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*Research Article*

# Photosensitizers from Spirulina for Solar Cell

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Spirulina is a kind of blue-green algae with good photosynthetic efficiency and might be used for photovoltaic power generation. So this paper used living spirulina as novel photosensitizer to construct spirulina biosolar cell. The results showed that spirulina had the photoelectric conversion effect, and could let the spirulina biosolar cell have 70 $\mu$A photocurrent. Meanwhile, adding glucose sucrose or chitosan in the spirulina anode chamber, they could make the maxima current density of the cell greatly increased by 80 $\mu$A, 100 $\mu$A, and 84 $\mu$A, respectively, and the sucrose could improve the maximum power density of the cell to 63 mW/m$^{-2}$. Phycobiliprotein played an important role in the photosynthesis of spirulina. So in this paper phycobiliprotein was extracted from spirulina to composite with squaraine dye to sensitize nanocrystalline $TiO_2$ photoanode for building dye sensitized solar cell, and the photoelectric properties of the cell also were investigated.

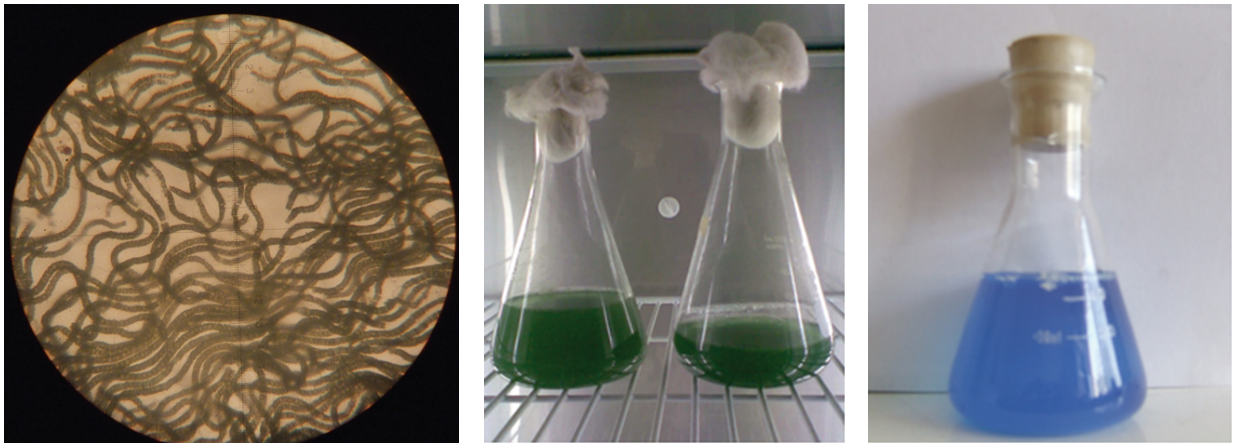
## 1. Introduction

Many photosensitizers [1–4] have been used to construct photo devices, such as organic dyes, inorganic nanomaterials, and biomass. Solar cells are the main photo devices that achieve the conversion of light energy into electrical energy. In particular, the solar cells based on photosynthesis principle of plants and algae, have great potential for the development and application [5–9]. In 1911, British botanist Potter discovered that microbes could produce current [10]. After the 1980s, electron transfer intermediates were widely used for improving output power of the microbial fuel cell greatly. In 1999, Tatsuo Yagishita et al. studied *Synechococcus* with glucose to make electricity production [11]. Researchers in University of Massachusetts found that iron reducing bacteria Rhodospirillum could metabolize carbohydrates and produce electricity [12]. US scientist Logan injected new vitality to the research of microbial fuel cell (MFC) by his studies in wastewater treatment and microbiological power generation [13–17]. Spirulina is ancient blue-green algae [18], and the growth and expansion of spirulina are rapid, easy, and convenient due to its cultivation pH 8.6–9.5 and lower demands for the environment [19, 20]. It has the solar energy utilization efficiency up to 18% and the photosynthetic efficiency up to 43% (more than 3 times high to those of advanced plants) due to its phycobiliprotein. So this paper intended to extract phycobiliprotein from spirulina and used it as photosensitizer to sensitize nano-$TiO_2$ to equip the dye sensitized solar cell [21]. Meanwhile, we applied the living spirulina to build the spirulina biosolar cell [22, 23] and investigated the electrical properties of the cell and the influence of carbohydrates on photoelectric performance of the cell.

## 2. Experimental

*2.1. Spirulina Cultivation and Extraction of Phycobiliprotein.* Spirulina was cultivated with medium Zarrouk or medium spirulina at 28°C under 3000 lx light and 12 L/12 D photoperiod and was trained for 20 days [24] for the experiment. Phycobiliprotein was extracted from the spirulina by repeated freezing and melting technology under ultrasonic.

*2.2. $TiO_2$ Film and Its Sensitization with the Phycobiliprotein and Phycobiliprotein Squaraine.* Nanometer $TiO_2$ film was prepared on glass electrode by sol-gel from butyl titanate,



(a) (b) (c)

Figure 1: The sample of live spirulina under microscope (a) and in incubator (b) and the phycobiliprotein extracted (c).

diethanolamine, ethyl alcohol, and PEG and was sensitized with the phycobiliprotein or phycobiliprotein squaraine by impregnated method, respectively. The squaraine dye with N-p-carboxybenzyl group was synthesized by the reference [25].

*2.3. Construction of Spirulina Biosolar Cell.* Spirulina biosolar cell consisted of anode chamber and cathode chamber separated by clapboard, and the clapboard was equipped with proton exchange membrane (Nafion, 14 $cm^2$). Two graphite electrodes in the anode and cathode chamber (about 10 $cm^2$) were placed closely to both sides of the proton exchange membrane, and Ag/AgCl reference electrode in the anode chamber was close to the anode. Spirulina in the culture medium (240 mL) with or without glucose, sucrose, or chitosan was added to the anode chamber, while the culture medium (240 mL) was in the cathode chamber.

*2.4. Detection of the Spirulina Biosolar Cell.* The spirulina biosolar cell was placed under a xenon light source with the distance of 22 cm to the surface of anolyte. Photoelectric conversion performance of the solar cell was detected at 28°C under xenon lamp by electrochemical workstation.

## 3. Results and Discussion

*3.1. Spirulina and Phycobiliprotein Photosensitizers.* Figure 1 showed that the spirulina cultivated was green and spirochete, while the phycobiliprotein extracted from spirulina was blue. The maximum fluorescence emission wavelength of the phycobiliprotein was 650 nm. The phycobiliprotein sensitized the nano-$TiO_2$ film anode and assembled it into the dye sensitized solar cell with $KI/I_2$ acetonitrile solution as electrolyte and graphite as cathode. The results showed that the phycobiliprotein could improve the photovoltage and current of the nano-$TiO_2$ film to 273 mV and 4.2 mA, while using the phycobiliprotein squaraine as the photosensitizer, they could be 407 mV and 5.7 mA.

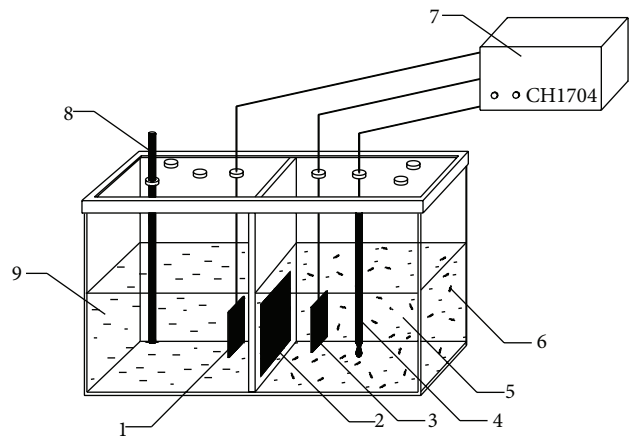



Figure 2: Schematic structure of the spirulina biosolar cell. 1: cathode, 2: proton exchange membrane, 3: anode, 4: reference electrode, 5: anolyte, 6: spirulina, 7: electrochemical workstation, 8: intake tube, and 9: catholyte.

*3.2. The Spirulina Biosolar Cell and Its Working Principle.* Structure and working principle of the spirulina biosolar cell were shown in Figures 2 and 3. Spirulina as electricity generation algae in the anolyte emitted electrons by its photosynthesis and respiration metabolism under light, and the electrons were transferred to the anode. At the same time, the protons were produced, then transferred to the cathode surface after penetrating the proton exchange membrane, and at last the protons reacted with oxygen and electrons to form water.

*3.3. Photocurrent of the Spirulina Biosolar Cell.* Figure 4 showed changing curves of the current with time for the cells under the dark and light. B1 represented the curve for the cell with 240 mL culture medium in each of the chambers, while S1 for the cell with 240 mL spirulina cultivated for twenty days in anode chamber and 240 mL culture medium in

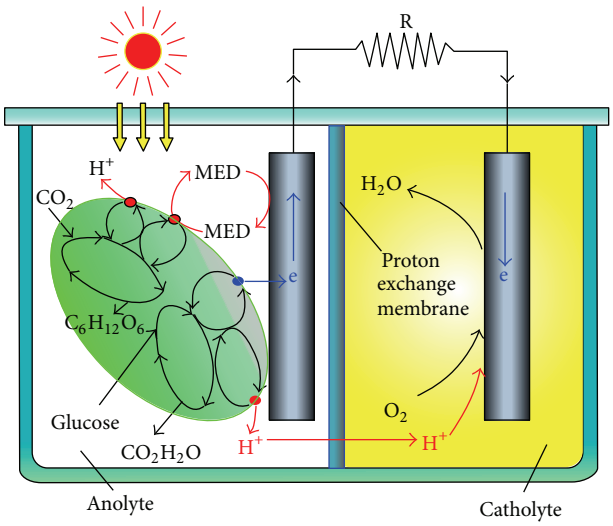



Figure 3: Electrons transfer mechanism of the spirulina biosolar cell.

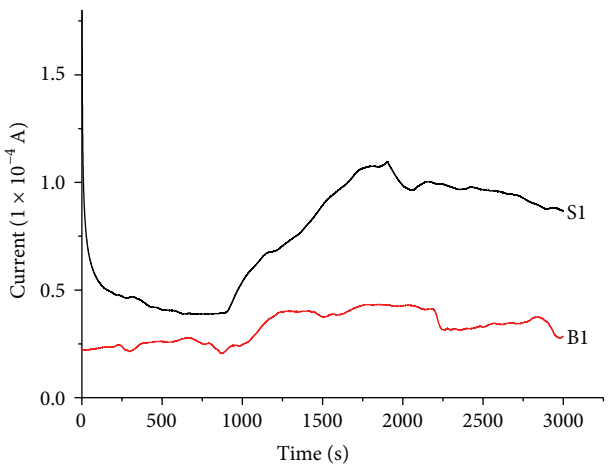



Figure 4: Current-time curves of the solar cell with and without spirulina under light and dark. B1: without spirulina; S1: with spirulina.

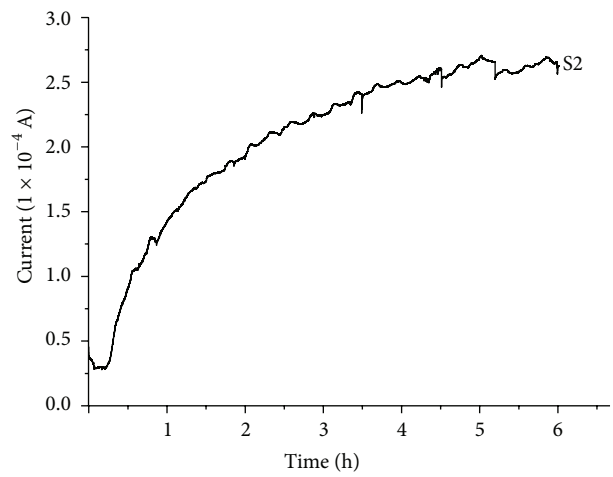



Figure 5: Current-time curve of the spirulina biosolar cell under the light for 6 h.

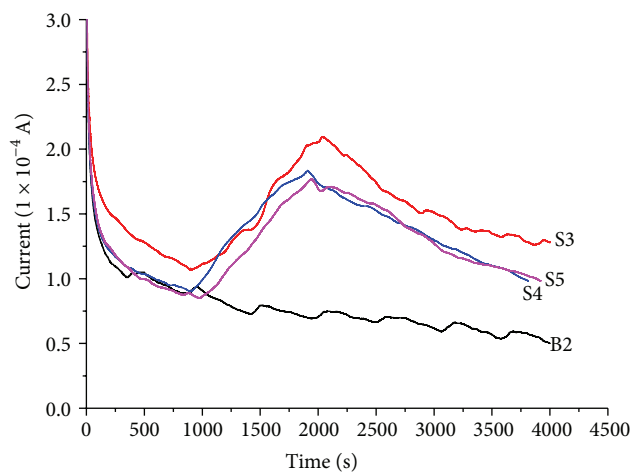



Figure 6: Current-time curves of the solar cell with sucrose in the anode chamber under the light and dark for three times. With spirulina, S3: the first time, S4: the second time, S5: the third time; B2: without spirulina.

the cathode chamber. There was no light in 900 s. When lighting at the 900 s, the current rose, and fell when the lighting was removed at the 1900 s. B1 indicated that polarization current of the cell increased 19 $\mu$A due to the elevated temperature of the solution and the reduction of internal resistance in solution under the illumination. The current of the cell under illumination had largely been increased (S1) by 70 $\mu$A due to the electron produced from spirulina by photosynthesis, and after the light was removed, the current decreased a little. Figure 5 showed that the current of the spirulina biosolar cell should be increased by 240 $\mu$A under the light for 6 h.

*3.4. Influence of Carbohydrates on Photocurrent of the Solar Cell.* Figure 6 showed the influence of carbohydrates on photocurrent of the spirulina biosolar cell under the dark and light. B2 indicated the changing of current with time for the cell with 2 g sucrose in 240 mL culture medium anode chamber. S3 showed that the current generated by the spirulina biosolar cell with 2 g sucrose in anode chamber had been increased by 100 $\mu$A and indicated that the presence of sucrose could promote the electrons production significantly in photosynthesis of spirulina. After the light was removed, the current of the cell had a slight decrease. S4 and S5 explained that the maxima current only had a little decrease while repeating the experiments due to the slight loss of spirulina. Figure 7 showed that the photocurrent of the spirulina biosolar cell with 3.8 g sucrose in anode chamber was increased 389 $\mu$A under the light for 4 h.

The influence of other carbohydrates on photocurrent of the spirulina biosolar cell was investigated. The results were shown in Table 1. The date indicated that glucose and chitosan made the photocurrent of the solar cell increase about 80 $\mu$A

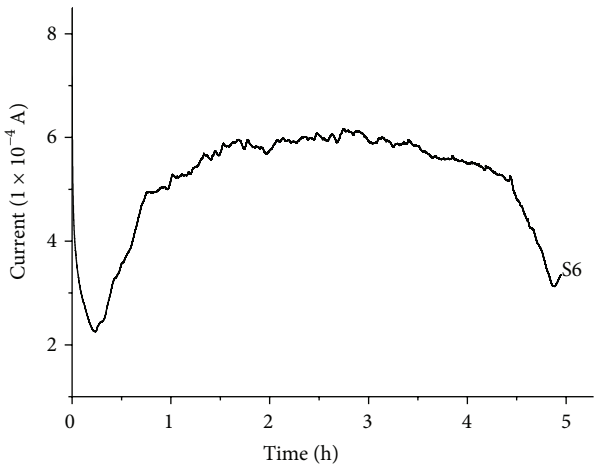



Figure 7: Current-time curve of the spirulina solar cell with sucrose under the light for 4 h.

Table 1: Current of the biosolar cell with spirulina and carbohydrates.

| Anolyte | $I_1$ ($\mu$A) | $I_2$ ($\mu$A) | $\Delta I$ ($\mu$A) |
|---|---|---|---|
| C | 20 | 39 | 19 |
| C + S | 32 | 102 | 70 |
| C + S + Glucose | 114 | 194 | 80 |
| C + S + Sucrose | 101 | 201 | 100 |
| C + S + Chitosan | 82 | 166 | 84 |

C: culture medium, S: spirulina, $I_1$: current at 900 s, $I_2$: current at 1900 s, and $\Delta I$: the photocurrent difference.

and 84 $\mu$A, respectively. Among them, the photoelectric conversion effect of the spirulina biosolar cell with sucrose was the best and could be improved approximately by 100 $\mu$A.

Carbohydrates might improve the photosynthesis rate and photoelectric conversion of the spirulina biosolar cell due to their improving of the activity of hexokinase (an enzyme relating to the cyanobacterial photosynthesis). In the process, the carbohydrates were likely to compensate for lack of a carbon source and conducive to consumption reducing of ATP and NADPH in carbon utilization of the cells. These exogenous carbohydrates provided electrons as the endogenous starch or glucose did and made the electrons flow to PS I. Meanwhile, they improved proton gradient of crossing thylakoid membrane, photosynthetic phosphorylation level of cell, and the efficiency of emitting electrons from spirulina.

## 4. Conclusions

Phycobiliprotein-squaraine composite had good efficiency for widening and strengthening the UV-Vis light absorption and fluorescence emission of $TiO_2$ film and improving the photovoltage and photocurrent of the DSSC. Living spirulina had photoelectric conversion effect and could transmit the photoelectrons by its photosynthesis out of its cytomembrane in spirulina biosolar cell. Carbohydrates could improve the photocurrent of the solar cell further. Among them, sucrose was the best additive and could let the current and the power density of the spirulina biosolar cell increase by 100 $\mu$A and 30 mW/m$^{-2}$, respectively. Spirulina biosolar cell will have a large potential for practical applications.

## Conflict of Interests

The authors declare that they have no direct financial relation with the commercial identities mentioned in this paper that might lead to a conflict of interests for any of them.

## Acknowledgments

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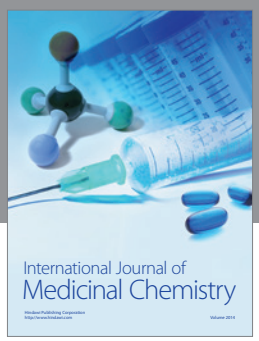

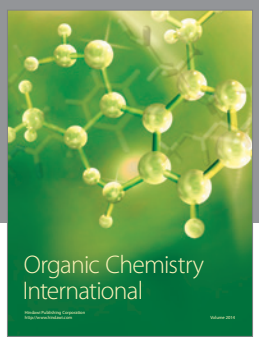

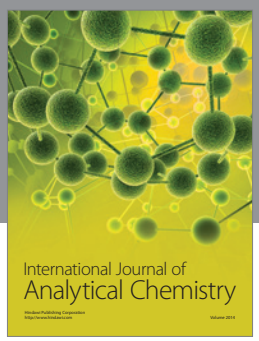

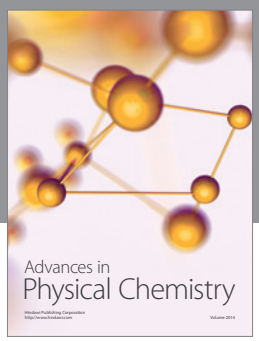

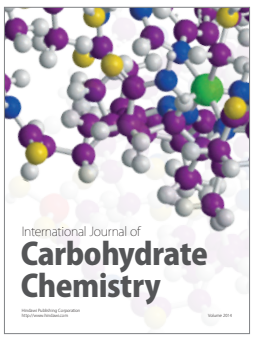

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