Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 76 (2008) 327–331

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

The synergistic effect of two photosynthetic pigments in dye-sensitized mesoporous TiO_2 solar cells

Bao-Qi Liu, Xiao-Peng Zhao*, Wei Luo

Department of Applied Physics, Institute of Electrorheological Technology, Northwestern Polytechnical University, Xi'an 710072, PR China

Received 24 August 2006; received in revised form 9 September 2006; accepted 12 September 2006

Abstract

Chlorophyll and xanthophyll were extracted from different plants for use as sensitizer colorants; cells were sensitized using chlorophyll, xanthophyll and a mixture of the two pigments. It was found that energy conversion efficiency (η) and maximum output power (P_{max}) were 15.16% and 8.31% higher than that achieved by the linear superposition of the cells sensitized by individual pigments. This indicates that the mixed pigment co-sensitization entails a synergistic effect in the energy transfer of the pigment-sensitized mesoporous TiO_2 solar cells. Fluorescence analysis revealed that the electron transfer between chlorophyll and xanthophyll in the mixed pigment co-sensitized mesoporous TiO_2 solar cells was similar to that in 'zigzag chains' of photosynthesis.

Keywords: Dye-sensitized solar cells; Photosynthetic pigments; Synergistic effect; Artificial photosynthesis

---

1. Introduction

Since Grätzel first reported dye-sensitized nanocrystal film solar cells (DSSCs) in 1991, this new kind of solar cell has attracted great attention due to its low-cost and simple fabrication. DSSCs, which are based on the principle of primary energy conversion in photosynthesis, consist of TiO_2 film (anode), a synthetic ruthenium bipyridyl-based dye, electrolyte and counter electrode (cathode). While the overall efficiency of this kind of cell is close to that of p–n junction solar cells [1,2], it is far inferior to the primary energy conversion efficiency in natural photosynthesis. Due to the increasing energy crisis, in recent years many researchers have devoted themselves to exploring methods for enhancing the energy conversion efficiency (η) and stability of DSSCs [3–6]. Research has focused on the synthesis of new sensitizers [7], low-cost natural dyes, co-sensitizing using multicolor dyes and the mechanism of energy conversion [5,8]. Masaki and coworkers improved η by using the synthetic dye *3-aryl-4-hydroxycyclobut-3-ene-1,2-dione* as sensitizer [6]; however, synthetic dyes are not ideal non-toxic and low-cost materials. Sayama greatly ameliorated the light capture efficiency of the cells by using red, yellow and blue dyes for co-sensitizing solar cells; however, the increase in η was not remarkable compared with single dye sensitizing [8].

In the primary energy conversion process of natural photosynthesis, the quantum efficiency is nearly 100%. The process is co-performed by photosystem I (PSI) and photosystem II (PSII) which are linked like a 'Z' by middle electron transport [9]. This paper concerns a new method for enhancing the energy conversion efficiency in DSSCs using a model of simulating 'zigzag chains' of photosynthesis.

2. The model of simulating 'zigzag chains' of photosynthesis in DSSCs

Fig. 1 is a sketch map of the 'zigzag chains' in natural photosynthesis. The PSI and PSII are linked via 'zigzag chains' by middle electron transport and can be excited, synchronously,

---

* Corresponding author. Tel./fax: +86 29 88495950.
E-mail address: xpzhao@nwpu.edu.cn (X.-P. Zhao).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.09.004

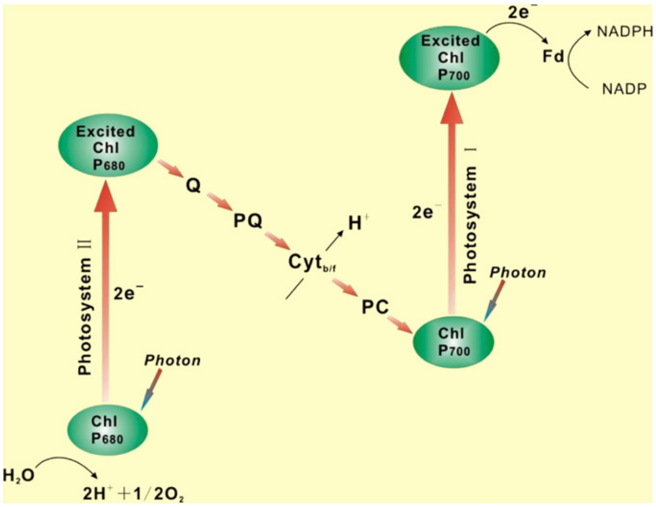

Fig. 1. Sketch map of ‘zigzag chains’ in natural photosynthesis.

by visible light and co-perform relay-like electron transfer from H_2O to $NADP^+$ in series-wound mode [9]. As a result of the synergistic interaction between PSI and PSII, the quantum efficiency is nearly 100% in natural photosynthesis. Inspired by the ‘zigzag chains’, we developed a model mesoporous TiO_2 solar cells comprising two photosynthetic pigments which are synergistically co-sensitized, so as to simulate high efficiency energy transfer. As chlorophyll and xanthophyll are key photosynthetic pigments, displaying high efficiency energy transfer between the two pigments [10–14], we used chlorophyll and xanthophyll as sensitizers to replace PSII and PSI, respectively, in DSSCs (Fig. 2). The two pigments can be excited synchronously by visible light and electron transfer can be achieved between the two pigments. In this kind of DSSC, xanthophyll can not only be excited by absorbed light but also can accept energy from the excited triplet state of chlorophyll. Hence, as the energy dissipation of the excited chlorophyll decreases, the energy transfer efficiency increases. The principle involved differs to that of extending the visible light absorption spectrum by using co-sensitizing multicolor dyes.

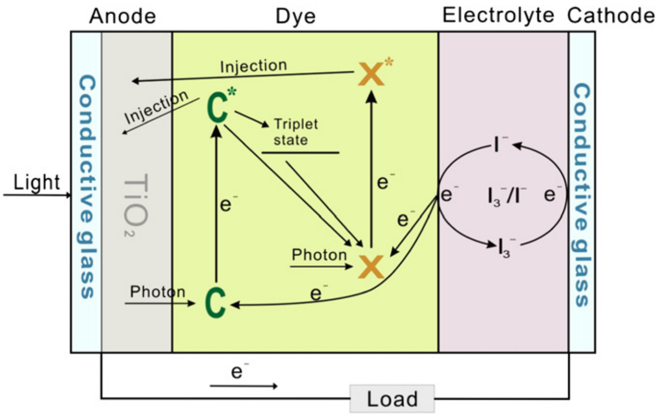

Fig. 2. The model of simulating ‘zigzag chains’ of photosynthesis in DSSCs. C: chlorophyll; X: xanthophylls.

3. Experimental section

3.1. Instruments and materials

ITO conductive glass (2.5 cm × 2.5 cm, indium doped SnO_2, sheet resistance $10.560\ \Omega\ cm^{-2}$, transmittance 85% in visible) was obtained from Shenzhen Conducting Film Corporation, China. Anhydrous ethanol, acetone, petroleum ether were of analytical grade. A mixture of 0.5 M KI and 0.05 M I_2 in water-free ethylene glycol was used as electrolyte. Chlorophyll and xanthophyll were obtained from the leaves of Chinar (*Platanus orientalis* L.) and petals of yellow chrysanthemum (*Dendranthema morifolium*) (rich in the xanthophyll), respectively. A NOVA 2000e Surface Area and Pore Size Analyzer was used to determine the surface area of TiO_2. A potentiometer, a microammeter, a variable resistor (47 kΩ) and a light source (35 W tungsten lamp: radiation in the spectral region of 400–1000 nm, spectral peak of 610 nm) were used to measure the output characteristics of the cells. An F-4500 Fluorescence Spectrophotometer was used to measure the fluorescence properties of the pigments.

3.2. Extraction of the pigments and visible light absorption measurement

Chlorophyll was extracted from the fresh and tender leaves of Chinar. The leaves were dried by airing and moved out from the nervure after washing. Five grams of prepared leaves were crushed in a mortar, and then transferred to a beaker after a small amount of petroleum ether had been added. Twenty milliliters of petroleum ether were then added and the mixture was filtered after being subjected to 15 min of ultrasound; the ether filtrate was discarded. The solid was air-dried and then 20 ml of acetone were added and the mixture was filtered after being subjected to 15 min of ultrasound; the acetone filtrate, which contained chlorophyll, was collected [15]. The solution was stored in the dark at 4 °C.

Xanthophyll was extracted from the clean and fresh petals of yellow chrysanthemum. Five grams of petal were ground in a mortar after a little solvent (60% anhydrous ethanol + 40% petroleum ether) was added; the mixture was transferred to a beaker and subjected to 15 min of ultrasound. After filtration, the resulting solution was further extracted for 15 min under ultrasonic condition. Finally, the solution was filtered and the filtrate further diluted to 20 ml using the solvent (60% anhydrous ethanol + 40% petroleum ether) [16,17]. The solution was stored in the dark at 4 °C.

The concentration of the pigments was calculated using Beer’s law. The chlorophyll solution and xanthophyll solution were first diluted to the required concentration with the appropriate solvent, respectively, and the chlorophyll solution and xanthophyll solution were then mixed together. The solution was stored in the dark at 4 °C.

The visible light absorption characteristics of the pigments in the range 400–700 nm were determined using the appropriate solvent as reference. Un-sensitized TiO_2 electrode was used as reference for the determination of the absorption character of the pigments on a TiO_2 electrode.

3.3. Preparation of the pigment-sensitized electrode

Nanocrystalline mesoporous anatase TiO_2 was prepared as described in Ref. [18]. Its surface area was 166.89 m^2/g, average pore diameter 7.9 nm and the average pore volume 0.34 cm^3/g. One gram of mesoporous TiO_2 were ground in an agate mortar while, simultaneously, 5 ml acetic acid was added.

Conductive glass was cleaned by using ultrasound with anhydrous ethanol under ultrasonic condition for 15 min after being washed with distilled water and then it was air-dried naturally. TiO_2 was deposited on the conductive glass using the method reported earlier [15]. The TiO_2-coated conductive glass was immersed in each of the pigment solution in order for the mesoporous TiO_2 to fully absorb the pigment molecules.

3.4. Assemble device and measurement of output properties

A piece of conductive glass was used as counter electrode. The device was assembled as described in Ref. [19]. The sandwich type solar cell was irradiated using a 35 W tungsten lamp (Fig. 3). The distance between the lamp and cell was 15 cm. The photocurrent and photovoltage were controlled using a 47 kΩ variable resistor.

4. Results and discussion

4.1. Absorption characteristics of the pigments in drawing solvent

Fig. 4 shows the visible light absorption spectrum of chlorophyll, xanthophyll and a mixture of chlorophyll and xanthophyll; the molar concentrations of chlorophyll and xanthophyll were both 0.42 μmol/l. The visible light absorption of xanthophyll was much stronger than that of chlorophyll because the molar absorption coefficient of xanthophyll is greater than that of chlorophyll. The absorption peak of the mixed pigments lay between that of chlorophyll and xanthophyll and there was no new absorption peak or peak shift. It is evident that the visible light absorption of the mixed pigments in solution is the linear superposition of two single pigments.

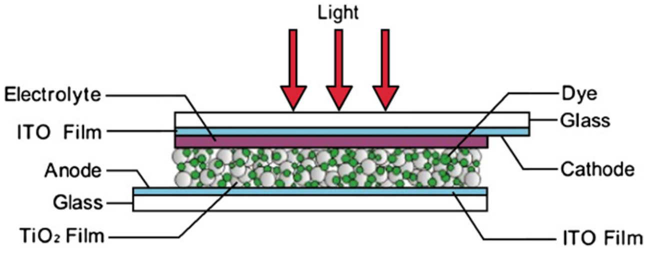

Fig. 3. Structure of photosynthetic pigments-sensitized TiO_2 solar cell.

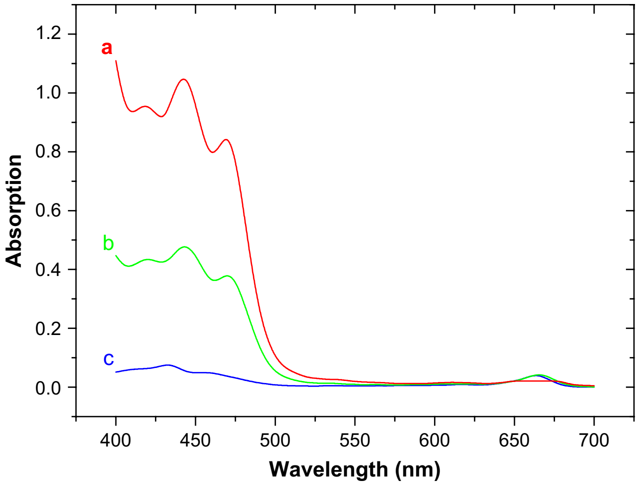

Fig. 4. Absorption spectra of different pigments at same concentration. a: Xanthophyll; b: mixture of chlorophyll and xanthophyll; c: chlorophyll.

4.2. Absorption characteristics of the pigments on TiO_2 electrode

Fig. 5 shows the visible light absorption characteristics of chlorophyll, xanthophyll and a mixture of chlorophyll and xanthophyll on the mesoporous TiO_2 electrode. Before being used, the mesoporous TiO_2 electrodes had been dipped in solutions of chlorophyll (155.5 μmol/l), xanthophyll (0.68 μmol/l) and a mixture of chlorophyll and xanthophyll (1:1 in volume fraction) for 10 h. Fig. 3 shows that the absorption characteristics of the pigments on mesoporous TiO_2 electrode are different from that in the solution. The absorption curve is much smoother than that in Fig. 2, and there is no obvious absorption peak. This demonstrates that the absorption spectrum of the pigments has been expanded in the visible region. Secondly, on the mesoporous TiO_2 electrode, the absorption of the mixed pigments is obviously stronger than that of the single pigments. These phenomena may be attributed to the

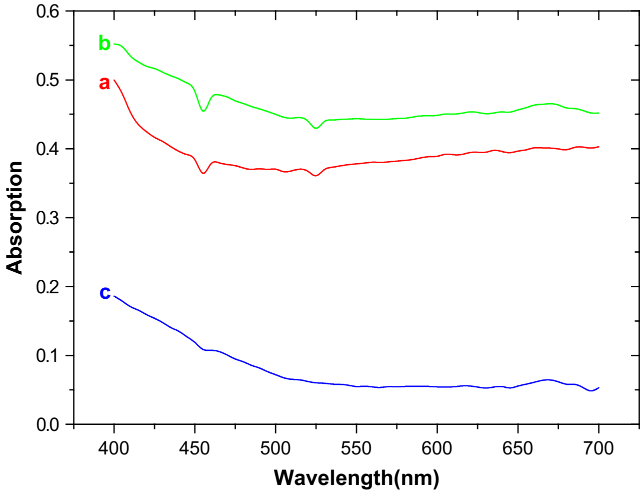

Fig. 5. Absorption spectra of pigments on TiO_2 electrode. a: Xanthophyll; b: mixture of chlorophyll and xanthophyll; c: chlorophyll.

interactions between TiO_2 and the pigment molecules on the mesoporous TiO_2 electrode. For instance, the pigment molecules combine with TiO_2 resulting in electron transfer between pigment molecules and the conduction band of TiO_2 [20]. The interactions between the pigments and TiO_2 are very complicated, further studies of their mechanism are in progress.

4.3. Photoelectrochemical characteristics of the cells

Table 1 shows the photoelectrochemical properties of the cells sensitized by different pigments. The cell sensitized by the mixed pigment displays the largest photovoltage and photocurrent. In the photosystems of green plants, xanthophyll is generally not photoelectrochemically reactive, but rather, serves as the light-harvesting antenna pigment which captures and transmits light energy to the pigment molecules in the reaction centre [9,21–23]. Contrarily, when deposited on the TiO_2 electrode, xanthophyll displays active photoelectrochemical activities, the J_{sc} and V_{oc} of the cells sensitized by xanthophylls being 15.65 μA and 479 mV, respectively, which are higher than those of the cells sensitized by chlorophyll.

The V_{oc} and J_{sc} of the cell sensitized by mixed pigment are 502 mV and 21.50 $\mu A/cm^2$, respectively, and η is 5.8 times that of the cell sensitized by chlorophyll and 1.4 times of the cell sensitized by xanthophyll. The η of the cell sensitized by the mixed pigments is not only higher than other cells but also is higher than the linear superposition of the cells sensitized by each single pigment, as is the P_{max}. This indicates that the co-sensitization with two pigments involves synergism in terms of the energy transfer of the pigment-sensitized TiO_2 solar cells.

4.4. Interaction between chlorophyll and xanthophyll in DSSCs

Xanthophyll acts as a light-harvesting pigment in the photosynthetic antenna pigment–protein complexes, which efficiently transfers energy to chlorophyll [9,22]. Another important function of xanthophyll is photoprotection in which it effectively quenches the chlorophyll triplet state [10,11,24]. It is believed that outside the plant body, xanthophyll has the function of chlorophyll fluorescence quenching, this having been observed in solution (Fig. 6) and on a TiO_2 electrode (Fig. 7).

The results in these works indicate that both the η and P_{max} of the cells sensitized by the mixed pigments are 15.16% and 8.31% higher, respectively, than that of the linear superposition of the cells sensitized by individual pigment (Table 1). This suggests that the quenching effect resulted from energy transfer between chlorophyll molecules and xanthophyll molecules. In DSSCs, the high-energy electrons produced by the excited chlorophyll which had not been injected into the conductive band of TiO_2, and they were captured by xanthophyll. In this way, xanthophyll inhibits the recombination of photoinduced electron–hole pairs of the excited chlorophyll and so the dark current of the cell decreases. Thus, in DSSCs, the molecules of xanthophylls could be excited by visible light and they inject electrons into the conductive band of TiO_2, which contributes to energy conversion of DSSCs, they also could reduce energy dissipation by quenching chlorophyll fluorescence.

Table 1
The photoelectrochemical properties of cells sensitized by different pigments

Pigment	J_{sc} ($\mu A/cm^2$)	V_{oc} (mV)	FF (%)	η (%)	P_{max} (μW)
Chlorophyll	11.92	468	4	0.55	0.87
Xanthophyll	15.65	479	11	2.22	3.46
Mixture of chlorophyll and xanthophyll	21.50	502	11	3.19	4.69

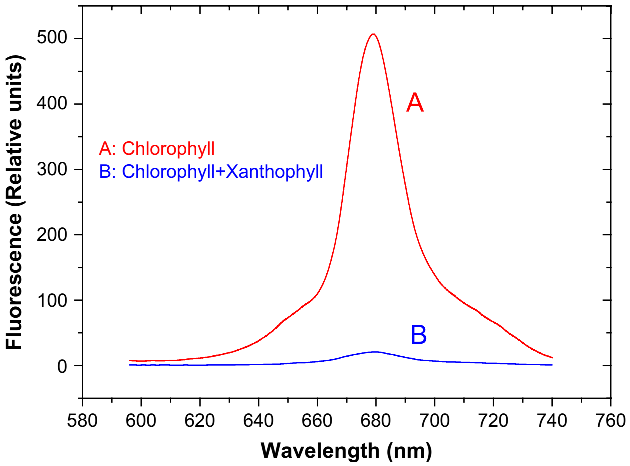

Fig. 6. Fluorescence emission spectra of chlorophyll and mixture of chlorophyll and xanthophyll in acetone solution.

5. Conclusions

The V_{oc} of the cell sensitized by xanthophyll was 594 mV; xanthophyll displays active photochemical activities when present on the mesoporous TiO_2 electrode. In the cells co-sensitized with xanthophyll and chlorophyll, xanthophyll can

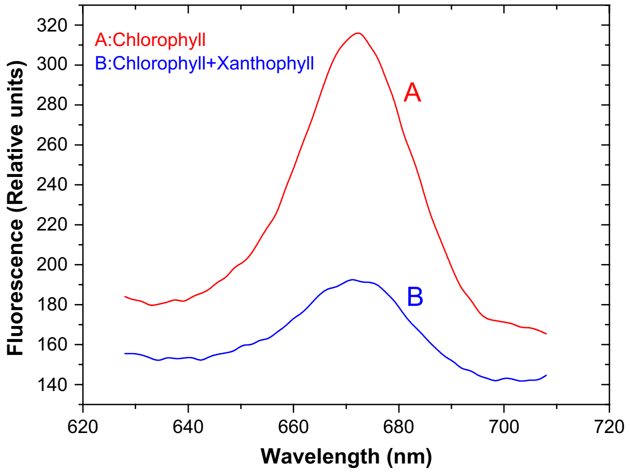

Fig. 7. Fluorescence emission spectra of chlorophyll and mixture of chlorophyll and xanthophyll on TiO_2 electrode.

synchronously accept the energy from the incident light and the excited chlorophyll, and the energy dissipation of excited chlorophyll decreases. The mechanism of energy conversion in this kind of cell is similar to that in the ‘zigzag chains’ of natural photosynthesis and is different from that of multicolor dye co-sensitizing. The η and $P_{\max}$ of the cell sensitized using the mixed pigment show nonlinear superposition effect compared with the cells sensitized by each single pigment. The two photosynthetic pigments showed a synergistic effect in energy transfer.

Acknowledgements

The authors gratefully acknowledge financial support by National Natural Science Foundation of China for Distinguished Young Scholars Program (no. 50025207).

References

[1] O’ Regan B, Grätzel M. A low-cost high-efficiency solar cell based on dye-sensitized colloidal TiO_2 film. Nature 1991;353:737–9.

[2] Dai Songyuan, Wang Kongjia, Wu Qinchong. Investigation of high photoelectric-efficiency under the solar spectrum about NPC. Acta Ener Sol Sin 1996;17(3):220–5.

[3] Kim Seok-Soon, Yum Jun-Ho, Sung Yung-Eun. Flexible dye-sensitized solar cells using ZnO coated TiO_2 nanoparticles. J Photochem Photobiol A Chem 2005;171:273–7.

[4] Xu Lin, Zhang Hongyu, Wang Enbo, Wu Aiguo, Li Zhuang. Preparation and characterization of photoluminescent ultrathin films based on polyoxometalates. Mater Chem Phys 2003;77(2):484–8.

[5] Tedeschi Concetta, Caruso Frank, Möhwald Helmuth, Kirstein Stefan. Adsorption and desorption behavior of an anionic pyrene chromophore in sequentially deposited polyelectrolyte-dye thin films. J Am Chem Soc 2000;122(24):5841–8.

[6] Liu Yangjing, Wang Youxiong, Lu Hongxia, Claus RO. Electrostatic self-assembly of highly-uniform micrometer-thick fullerene films. J Phys Chem B 1999;103(12):2035–6.

[7] Matsui Masaki, Mase Haruhiko, Jin Ji-Ye, et al. Application of semisquaric acids as sensitizers for zinc oxide solar cell. Dyes Pigments 2006;70:48–53.

[8] Sayama Kazuhiro, Tsukagoshi Shingo, Mori Tohru. Efficient sensitization of nanocrystalline TiO_2 films with cyanine and merocyanine organic dyes. Solar Energy Mater Solar Cells 2003;80:47–71.

[9] Kuang Tingyun. Mechanism and regulation of primary energy conversion process in photosynthesis. Jiangsu Science and Technology Publishing House; 2003. P18–P19, P200.

[10] Peterman EJG, Gradinaru CC, Calkoen F, Borst JC, van Grondelle R, van Amerongen H. Xanthophylls in light-harvesting complex II of higher plants: light harvesting and triplet quenching. Biochemistry 1997;36(40):12208–15.

[11] Barzda V, Peterman EJG, Van Grondell R, van Amerongen H. The influence of aggregation on triplet formation in light-harvesting chlorophyll *a*/*b* pigment–protein complex II of green plants. Biochemistry 1998;37:546–51.

[12] Peterman EJG, Monshouwer R, Van Stokkum IHM, van Grondelle R, van Amerongen H. Ultrafast singlet excitation transfer from carotenoids to chlorophylls via different pathways in light-harvesting complex II of higher plants. Chem Phys Lett 1997;264:279–84.

[13] Connelly JP, Muller MG, Bassi R, Croce R, Holzwarth AR. Femtosecond transient absorption study of carotenoid to chlorophyll energy transfer in the light-harvesting complex II of photosystem. Biochemistry 1997;36(2):281–7.

[14] Croce R, Muller MG, Bassi R, Holzwarth AR. Carotenoid-to-chlorophyll energy transfer in recombinant major light-harvesting complex (LHCII) of higher plants. I. Femtosecond transient absorption measurements. Biophys J 2001;80(2):901–15.

[15] Smestad GP, Gratzel M. Demonstrating electron transfer and nanotechnology: a nature dye-sensitized nanocrystalline energy converter. J Chem Educ 1998;75:752–6.

[16] Takagi Shigeaki. Determination of green leaf carotenoids by HPLC. Agric Biol Chem 1985;49(4):1211–31.

[17] Craft NE, Scared JH. Relative solubility, stability, and absorbtivity of lutein and β-carotene in organic solvents. J Agric Food Chem 1992;40:431–4.

[18] Yin Jan Bo, Zhao Xiao Peng. Giant electrorheological activity of high surface area mesoporous cerium-doped TiO_2 templated by block copolymer. Chem Phys Lett 2004;398:393–9.

[19] Dai Songyuan, Weng Jian, Sui Yifeng, Shi Chengwu, Huang Yang, Chen Shuanhong, et al. Dye-sensitized solar cells from cell to module. Solar Energy Mater Solar cells 2004;84:125–33.

[20] Pan Jie, Benko Gabor, Xu Yunhua, Pascher Torbjörn, Sun Licheng, Sundström Villy, et al. Photoinduced electron transfer between a carotenoid and TiO_2 nanoparticle. J Am Chem Soc 2002;124:13949–57.

[21] Liu Zhenfeng, Yan Hanchi, Wang Kebin, Kuang Tingyun, Zhang Jiping, Gui Lulu, et al. Crystal structure of spinach major light-harvesting complex at 2.72 Å resolution. Nature 2004;428:287–92.

[22] Wang Shuicai, Cai Xia, He Junfang, et al. Study on molecule energy transfer from light-harvesting antenna to reaction center. Acta Photo Sin 2003;32(6):641–5.

[23] Wang Shuicai, Cai Xia, He Junfang, et al. Study on molecule energy transfer from core antenna to reaction center. Acta Photo Sin 2003;32(7):848–52.

[24] Dreuw Andreas, Fleming Graham R, Head-Gordon Martin. Chlorophyll fluorescence by xanthophylls. Phys Chem Chem Phys 2003;5:3247–56.