Int. J. Electrochem. Sci., 13 **(2018)** 1945 – 1955, doi: 10.20964/2018.02.38

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Studies on Photoelectric Performance of Natural Dyes from Safflower

Su-Qing Zhao[1], *Yu-Long Xie*[2,*], *Zheng-Xing Qi*[2], *Peng-Cheng Lin*[3]

[1] School of Physics and Electronic Information Engineering, Qinghai Nationalities University, Xining, Qinghai, 810007, China
[2] School of Chemistry and Chemical Engineering, Qinghai Nationalities University, Xining, Qinghai, 810007, China
[3] College of Pharmacy, Xining, Qinghai, Key Laboratory of Plant Resources of Qinghai-Tibet Plateau in Chemical Research, 810007, China
[*]E-mail: yulongxie2012@126.com

Received: 1 October 2017 / *Accepted:* 10 December 2017 / *Published:* 28 December 2017

The TiO_2 nanoparticles thin films was used to prepare the dye-sensitized solar cells (DSSCs) as photoelectrode and natural dyes as photosensitizers. The sensitized TiO_2 based solar cell used nature dye carthain and hydroxysafflor yellow A as sensitizer, which were extracted from the abundant Hehuang safflowers in Qinghai province of China. The DSSCs exhibited short-circuit photocurrent density (J_{sc}) value of 2.193 $mA\cdot cm^{-2}$, open-circuit photovoltage (V_{oc}) of 0.61 V, the fill factor (FF) of 0.50 and solar energy-to-electricity conversion yield (η) of 0.664 %. Natural dyes as sensitizers for DSSCs are promising because of their environmental friendliness, low-cost and designable polychrome modules.

Keywords: Natural dye, Dye-sensitized solar cells, Safflower

1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) have attracted great interest in both academic research and industrial applications owing to its low cost, easy handling and relatively high conversion efficiency [1, 2]. DSSC is a semiconductor material which owns a mesoporous structure of a wide band (e.g., titanium oxide (TiO_2), zinc oxide (ZnO)) sensitized by a light harvesting material (usually metal-organic Ru-based dyes), permeated with a redox electrolyte, with counter electrodes like sandwich [3]. There are two electrodes in the DSSCs, which are the photo-eletrode (negative) and the counter-electrode (positive). There is titanium dioxide nanoparticles in the photo-electrode (sintered on a conducting glass substrate). Dye molecules are attached on the surface of the titanium dioxide nanoparticles which can absorb sunlight in the visible spectrum region. The counter-electrode can be a conducting glass (coated on the surface with a thin layer of platinum catalyst or carbon nanoparticles) or a carbon electrode [4-7]. One of the key elements in DSSCs is photosensitizer. Ruthenium (Ⅱ) polypyridyl complexes are the most successful photo-induced electron transfer sensitizers in DSSCs so far [8]. Yet, ruthenium complexes are expensive and hard to get. So, Searching for cheaper, simpler, and safer sensitizers has become an urgent scientific problem Chlorophyll, anthocyanin, nasunin, and carotenoids, such natural pigments can fulfill those requirements, and TiO_2 sensitized by natural pigments have been reported [8-14].

Natural extracts from leaves, flowers, and fruits are superior to rare metal complexes and organic dyes. The natural dyes are in wide existence, easy to extract, cheap, and environment friendly [8, 15]. Many researchers have investigated the use of natural dyes in solar cells, such as those obtained from extracts of hibiscus [16], mulberry [17], red cabbage [18] and achoite seeds [19, 20]. The function of dye is to absorb light, inject electrons into the TiO_2 conduction band, and then accept electrons from the redox mediator in the electrolyte [20]. Safflower (*Carthamus tincttiorius* L.) is one of the world's oldest crops, highly branched, herbaceous, thistle like annual herb with yellow to red petals [21]. In this work, we made an effort to collect yellow pigment and red pigment from Hehuang safflower, for these plants are abundant in Chinese Qinghai province. Natural dyes sensitized TiO_2 nanoparticles thin films were fabricated by doctor blade method. Furthermore, the photoelectrical properties were studied on assembly DSSCs.

2. EXPERIMENTAL

The red and yellow pigments were extracted by a microwave-assisted extraction method from Hehuang safflowers. The raw natural Hehuang safflowers were washed with distilled water and then dried at 60 °C. The method of extraction and separation of the yellow pigment is as follows. The method is ultrasonic extraction with water as the solvent. The processing condition is material ratio of 1:30, extraction temperature of 70℃, extraction time of 45min, extracting twice. The combined filtrates is separated and purified by HPD-400 Macroporous resin. the flow rate of adding samples to it is 3BV/h. After 2 hours, it will be eluted with distilled water of pH=3 at a speed of 6BV/h until the molish reaction was negative. Of which the aim is to remove the high polar impurity, such as sugar, protein, and amino acid. Then, it is eluted with 50% ethanol of pH=3 at a speed of 6BV/h and the eluant is collected.Last,the eluant is concentrated under vacuum to a little(whose density is about 1.08),then it is freeze-dried into powder, which is the safflower yellow pigment. The method of extraction and separation of red safflower pigment is as follows. First, soak the safflower with 100 times distilled water, which will be repeated over and again until there is no Safflower Yellow. Then, soak the residue in 90% ethanol for 2 hours at 60℃ with solid-liquid ratio1:30, twice. The combined filtrates is separated and purified by X-5 Macroporous resin.the flow rate of adding samples to it is 4.5BV/h. After 2 hours, it is eluted with 80% ethanol at a speed of 2BV/h and the eluant is collected. Last, the eluant is concentrated under vacuum and freeze-dried into powder, which is the safflower red pigment.

The electrochemistry properties were examined by Ivium Stat electrochemical analyzer while a platinum electrode served as a working electrode, Ag/Ag^+ electrode served as reference electrode and a platinum wire served as counter electrode. The scan rate was 50 mV/s. Dry and purified MeCN was used as solvent and 0.1 M $(nBu_4N)[PF_6]$ was used as a supporting electrolyte. Potentials was given vs the Fc^+/Fc couple which was used as internal standard.

FTO conductive glass sheets were of 0.8 cm × 1.6 cm dimensions pieces. The glasses were ultrasonic cleaned in detergent solution for 15 min, rinsed with water and ethanol, and then dried. The TiO_2 paste was fabricated by adding 0.062 g of TiO_2 nano-powder and 0.072 g of polyethylene glycol with grinding for half an hour until a homogeneous paste was obtained. Thin layers of the prepared TiO_2 paste were spread on the transparent conducting FTO coated glasses by employing doctor blade method. Samples were then dried in an oven at 70 °C for 20 min. Finally, the samples were sintered at 400 °C for 40 min then cooled down to room temperature before placing in dye solutions for one day under dark. The redox electrolyte with $[I_3^-]/[I^-]$ 1:9 was prepared by dissolving 0.5 M LiI and 0.05 M I_2 in acetonitrile solvent. Since LiI is extremely hygroscopic, electrolytes were prepared in a dry room maintained. The counter electrode was prepared using platinus chloride, it was made as follows: In the H_2PtCl_6 solution was isopropanol (2 mg/ml), which was deposited onto the ITO glass by spin coating method. The UV-VIS absorption spectra of the dyes were measured using a UV-VIS spectrophotometer (UV-2450 SHIMADZU). The wavelength range of absorption spectra analysis extends from 300 nm to 900 nm. Photovoltaic measurements were made using an AM 1.5 illumination provided by a xenon lamp (150 W) with an optical filter (AM 1.5G) under a power of 100 $mW \cdot cm^{-2}$ (calibrated by a standard silicon solar cell). The Ivium Stat electrochemical analyzer was employed to measure the photocurrent and voltage (J–V) obtained from an illuminated area of 0.5 cm × 0.5 cm. The incident photon to current efficiency (IPCE) spectra were recorded using a computer-controlled setup consisting of a xenon light source, a monochromator, and a potentiostat, calibrated using a certified reference solar cell.

Theoretical calculations were performed for red and yellow pigments compound by the ADF2013.01 (XC potential. In SCF:GGABPE). The exchange correlation was determined by using the DZP functional. The above functional and orbital basis sets were used to provide an accurate description of the compounds. A full optimization was performed in each case, and the total structure optimization together with the vibrational analysis was derived in order to determine whether they confirmed to a maximum and a minimum in the potential energy curve. Structural and electronic parameters for the neutral and protonated structures of red and yellow pigments were calculated by using molecular orbital theory.

3. RESULTS AND DISCUSSION

The Hehuang safflowers were harvested in Qinghai province of China. The red and yellow pigments produced from Hehuang safflowers are mainly used for dye raw material. Flower color investigation was carried out on Hehuang safflower, so far the most important compositions are hydroxysafflor yellow A (yellow pigment) and carthain (red pigment). The chemical structures of hydroxysafflor yellow A and carthain in Hehuang safflower are illustrated in Fig. 1. Fig. 1a is the structure of hydroxysafflor yellow A. Fig. 1b is the structure of carthain.

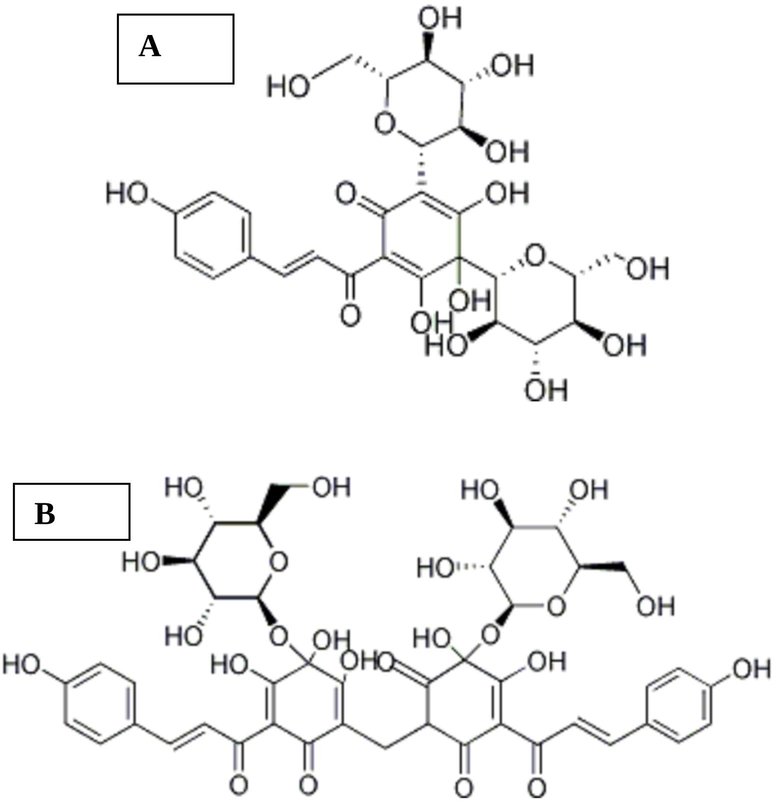
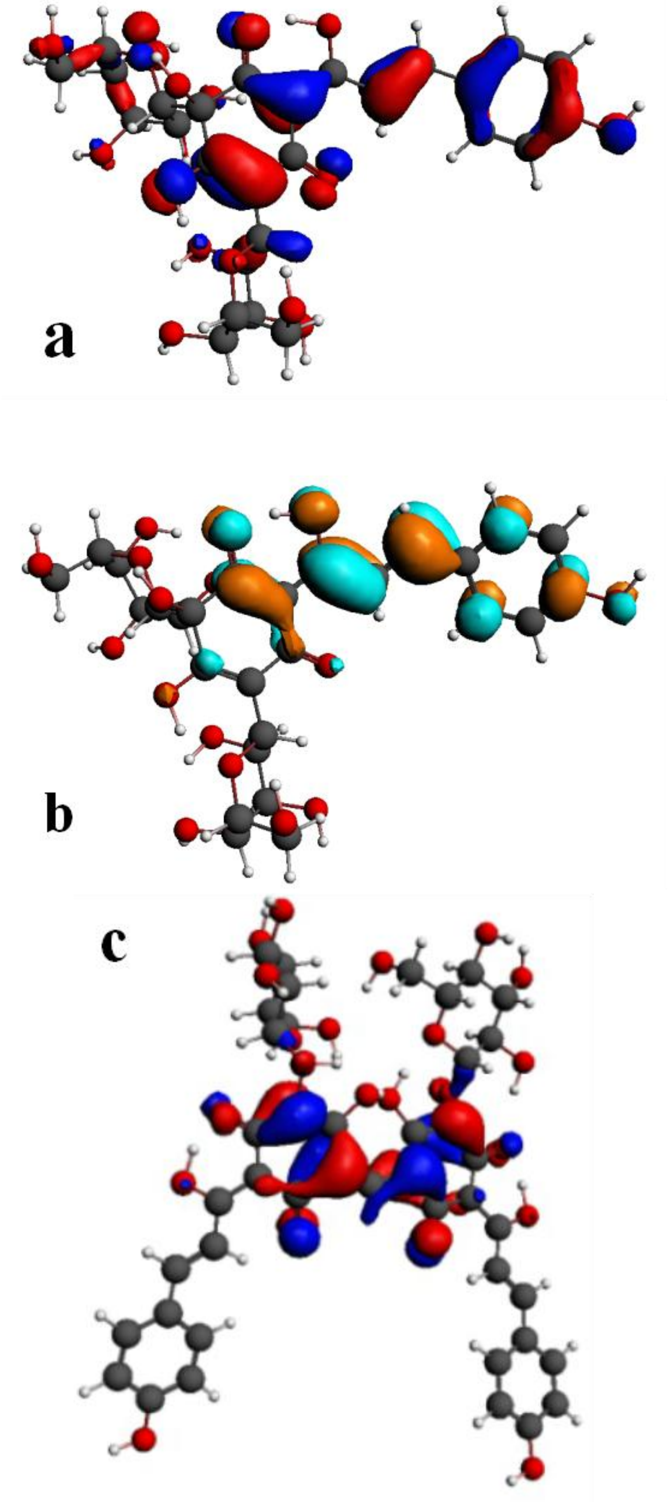


Figure 1. Chemical structure of a. hydroxysafflor yellow A and b. carthain.

All the calculations were performed with the ADF2013.01 (XC potential. In SCF:GGABPE). First of all, geometric parameters (bond lengths, angles and dihedral angles) of ground-state geometry optimization were performed on a model from the geometric parameters (bond lengths, angles and dihedral angles). Then, from the optimized structure, molecular orbitals were calculated and excitation energies were evaluated by means of the time-dependent density functional theory (TD-DFT) with the same functional and basis set. It is useful to examine the highest occupied orbitals and the lowest virtual orbitals of these molecular because the relative position of the occupied and virtual orbitals provides a reasonable qualitative indication for the excitation properties and ability of electron or hole transport [22-24]. As the first dipole-allowed electron transitions, that is to say, the strongest electron transitions with largest oscillator strength, corresponded almost exclusively to the promotion of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).We have plotted the contour plots of HOMO and LUMO in Fig. 2. Fig. 2a is the HOMO of hydroxysafflor yellow A. Fig. 2b is the LUMO of hydroxysafflor yellow A. Fig. 2c is the HOMO of carthain. Fig. 2d is the LUMO of carthain. The frontier orbitals in these molecules spread over the whole p-conjugated backbone. In general, the HOMO possesses an anti-bonding character between the subunits. This may explain no planarity observed for these molecules in their ground states. On the other hand, the LUMO of all the molecules generally shows a bonding character between the subunits. This implies that the singlet excited state involving mainly the promotion of an electron from the HOMO to the LUMO should be more planar.



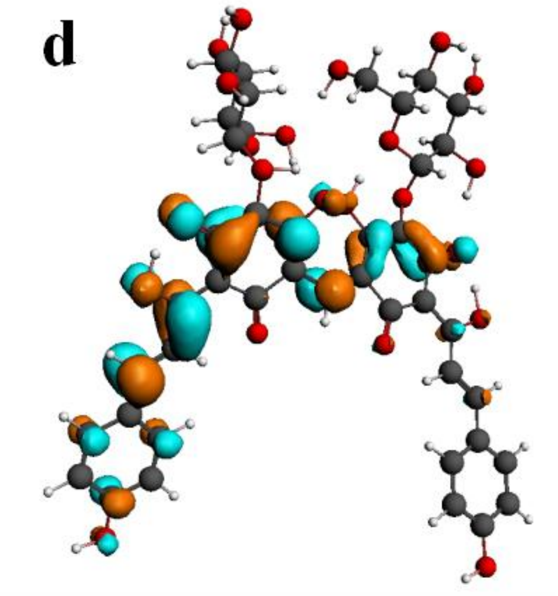


Figure 2. Isodensity plots of HOMO and LUMO molecular orbitals for hydroxysafflor yellow A (a and b) and carthain (c and d).

The electronic properties depend essentially on the HOMO, the LUMO energy levels, and the electron hole mobility. It is known that the energy of the band gap (E_{gap}) between the HOMO and LUMO energies is an important parameter that determines the molecular admittance, because it is a measurement of the electron density. For a better understanding of the electronic properties of the studied molecules, the calculated electronic properties parameters of HOMO and LUMO energy levels and band gap based on the presented results were present in Table 1.

Table 1. The HOMO, LUMO and E_{gap} (eV) energies of the studied compounds.

Sample	**UV-Vis and CV Calculations (eV)**			**Computational Calculations(eV)**		
pigments	E_{HOMO}	E_{LUMO}	E_{gep}	E_{HOMO}	E_{LUMO}	E_{gep}
hydroxysafflor yellow A	–5.135	–2.874	2.261	–5.730	–3.529	2.201
carthain	–4.458	–2.526	1.932	–5.254	–3.068	1.646

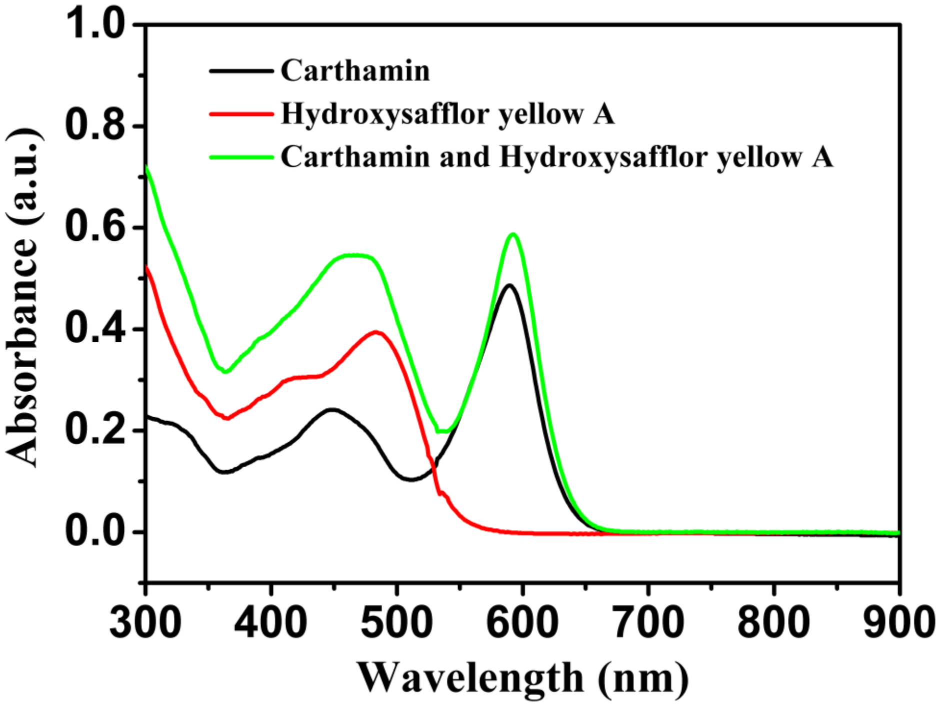


Figure 3. UV-Vis spectra of carthain and hydroxysafflor yellow A in ethanol.

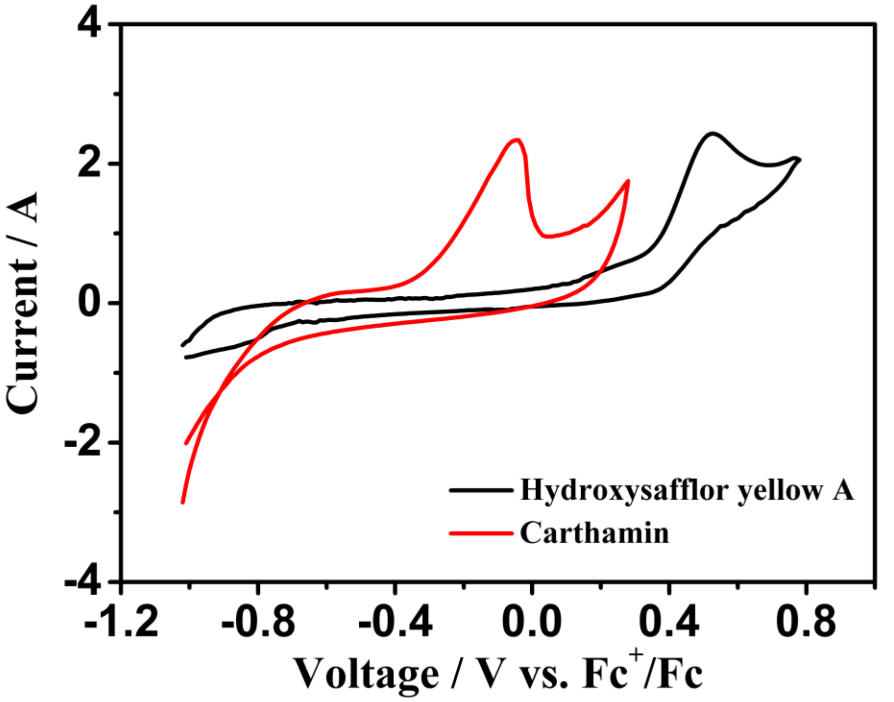


Figure 4. Cyclic voltammograms of the carthain and hydroxysafflor yellow A.

As shown in Fig. 3, UV-Vis absorption spectra of carthain and hydroxysafflor yellow A were investigated. The band-gap of hydroxysafflor yellow A was calculated and obtained value of 2.261 eV. The band-gap value of carthain showed 1.932 eV. The absorption bands of the mixture of carthain and hydroxysafflor yellow A are broadened, compared with hydroxysafflor yellow A or carthain. At the same time, the intensity of absorption is enhanced.

Cyclic voltammorams were schemed to calculate HOMO energy levels of carthain and hydroxysafflor yellow A using oxidation energy potential. The energy potential values can be acquired from oxidation onset point in Fig. 4. The corresponding HOMO energy levels were calculated using oxidation onset potentials. From the calculation results shown in Table 1, little difference was observed from the calculated values of the UV-Vis absorption spectra and oxidation onset potentials.

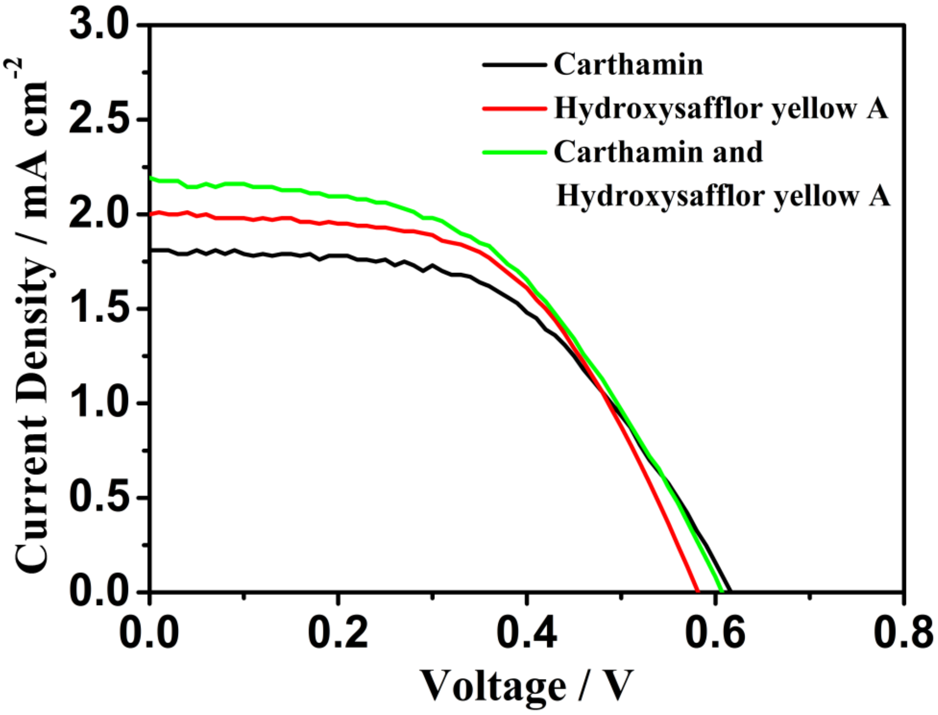


Figure 5. *I–V* characteristic curves of different DSSC.

The co-sensitized DSSCs were prepared by using the co-adsorbed TiO_2 electrode with carthain and hydroxysafflor yellow A, Pt-coated glass as a counter electrode, and an acetonitrile solution with iodine (0.05 M), lithium iodide (0.1 M), and 1,2-dimethyl-3-propylimidazolium iodide (0.6 M) as electrolyte. The photocurrent-voltage (*I–V*) characteristics were measured under simulated solar light (AM 1.5, 100 mW·cm^{-2}). The *I–V* curves are shown in Fig. 5. The photovoltaic performance parameters of DSSCs based on only hydroxysafflor yellow A or carthain and co-sensitized DSSCs based on carthain and hydroxysafflor yellow A are collected in Table 2. The *I–V* curves show that the short-circuit photocurrent density (J_{sc}) and solar energy-to-electricity conversion yield (η) of co-sensitized DSSCs based on carthain and hydroxysafflor yellow A (2.193 mA·cm^{-2} and 0.664%) are much higher than those of DSSCs based on only carthain (1.810 mA·cm^{-2} and 0.597%) or only hydroxysafflor yellow A (2.005 mA·cm^{-2} and 0.644%). On the other hand, the open-circuit photovoltage (V_{oc}) value (610 mV) of co-sensitized DSSCs based on carthain and hydroxysafflor yellow A is higher than that of hydroxysafflor yellow A (580 mV).

Table 2. Photoelectrochemical parameters of two kinds of natural dyes sensitized DSSCs and co-sensitized solar cell.

Sensitizer	J_{sc} (mA·cm^{-2})	V_{oc} (V)	**FF**	η (%)
carthain	1.810	0.61	0.54	0.597
hydroxysafflor yelloA	2.005	0.58	0.55	0.644
co-sensitizer	2.193	0.61	0.50	0.664

Under different wavelengths, photocurrent behavior of natural dyes sensitized TiO2 nanoparticle electrodes were investigated, experiments were performed to obtain the incident photon to current efficiency (IPCE). IPCE was also considered as external quantum efficiency (EQE), which is the ratio of electrons collected per incident photon, and can be used as a reference in the charge transport efficiency [25].

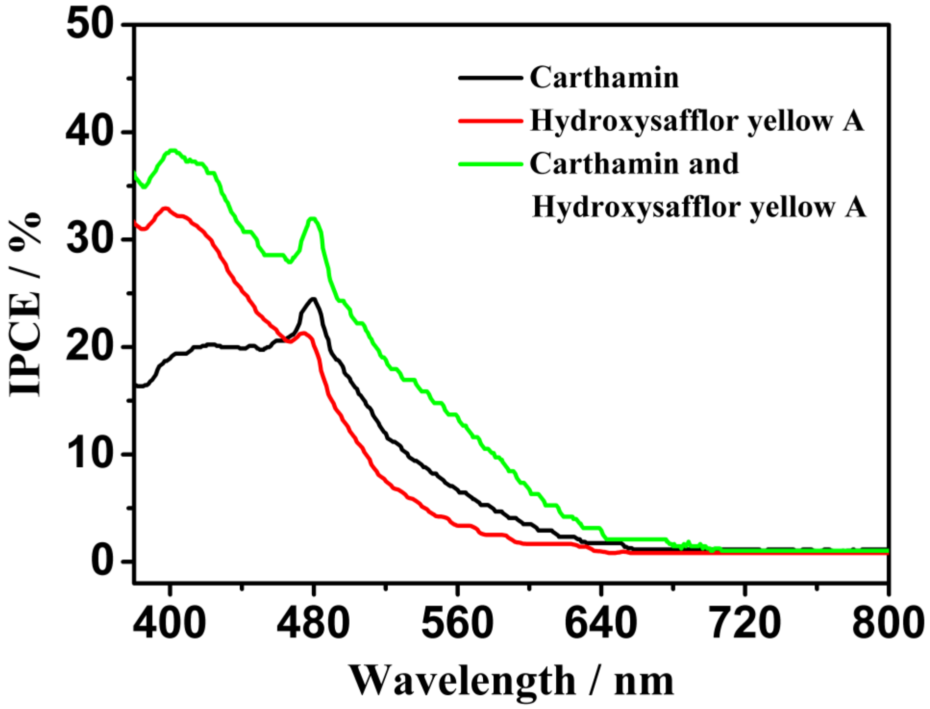


Figure 6. IPCE spectra of DSSCs based on different samples.

Fig. 6 demonstrate that the sensitization by carthain and hydroxysafflor yellow A distinctively expands the photo-response region of TiO_2 nanoparticle electrode. The absorbance of the carthain and hydroxysafflor yellow A co-sensitized TiO_2 film is higher than hydroxysafflor yellow A or carthain alone sensitized film. The enhanced absorption likely indicates that the carthain and hydroxysafflor yellow A co-sensitized TiO_2 have complementary and enhancement effects because of the wider absorption spectrum of carthain and hydroxysafflor yellow A. Co-sensitization using both the carthain and hydroxysafflor yellow A showed much higher photoresponse compared to the single hydroxysafflor yellow A or carthain sensitized TiO_2, and the co-sensitized TiO_2 electrode exhibits a maximum of IPCE. For co-sensitized TiO_2 electrode by both the carthain and hydroxysafflor yellow A, there is a significant increase in IPCE comparing to the single dye sensitized TiO_2 electrodes. The high performance of the co-sensitized TiO_2 electrode by both the carthain and hydroxysafflor yellow A is mainly attributed to a synergistic effect between the high electron injection efficiency of the hydroxysafflor yellow A and the wide light harvesting range of the carthain.

4. CONCLUSIONS

To provide a new co-sensitization approach in DSSCs, we have developed a co-sensitization method utilizing the natural dye sensitizer from Hehuang safflowers. The feasibility of assembling DSSCs with TiO_2 nanoparticles sensitized with two kinds of natural dyes have been demonstrated. Successful conversion of visible light into electricity was achieved. Compared with single hydroxysafflor yellow A or carthain, co-sensitizer (carthain and hydroxysafflor yellow A) has a higher absorbance of visible light spectrum, so the solar cell sensitized by carthain and hydroxysafflor yellow A has a higher photovoltaic conversion efficiency than single dye. The efficiencies of the solar cells sensitized with carthain, the hydroxysafflor yellow A, and co-sensitizer were up to 0.597%, 0.644%, and 0.664%, respectively. Even though the values of co-sensitized(carthain and hydroxysafflor yellow A)DSSCs are lower than those of the reference solar cells(chemical dye N719), natural dyes are still a promising sources of sensitizers for DSSCs because of the simple extraction procedure, low cost, wide availability, and environmentally friendliness. By improving extraction and refining procedure, there will be a better efficiency for natural dyes.

ACKNOWLEDGEMENTS
This work was supported by the Research Program of Application Foundation of Qinghai Province (No. 2015-ZJ-738).

References

1. B. O'Regan, M. Grätzel, *Nature*, 353 (1991) 737.
2. Y.-L.Xie, Z.X. Li, Z.G. Xu, H.L. Zhang, *Electrochem. Commun.*, 13 (2011) 788.
3. Y.-L. Xie, J. Yuan, P. Song, S.Q. Hu, *J. Mater. Sci: Mater. Electron.*, 26 (2015) 3868.
4. E. Ramasamy, W. J. Lee, D. Y. Lee, J.S. Song, *Electrochem. Commun.*, 10 (2008) 1087.
5. W. J. Lee, E. Ramasamy, D. Y. Lee, J.S. Song, *ACS Appl. Mater. Interfaces,* 1 (2009) 1145.

6. J. Chen, K. Li, Y. Luo, X. Guo, D. Li, M. Deng, S. Huang, Q. Meng, *Carbon*, 47 (2009) 2704.
7. F.-F. Ajayi, K.-Y. Kim, K.-J. Chae, M.-J. Choi, I. S. Chang, I.S. Kim, *Photochem. Photobiol. Sci.*, 9 (2010) 349.
8. N. Li, N. Pan, D. Li, S. Lin, *Int. J. Photoenergy*, 2013 (2013) 1.
9. N. J. Cherepy, G. P. Smestad, M. Grätzel, J. Z. Zhang, *J. Phys. Chem. B*, 101 (1997) 9342.
10. K. Wongcharee, V. Meeyoo, S. Chavadej, *Solar Energ. Mater. Solar Cells*, 91 (2007) 566.
11. G. Calogero, G. D. Marco, *Solar Energ. Mater. Solar Cells*, 92 (2008) 1341.
12. E. Yamazaki, M. Murayama, N. Nishikawa, N. Hashimoto, M. Shoyama, O. Kurita, *Solar Energy,* 81 (2007) 512.
13. Q. Dai, J. Rabani, *Chem. Commun*., 20 (2001) 2142.
14. W. M. Campbell, A. K. Burrell, D. L. Officer, K. W. Jolley, *Coordin. Chem. Rev.,* 248 (2004) 1363.
15. G.P. Smestad, *Sol. Energy Mater. Sol. Cells*, 55 (1998) 157.
16. M. Thambidurai, N. Muthukumarasamy, D. Velauthapillai, C. Lee, *Mater. Lett*., 92 (2013) 104.
17. M. Thambidurai, N. Muthukumarasamy, D. Velauthapillai, N. Sabari Arul, S. Agilan, R. Balasundaraprabhu, *J. Mater. Sci. Mater.s in Electron*., 22 (2011) 1662.
18. S. Furukawa, H. Iino, T. Iwamoto, K. Kukita, S. Yamauchi, *Thin Solid Films*, 518 (2009) 526.
19. N.M. Gómez-Ortíz, I.A. Vázquez-Maldonado, Aida R Pérez-Espadas, Gerko Oskam, *Solar Energ. Mater. Solar Cells*, 94 (2010) 40.
20. N. Gokilamani, N. Muthukumarasamy, M. Thambidurai, A. Ranjitha, D. Velauthapillai, T. S. Senthil, R. Balasundaraprabhu, *J. Mater. Sci.: Mater. Electron*., 24 (2013) 3394.
21. G.M. Machewad, P. Ghatge, V. Chappalwar, B. Jadhav, A. Chappalwar, *J. Food Process Technol*., 3 (2012) 172.
22. A. De Oliveira Marcos, A. Duarte Hélio, J.M. Pernaut, B.D.A. Wagner, *J. Phys. Chem. A*, 104 (2000) 8256.
23. Y. Ait Aicha, S. Mohamed Bouzzine, Z. Mohyieddine Fahim, T. Zair, M. Bouachrine, M. Hamidi, *Comput. Theor. Chem*., 1036 (2014) 22.
24. H. Nikoofard, M. Gholami, *Comptes Rendus Chimie*, 17 (2014) 1034.
25. Y.-L. Xie, P. Song, *J. Electron. Mater.*, 45 (2016) 4952.