present in photosynthetic aerobic organisms. PBSs are able to efficiently transfer absorbed solar light to the chlorophylls of photosynthetic reaction-center complexes. PBSs were first observed in the unicellular red alga *Porphyridium cruentum* [3,4]. Biochemically, PBSs are made up of water-soluble phycobiliproteins (PBPs) and linker polypeptides [5]. The diversity of PBPs also plays an important role in the evolution of algae [6]. Because of their unique composition and structure, PBPs have the ability to capture sunlight in the wavelength range of 480–650 nm [1]. PBPs are mainly divided into three categories, including phycoerythrin (PE; maximum absorption wavelength of about 565 nm), phycocyanin (PC; maximum absorption wavelength of about 617 nm), and allophycocyanin (APC; maximum absorption wavelength of about 650 nm). The energy from sunlight is transmitted in the single direction PE → PC → APC → photoreaction center with almost 95% efficiency. The energy transfer mechanism of PBSs is generally considered to be Förster resonance energy transfer, which endows the PBSs of marine red algae and cyanobacteria with strong light-harvesting efficiency under low light. These features allow marine cyanobacteria and red algae to effectively adapt to the special light environment of the ocean [7–10].

Solar energy is a resource-rich renewable energy. The development of solar energy technology can partly solve the environmental problems and energy crisis the world faces. Since the 1990s, the invention of solar cells has promoted research on the use of biomacromolecules in dye-sensitized solar cells (DSSCs) [11–15]. The low cost, environmental friendliness and simple fabrication of DSSCs mean that they have good application prospects. One of the core materials of a DSSC is the sensitizing dye, and the performance of the sensitizing dye strongly affects the photoelectric conversion efficiency of the DSSC [16–22]. Sensitizing dyes must be stable in electrolyte solutions, bond tightly to the semiconductor surface, and have both a high optical absorption coefficient and a wide light absorption spectrum. Although researchers have synthesized thousands of sensitizing dyes since the 1990s, only a few of them have good optoelectronic properties. Recently, researchers have developed a number of biological dye sensitizing layers [23–25]. With the discovery of the nanoscale fine structure of supramolecular photosynthetic protein complexes, biomacromolecule-based DSSCs have been paid increasing attention by scientists [26]. Recent research has focused on the use of bacterial rhodopsin, bacterial photoreaction center complex, photosystem I and II, and light-harvesting complex to fabricate photovoltaic converters [27–31].

The efficient use of solar energy in algae mainly originates from PBPs, which are special light-harvesting proteins. PBPs are good sensitizing dyes for DSSCs. Zhang et al. [32,33] used Chlorin e_6 coupled with a PBS from *Spirulina platensis* as a sensitizing dye to assemble a DSSC on a titanium dioxide (TiO_2) film. The PBS markedly improved the photoelectric performance of Chlorin e_6. The short-circuit current density and photoelectric conversion efficiency of the device were 0.50 mA/cm^2 and 0.19%, which were 44% and 1.6 times higher than the corresponding parameters for the Chlorin e_6-sensitized DSSC. However, their poor stability and scalability limit further applications of PBS-based DSSCs. Therefore, the artificial synthesis of PBPs has received extensive attention. In our previous research, we used a recombinant APC trimer to sensitize a TiO_2 nanophotoanode and constructed a DSSC based on the recombinant PBP [34]. The short-circuit current density and photoelectric conversion efficiency of the DSSC were 0.73 mA/cm^2 and 0.26%, respectively under a light intensity of 100 mW/cm^2.

In recent years, underwater equipment, including autonomous underwater vehicles and submarine observation networks, has become a new research hotspot. Photovoltaic technology is also expanding from photovoltaic power plants and space craft to the marine field. The unique low-light capture mechanism of seaweed provides a good reference for the development of artificial solar capture devices. In this paper, DSSCs are constructed using PBPs with different structural and optical properties as sensitizing materials. The characteristics of the PBP-modified electrode surfaces are characterized by confocal laser scanning microscopy (CLSM) and scanning electron microscopy (SEM). The photocurrent characteristics of the assembled solar photovoltaic cells are studied, allowing the PBP that gave the highest photoelectric conversion efficiency to be identified. The incident photo-to-current conversion efficiency (IPCE) and the incident conversion efficiency (ICE) are collected to aid discussion of the efficient capture of low light underwater by the PBP-based DSSCs.

**Experimental details**

**Materials**

**Natural PBPs.** C-PC from *Spirulina platensis* was provided by Xindaze Spirulina Co. Ltd, China. B-PE from *Porphyridium* was isolated and purified by our laboratory [35].

**Artificial PBPs.** All artificial PBPs were prepared in our laboratory. Hx is a His-tagged recombinant PC α subunit (His-PC-A) [36]. MF0 is a double-tagged recombinant PC α subunit (His-MBP-PC-A) [37]. MAC is a double-labeled PC α subunit (MBP-streptavidin-PC-A) [38]. SASB is a double-labeled APC α subunit and β subunit monomer (His-strepII-PC-A, His-strepII-PC-B). rAPC is a recombinant APC trimer (αβ)_3 [39,40].

**Construction and sensitization of TiO_2 electrodes**

A TiO_2 photoanode was placed in a muffle furnace, heated at 400 °C for 30 min, and then cooled to 50 °C. The activated electrode was taken out, immersed in PBP solution (pH = 7.0, 50 mmol/L phosphate-buffered saline, PBP concentration was 5 mg/mL), protected from light, and stood at...
room temperature for 24 h. The sensitized TiO$_2$ photoanode was taken out of the PBP solution, rinsed with 50 mmol/L phosphate-buffered saline to remove the PBPs that were not strongly adsorbed, and then vacuum-dried in the dark.

**Assembly and performance testing of PBP-sensitized solar cells**

TiO$_2$ electrodes sensitized with different PBPs were used as photoanodes in the DSSCs. Pt-plated fluorine doped tin oxide (FTO) glass (10 Ω/sq, Asahi glass, Japan) was used as the counter electrode. A hollow Surlyn heat seal film (25 μm) was placed between the two electrodes to form a closed square cavity. The electrolyte (0.5 mol/L LiI, 0.05 mol/L I$_2$, 0.3 mol/L DMPII, 0.5 mol/L 4-TBP and 0.1 mol/L GNCS in acetonitrile) was then injected into the cavity through a small hole in the surface of the electrode. After assembly of the cell, as an effective irradiation area of 0.24 cm$^2$, its photoelectric performance was measured by a current–voltage (I–V) test station 2000 (Crown Tech IV Test Station 2000). Each DSSC photoanode was irradiated with a light intensity of 100 mW/cm$^2$, and the voltage and current were monitored using a Keithley 2400 sourcemeter. From the obtained I–V curves, because a large number of images were obtained and the adsorption of the seven PBPs on the photoanodes was similar in each case, we selected the images of the B-PE-sensitized photoanode for analysis (Fig. 3).

**Characterization of TiO$_2$ photoanode surfaces after PBP sensitization**

According to the spectral characteristics of the PBPs (the absorption peaks and maximum fluorescence emission peaks of the seven PBPs are summarized in Supplementary Figure S1 and Supplementary Table S1), the sensitized photoanodes were excited by lasers with emission wavelengths of 559 and 635 nm. Fluorescence photographs of the sensitized photoanodes from 570 to 670 nm were obtained by CLSM. The sensitized TiO$_2$ electrodes were cut and plated with platinum. The surface and cross section of the sensitized photoanodes were observed by SEM (Hitachi S-4800).

**Spectral response test of PBP sensitized solar cells**

The spectral range of the illumination source was set to 300–800 nm, and the constructed DSSCs were tested using a solar cell spectral response test system. IPCE and ICE spectra were obtained based on the changes in photoelectric conversion efficiency and short-circuit current density with illumination wavelength.

**Results and discussion**

**CLSM characterization of the surface of TiO$_2$ photoanodes after PBP sensitization**

CLSM is a sensitive and simple method for detecting the adsorption state of PBPs with fluorescent emission in sensitized photoanodes. The surface of the electrode after B-PE sensitization was red, and the other electrode surfaces were blue. CLSM images of unsensitized and sensitized TiO$_2$ photoanodes are shown in Figs. 1 and 2. When excited at 635 and 559 nm, the blank photoanode did not fluoresce in the dark field (Figs. 1a and 2a). When the PBP-sensitized TiO$_2$ photoanodes were excited at different wavelengths, the entire photoanodes emitted very bright orange-red light. To capture clear pictures, the intensity of the excitation light was lowered (Figs. 1c, g, i, k, m, o, and 2m, o). The CLSM results indicate that all seven of the PBPs were adsorbed on the surface of the TiO$_2$ photoanodes and retained their ability to absorb light.

**SEM characterization of PBP-sensitized TiO$_2$ photoanodes**

SEM was used to observe the photoanodes at magnifications of 10000–100000×. Because a large number of images were obtained and the adsorption of the seven PBPs on the photoanodes was similar in each case, we selected the images of the B-PE-sensitized photoanode for analysis (Fig. 3).

**Results and discussion**

**Photoelectric properties of DSSCs**

The photoanode and platinum electrode sensitized with PBPs were assembled into solar cells, and then their photoelectric properties were measured. Fig. 5 depicts I–V curves of DSSCs sensitized by different PBPs at a light intensity of 100 mW/cm$^2$. 

**Spectral response test of PBP sensitized solar cells**

The spectral range of the illumination source was set to 300–800 nm, and the constructed DSSCs were tested using a solar cell spectral response test system. IPCE and ICE spectra were obtained based on the changes in photoelectric conversion efficiency and short-circuit current density with illumination wavelength.
The open circuit voltage and short circuit current density of the cell with B-PE are much higher than those of the cells with C-PC and artificial PBPs. The parameters of the DSSCs with different PBPs are listed in Table 1, which is sorted from high to low in terms of photovoltaic conversion efficiency. The short-circuit current densities of the six cells containing PBPs based on phycocyanobilin (PCB) ranged from 0.32 to 0.88 mA/cm², and the open circuit voltage ranged from 0.38 to 0.46 V. The short-circuit current density of the device with B-PE was the highest of the cells, reaching 3.236 mA/cm², and its open circuit voltage was also the highest at 0.545 V.

The photovoltaic conversion efficiency of the cells sensitized with various PBPs at a light intensity of 100 mW/cm² is shown in Fig. 6. The photovoltaic conversion efficiency of the cell with B-PE exceeded 1%. In contrast, the photovoltaic conversion efficiencies of the DSSCs with C-PC and artificial PBPs were between 0.1% and 0.25%. Therefore, the photovoltaic conversion efficiency of the B-PE-based device was four to ten times that of other PBPs.

Above SEM results confirmed the multilayer absorption of B-PE on sensitized photoanode. Previous studies revealed that the multilayer proteins architecture, in certain range, can improve photocurrent density, because of enhancing light-harvesting and charge-separating [43–46]. However there was a little change in the absorbance spectrum. As long as absorption, the thickness of multilayer was thicker. The performance of short-circuit current densities was linearly enhanced with the thickness of PBP multilayer [43]. In addition, our experiment results show that the B-PE adsorption on the FTO glass has good fluorescence properties, but the fluorescence peak disappeared after B-PE adsorption on TiO₂ electrode (Supplementary Figure S2). This indicates that TiO₂ electrode has a significant fluorescence quenching effect on B-PE. The energy absorbed by the B-PE can be transferred to the TiO₂ electrode.
Fig. 2 — Confocal fluorescence images (559 nm) and bright-field images of TiO$_2$ photoanodes with and without PBPs. Blank photoanode (a), bright-field image of blank photoanode (b), bright confocal fluorescence image of sensitized photoanodes (c, e, g, i, k, m, o), bright-field images of sensitized photoanodes (d, f, h, j, l, n, p).

Fig. 3 — SEM images of blank control and B-PE-sensitized photoanodes at different magnifications. 10 K (a), 20 K (c), 50 K (e), 100 K (g) FE-SEM image of blank control; 10 K (b), 20 K (d), 50 K (f), 100 K (h) FE-SEM image of sensitized photoanode.
Spectral responses of the PBP-sensitized solar cells

To study the responses of the PBP-sensitized DSSCs to different wavelengths of monochromatic light, IPCE spectroscopy was conducted. The photoelectric conversion efficiencies and short-circuit current densities of the devices at different illumination wavelengths were obtained.

The photoelectric conversion efficiencies originating from the PBPs in the visible light region are presented in Fig. 7. The maximum photoelectric conversion efficiency peaks of all devices were blue or red-shifted relative to their respective absorption peaks (blue vertical lines). The maximum efficiencies of the DSSCs with B-PE and C-PC were obviously higher than those of the other devices.

Fig. 7a shows that the DSSC based on B-PE exhibits its highest photoelectric conversion efficiency between 525 and 570 nm. B-PE is composed of three subunits (α, β, and γ). The γ subunit contains PEB, the absorption maximum of which is at 525 nm. Glazer and co-workers found that an exciton pair (PEB82α/PEB82β) in B-PE absorbs at 570 nm [47]. This exciton pair is caused by the influence of the γ subunit on the spatial structure of PEB82β. Therefore, the two peaks in the photoelectric conversion efficiency spectrum of B-PE are closely related to the γ subunit.

As shown in Fig. 7b, the maximum photoelectric conversion efficiency of the DSSCs with various genetic artificial PBPs is around 690 nm, and that is the second largest photoelectric conversion efficiency of the DSSCs with C-PC. Previous studies revealed that the absorption peak of PCB in acidic methanol is also around 690 nm. The spatial structures of the PCB-based PBPs used in this experiment are similar. Therefore, it is speculated that the protein in the electrolyte environment will be denatured, resulting in a change in the conformation of the chromophore. Because B-PE is the only PBP that contains a γ subunit in this experiment, it is presumed that the γ subunit can maintain the structural stability of B-PE in the electrolyte environment.

To more intuitively reflect the magnitude of the current generated by PBP absorption, we measured the ICE spectra of the devices (Fig. 8). The photocurrent generated by this DSSC was mainly produced by the sensitization of B-PE. The results in Fig. 8a illustrate that the photocurrent intensity of the device with B-PE is much higher than that of devices with PBPs based on PCB.

The maximum photocurrent of the DSSC based on B-PE was observed between 525 and 570 nm, whereas the
maximum photocurrent of the DSSCs based on artificial PBPs was observed at 690 nm. In addition, the DSSC based on C-PC exhibited a peak at 565 nm, and the DSSC based on B-PE had a shoulder peak at 690 nm. Blue or red shifts occur with respect to the respective absorption peaks (Fig. 8a and b). Interestingly, the photocurrent intensity of the DSSC based on B-PE at 525 nm is lower than that at 570 nm. However, in Fig. 7, the photoelectric conversion efficiency of the DSSC based on B-PE at 525 nm is higher than that at 570 nm. This may be because the single photon energy absorbed by B-PE at 525 nm is higher than that at 570 nm.

In the ICE spectra, the DSSC based on C-PC displayed its maximum current at 565 nm. In this experiment, we used six PBPs based on PCB. Hx, MF0, and MAC are α subunits of C-PC with different molecular labels. The α subunit of C-PC has a PCB chromophore attached to the 84α position. In contrast, rAPC and SASB are recombinant APCs. The α and β subunits of each recombinant APC also contain the PCB chromophore at the 84α and 84β positions. The difference between C-PC and the above five artificial PBPs is that C-PC contains a β subunit, which has another PCB chromophore at the 155β position. Therefore, it is likely that the absorption of energy by PCB at the β155 position results in the current peak at 565 nm in the ICE spectrum of the device with C-PC.

The high photoelectric conversion efficiency of the DSSC based on B-PE is interesting. The high-level structure of PBP is easily affected by the external environment, especially in electrolyte solutions where redox reactions occur repeatedly. Supplementary Figure S3 displays spectra of the monomer and trimer of rAPC. When the rAPC trimer dissociates to form the monomer, the spectrum exhibits a very large change. Therefore, the solution environment has a large effect on the structure of PBPs based on PCB. This in turn affects the photoelectric conversion efficiency and photocurrent of their devices. From the IPCE and ICE spectra, the DSSC based on B-PE displayed a small change with respect to absorption spectrum and maintained a high photoelectric conversion efficiency. The molecular structures of B-PE and C-PC are (αβ)6 and (αβ)6, respectively. The biggest difference between them is that there is a γ subunit in the central cavity of B-PE. The γ subunit in the hydrophobic environment of B-PE increases the structural stability of the protein, raises the light absorption of B-PE, regulates the energy transfer pathway, and performs photoprotection functions. Therefore, DSSCs based on B-PE have better application prospects than those with C-PC.
In this paper, DSSCs were constructed using PBPs with different structural and optical properties as sensitizing materials. For example, H₂ can penetrate into the voids of a TiO₂ electrode because it has a low molecular weight. Although MF₀ is twice as large as H₂, it has better water solubility. MAC and MF₀ have similar molecular sizes but MAC contains a streptavidin tag. Both SASB and rAPC are genetically recombined APCs. SASB is present primarily in the form of α and β monomers in solution because of the presence of biotin tags in SASB. Both B-PE from Porphyridium cruentum and C-PC from Spirulina platensis were derived from nature algae and are mainly present in the form of hexamers in their natural states.

The experimental results showed that the photoelectric conversion efficiencies of DSSCs based on PBPs containing PCB were between 0.1% and 0.25%, which are close to the reported photosynthetic protein efficiencies of PBSs. The DSSC based on B-PE displayed a short-circuit current density of 3.236 mA/cm², open circuit voltage of 0.545 V, fill factor of 0.569, and high photoelectric conversion efficiency of 1%. The IPCE and ICE spectra of the DSSC based on B-PE revealed that it has maximum photoelectric conversion efficiency and photocurrent between 525 and 570 nm. The light present in deep seawater is mainly blue-green light in the wavelength range of 480–570 nm (Fig. 9). Therefore, DSSCs based on B-PE will have great potential in underwater photovoltaic applications. We believe that in the future, artificial light-harvesting devices will be constructed using B-PE as a sensitizing material. High-efficiency light-harvesting devices for weak blue-green light will be developed because they have broad application prospects in offshore engineering. If their photoelectric conversion efficiency can be improved, DSSCs based on B-PE will be attractive for this purpose.

Acknowledgment

The authors gratefully acknowledge the financial support provided by the Marine Economic Innovation Development Demonstration Project (YHCX-SW-P-201701). This work was also supported by the National Natural Science Foundation of China (grant numbers 41176144), Key Project of Coal-based Science and Technology in Shanxi Province (Grant No. FT2014-01) and the Scientific Research Foundation of Ludong University (grant number ly2014041).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2018.10.176.
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