Journal of Photochemistry and Photobiology A: Chemistry 219 (2011) 188–194

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Dye-sensitized solar cells using 20 natural dyes as sensitizers

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ARTICLE INFO

Article history:
Received 24 June 2010
Received in revised form 4 February 2011
Accepted 17 February 2011
Available online 23 February 2011

Keywords:
Dye-sensitized solar cell
Natural dye
Extraction
Mangosteen
Effectual component

ABSTRACT

Twenty natural dyes, extracted from natural materials such as flowers, leaves, fruits, traditional Chinese medicines, and beverages, were used as sensitizers to fabricate dye-sensitized solar cells (DSCs). The photoelectrochemical performance of the DSCs based on these dyes showed that the open circuit voltages (*Voc*) varied from 0.337 to 0.689 V, and the short circuit photocurrent densities (*Jsc*) ranged from 0.14 to 2.69 mA cm^{-2}. Specifically, a high *Voc* of 0.686 V was obtained from the dye extracted from mangosteen pericarp sensitizer. The photo-to-electric conversion efficiency of the DSC sensitized by the ethanol extract of mangosteen pericarp without purification reached 1.17%. Moreover, various components of the ethanol extract were extracted using different organic solvents. The photoelectrochemical performance of these extracts demonstrated that rutin was the most effectual component of the sensitizer for DSC.

1. Introduction

Since Grätzel et al. developed dye-sensitized solar cells (DSCs), a new type of solar cells, in 1991 [1], these have attracted considerable attention due to their environmental friendliness and low cost of production. A DSC is composed of a nanocrystalline porous semiconductor electrode-absorbed dye, a counter electrode, and an electrolyte containing iodide and triiodide ions. In DSCs, the dye as a sensitizer plays a key role in absorbing sunlight and transforming solar energy into electric energy. Numerous metal complexes and organic dyes have been synthesized and utilized as sensitizers. By far, the highest efficiency of DSCs sensitized by Ru-containing compounds absorbed on nanocrystalline TiO_2 reached 11–12% [2,3]. Although such DSCs have provided a relatively high efficiency, there are several disadvantages of using noble metals in them: noble metals are considered as resources that are limited in amount, hence their costly production. On the other hand, organic dyes are not only cheaper but have also been reported to reach an efficiency as high as 9.8% [4]. However, organic dyes have often presented problems as well, such as complicated synthetic routes and low yields. Nonetheless, the natural dyes found in flowers, leaves, and fruits can be extracted by simple procedures. Due to their cost efficiency, non-toxicity, and complete biodegradation, natural dyes have been a popular subject of research. Thus far, several natural dyes have been utilized as sensitizers in DSCs, such as cyanin [5–17], carotene [18,19], tannin [20], and chlorophyll [21]. Calogero and Marco reported that a conversion efficiency of 0.66% was obtained using red Sicilian orange juice dye as sensitizer [13]. Wongcharee et al. employed rosella as sensitizer in their DSC, which achieved a conversion efficiency of 0.70% [8]. Roy et al. indicated that when using Rose Bengal dye as sensitizer, the *Jsc* and *Voc* of their DSC reached 3.22 mA cm^{-2} and 0.89 V, respectively, resulting in a 2.09% conversion efficiency [11]. Furthermore, Wang et al. carried out structural modification of coumarin and used the coumarin derivation dye as sensitizer in their DSC, which provided an efficiency of 7.6% [22–25]. Thus, optimization of the structure of natural dyes to improve efficiency is promising.

In this paper, 20 types of natural dyes were extracted from flowers, fruits, traditional Chinese medicines, and beverages, such as rhododendron, herba artemisiae scopariae, mangosteen pericarp, and coffee. To the best of our best knowledge, most of these natural dyes, especially traditional Chinese medicines, are reported as sensitizers of DSCs for the first time. These extracted dyes were characterized by UV–vis absorption spectra. The photoelectrochemical properties of the DSCs using these extracts as sensitizers were investigated. Additionally, stepwise purification of the extract obtained from mangosteen pericarp was performed. The photovoltaic properties of DSCs sensitized by the purified products were studied.

2. Experiment

2.1. Preparation of natural dye sensitizers

All dyes, except for rose, lily, coffee, and leaves of Chinese holly for which water was used as the extraction solvent, were extracted

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doi:10.1016/j.jphotochem.2011.02.008

with ethanol. The dyes extracted with ethanol were obtained by the following steps: fresh plants, fruits, Chinese medicines, and beverages were washed with water and vacuum dried at 60 °C. After crushing into fine powder using a mortar, these materials were immersed in absolute ethanol at room temperature in the dark for one week. Then the solids were filtrated out, and the filtrates were concentrated at 40 °C for use as sensitizers. The dyes obtained from rose, lily, coffee, and leaves of Chinese holly were extracted by the following steps: the materials were immersed in boiling water for 2–3 h, and the solids were filtrated out. The resulting filtrates were used as sensitizers.

2.2. Preparation of dye-sensitized solar cells

FTO conductive glass sheets (Asahi Glass, fluorine-doped SnO_2, sheet resistance: 15 Ω/sq), were first cleaned in a detergent solution using an ultrasonic bath for 15 min, rinsed with water and ethanol, and then dried. Ti-nanoxide-D pastes (Solaronix, Co. Ltd.) were deposited on the FTO conductive glass by doctor-blading technique in order to obtain a TiO_2 film with a thickness of 9 μm and an area of 0.2 cm^2. The TiO_2 film was preheated at 200 °C for 10 min and then sintered at 500 °C for 30 min. Subsequently, the TiO_2 film was treated in 40 mM $TiCl_4$ solution at 70 °C for 30 min and then at 500 °C for 30 min. After cooling to 80 °C, the TiO_2 electrode was immersed in an ethanol solution containing a natural dye for 10–12 h [26].

The dye-sensitized TiO_2 electrode and a sputtered-Pt counter electrode were assembled to form a solar cell by sandwiching a redox (I^-/I_3^-) electrolyte solution. The electrolyte solution was composed of 0.03 M I_2, 0.06 M LiI, 0.6 M 1,2-dimethyl-3-propylimidazolium iodine, 0.1 M guanidinium thiocyanate, and 0.5 M 4-tert-butylpyridine in acetonitrile [19].

2.3. Measurements

The UV–vis transmission and reflectance spectra of the dyes absorbed in the TiO_2 films were taken on a UV-550 using an integrating sphere setup. The solution spectra were referenced against the appropriate solvent by a HP 8453 UV–vis spectrophotometer. The electrochemical impedance spectra (EIS) experiment was carried out at −0.78 V bias in the dark with an electrochemical workstation (Zenium Zahner, Zahner). The measured frequency range was from 100 mHz to 1 MHz, and the AC amplitude was set at 10 mV. The current–voltage curves of the DSCs were obtained by applying an external bias to the cell and measuring the generated photocurrent under white light irradiation with a Keithley digital source meter (Keithley 2601, USA). The intensity of the incident light was 100 mW cm^{-2}, and the instrument was equipped with a 300 W solar simulator (Solar Light Co., Inc., USA) that served as the light source. The photon flux was determined by a power meter (Nova, Ophir optronics Ltd.) and a calibration cell (BS-520, *s*/*n* 019, Bunkoh-Keiki Co., Ltd.).

3. Results and discussion

3.1. Absorption of natural dyes

We attempted to use 20 kinds of colorful natural dyes as sensitizers for DSCs. Table 1 lists the UV–vis absorption data of the dyes extracted with ethanol or water from flowers, leaves, fruits, traditional Chinese medicine, and beverages. Fig. 1 shows the representative UV–vis absorption spectra for the ethanol extracts of flowery knotweed, Begonia, and Perilla. As shown in Table 1, the ethanol extracts of begonia and rhododendron, as well as the 0.1 M HCl ethanol extract of violet, exhibit an absorption peak of ca. 540 nm. This absorption ascribes to their identical components,

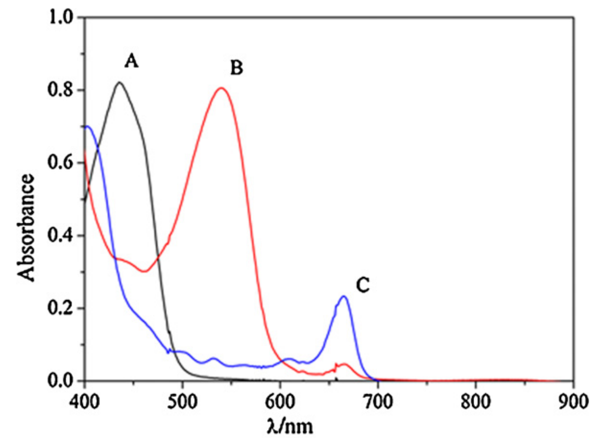

Fig. 1. UV–vis absorption spectra of (A) flowery knotweed, (B) begonia, and (C) perilla in ethanol solution.

namely, anthocyanins, a group of natural phenolic compounds. The chemical adsorption of these dyes is generally accepted to occur because of the condensation of alcoholic-bound protons with the hydroxyl groups on the surface of nanostructured TiO_2 [27].

Table 1 also demonstrates that the ethanol extracts of petunia, perilla, China loropetal, and China redbud, whose colors are green, reach a maximum absorption peak of 665 nm. The main component of these five extracts is chlorophyll. Furthermore, the absorption peaks for the ethanol extracts of yellow rose, tangerine peel, Fruct*us* lycii, marigold, and flowery knotweed in the 400–500 nm visible range may be attributed to xanthophyll, flavone, carotene, xanthophyll, and rhein, respectively. The ethanol extracts of rose and lily were found colorless; thus, water was used as the extraction solvent for rose and lily. The water extracts of rose, lily, coffee, and leaves of Chinese holly, as well as the ethanol extract of mangosteen pericarp, showed various colors, whereas no obvious maximum absorption peak in the visible light region was observed. This result can be attributed to the superposition of absorption peaks.

3.2. Photoelectrochemical properties of DSCs sensitized with natural dyes

Photovoltaic tests of DSCs using these natural dyes as sensitizers were performed by measuring the current–voltage (*I*–*V*) curves under irradiation with white light (100 mW cm^{-2}) from a 300 W solar simulator. The performance of natural dyes as sensitizers in DSCs was evaluated by short circuit current (*Jsc*), open circuit voltage (*Voc*), fill factor (*FF*), and energy conversion efficiency (η). The photoelectrochemical parameters of the DSCs sensitized with natural dyes are listed in Table 1. The typical *I*–*V* curves of the DSCs using the sensitizers extracted from mangosteen pericarp, rhododendron, perilla, leaves of Chinese holly, and herbal artenisiae scopariae are shown in Fig. 2.

As displayed in Table 1 and Fig. 2, the fill factors of these DSCs are mostly higher than 60%. The *Voc* varies from 0.337 to 0.689 V, and the *Jsc* changes from 0.14 to 2.69 mA cm^{-2}. Specifically, a high *Voc* (0.686 V) and *Jsc* (2.69 mA cm^{-2}) were obtained from the DSC sensitized by the mangosteen pericarp extract; the efficiency of the DSC reached 1.17%. These data are significantly higher than those of the DSCs sensitized by other natural dyes in this work. Moreover, as shown in Table 1, the *Voc* of the DSC using the mangosteen pericarp extract as sensitizer is comparable to that of the DSC sensitized by a Ru complex cis-$RuL_2(SCN)_2$ (*L* = 2,2′-bipyridyl-4,4′-dicarboxylic acid) (N-719), which is widely used in DSCs. This result regarding the mengosteen pericarp extract will be further discussed in Section 3.3. Chlorophyll plays an important role in plant photosyn-