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Red Spinach Dye Extracts as Photosensitizer in Solid State Dye Sensitizer Dye Solar Cells : Varying Relative Ratio of Co-solvents and Dye Extracting Temperature

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Abstract

The natural dye solutions were extracted from red Spinach leaves and used as photosensitizer in solid-state dye-sensitized solar cells (ssDSSCs). The optimal conditions for dye concentration and extracting temperature in ethanol and relative concentration of co-solvents (DMF and EtOH) were explored. With optimal dye concentration, the dyes extracted at 60 °C in ethanol and the dyes in DMF-rich solvent maximized the absorption of dye solutions. Following the study of dye absorption in solution, ssDSSCs were fabricated using red spinach dye extracts and their photovoltaic performances were examined against dye extracting temperature and relative ratio of co-solvents. It is found that the device efficiencies were insensitive to extracting temperature and a relatively higher efficiency of 0.10% was exhibited in the device with red spinach dye in ethanol.

Key words: red Spinach dye, photosensitizer, solid-state dye-sensitized solar cells

Introduction

Dye sensitized solar cell (DSSC) is a device for the conversion of light into electricity and its performance is based on the sensitization of wide band gap semiconductors [1]. It is a low-cost solar cell belonging to the group of thin film solar cells [2]. DSSC is one of the most promising photovoltaic technologies. Liquid electrolyte-based DSSCs have reached efficiencies as high as 11.1% [3]. However, these liquid based DSSCs suffer from potential leakage and corrosion which have sparked research in solid state hole transport materials (HTMs) instead of liquid electrolytes [4]. One of the most widely-used HTMs is

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spiro-OMeTAD(2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene) [5]. Solid-state dye-sensitized solar cells (ssDSSCs) with spiro-OMeTAD as HTM have attained efficiencies exceeding 5%, which is still far below the efficiency of liquid electrolyte DSSCs [6]. The lower efficiency is primarily a consequence of incomplete light harvesting. The highest-performing ssDSSCs to date have a 2-3 μm thick active layer [7], far thinner than the thickness needed to achieve good optical absorption. There are two factors that limit the ssDSSCs from being more efficient at thicknesses $> 2 \mu\text{m}$: electron-hole recombination and incomplete filling of the mesoporous TiO_2 films with spiro-OMeTAD. Studies on recombination show that recombination in ssDSSCs is two orders of magnitude faster than in liquid DSSCs [8] and the electron diffusion length (L_D) in mesoporous TiO_2 is 6-12 μm , much larger than the optimized 2 μm film thickness [9].

Experiment

The natural dye solutions were extracted from red Spinach leaves. The fresh red Spinach leaves were washed with distilled water, crushed and immersed and stirred in 10 ml EtOH (95 % absolute ethanol) at room temperature for 45 min. The solid residues in solution were then filtrated out, and the filtrates were concentrated for the use as sensitizers. The red Spinach dye solutions with different concentrations (0.05-0.55 g/ml) were prepared. In addition, the dyes were extracted at different temperature (45-70 $^{\circ}\text{C}$). Using the optimal dye concentration, the dye solutions were also prepared in the solvent mixture (various concentration of DMF in ethanol).

Fluorine-doped SnO_2 (FTO) coated glasses (2 cm x 10 cm) were etched with zinc powder and HCl (2M) to obtain the required electrode pattern. They were pre-treated with a 1M aqueous TiCl_4 at 70 $^{\circ}\text{C}$ for 30 min followed by washing with detergent (2% Hellmanex in water), distilled water, ethanol and acetone for 15 min each. Finally, they were blown with

N₂ gas for drying purpose and treated under UV Ozone for 20 min for removing the last traces of organic residues. The FTO sheets were subsequently coated with a compact layer of TiO₂ by aerosol spray pyrolysis deposition at 450 °C using a commercial titanium diisopropoxide bis(acetylacetonate) solution (75% in 2-propanol, Sigma-Aldrich) diluted in ethanol (volume ratio of 1:9) as precursor and oxygen as carrier gas. After cooling to room temperature they were treated in a 1M aqueous solution TiCl₄ for 30 min at 70°C, rinsed with distilled water and dried at 500°C for 30 min.

The mesoporous TiO₂ layer was developed to be used as working electrode in ssDSSC. A 3-μm-thick mesoporous TiO₂ layer composed of 30-nm-sized particles was deposited by screen printing using a commercial TiO₂ paste (Dyesol 18NRT, Dyesol). Mesoporous TiO₂ films were slowly heated to 500 °C (ramped over 30 min) and baked at this temperature for 30 min using tap control hot plate. The last step is to allow the TiO₂ films to cool down naturally to room temperature. They were cut into the dimension of 2×1.5 cm and rinsed with distilled water and ethanol each. They were blown with N₂ gas and treated under UV Ozone for 20 min. Prior to their use as electrode, they were again dried at 500 °C for 30 min using heat-blower.

In order to load the dye on the TiO₂ mesoporous electrode, the film electrodes were submerged in 3ml of a dye solution at room temperature for 12 hr in a dark place. The dye-adsorbed TiO₂ thin film was rinsed gently with distilled water to remove unwanted solids, and then with the ethanol which serves to remove water from the porous TiO₂.

The dyed films were rinsed briefly in acetonitrile and dried in air for 1 min. The HTM was then deposited by spin coating at 4000 r.p.m. for 30 s in nitrogen atmosphere. The 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) was dissolved in 1 ml chlorobenzene. After fully dissolving the hole transporter, 4-tert-

butylpyridine (tBP) was added with a volume-to-mass ratio of 1:26 $\mu\text{l mg}^{-1}$ tBP : spiro-OMeTAD. Lithium bis (trifluoromethylsulfonyl) imide salt (Li-TFSI) was pre-dissolved in acetonitrile at 170 mg ml^{-1} and added to the hole transporter solution at 1:12 $\mu\text{l mg}^{-1}$ of Li-TFSI solution : spiro-OMeTAD. The spin coating formulation was prepared by dissolving 180 mg (spiro-OMeTAD), 6.92 μl 4-tert-butylpyridine, 14.99 μl of a stock solution of 170 mg ml^{-1} lithium bis(trifluoromethylsulphonyl)imide in acetonitrile and 2.88 μl of a stock solution of 320 mg ml^{-1} tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) bis(trifluoromethylsulphonyl)imide (FK102) in acetonitrile in 1 ml chlorobenzene.

The concentration of spiro-OMeTAD in the solution, so that the ratio of spiro-OMeTAD to tBP, Li-TFSI and FK102 was kept constant. For spin-coating, a small quantity of the hole transporter solution (50 μl) was dispensed onto each substrate and left to wet the films for 5s before spin-coating. After spiro-OMeTAD infiltration, a chlorobenzene-soaked cotton swab was used the substrate that was not on top of the mesoporous TiO_2 film to remove the excess spiro-OMeTAD.

The films were left overnight in an air atmosphere before placing them in a thermal evaporator where 180-nm-thick gold electrodes were deposited through a shadow mask under high vacuum (10^{-6} mbar). Fig. 3.5(a) shows the thermal evaporator (EDWARDS AUTO 306). The active areas of the devices were defined by metal optical masks with 0.4 cm \times 0.5 cm apertures.

The optical transmission properties of multilayered TiO_2 and dye solution were measured by UV-vis spectrophotometry. The scanned range is from 300 nm to 900 nm with step interval of 0.5 nm. The UV-vis spectra were recorded with respect to an uncoated clean glass of the same type as the reference for solid samples and to the solvent used as the reference for solution samples. The power conversion efficiencies (PCE) of DSSCs were

evaluated by recording J-V characteristics of the device. It was measured using a computer-controlled digital source meter (Keithley 2400) under illumination with a Newport solar simulator (AM 1.5, 1000 Wm^{-2}). A Keithley source meter was used to supply an input voltage and measure the output current of DSSCs. The light source was a 450 W xenon lamp (Oriol) equipped with a Schott K113 Tempax sunlight filter (Praezisions Glas & Optik GmbH) to match the emission spectrum of the lamp to the AM 1.5 G standards. Before each measurement, the exact light intensity was determined using a calibrated Si reference diode.

Results and Discussion

Fig 1 (a) shows the absorption spectra of red Spinach extracts in ethanol in the wavelength range from 300 to 900 nm. First the characterization peaks in the absorption spectra were identified. In this figure, two peaks were found: the first one around 410 nm and the second one at 665 nm; they are attributable to the mixture of chlorophyll a and b. The absorption spectra of red Spinach extracts with different concentrations (0.05 g/ml - 0.55 g/ml) in ethanol. Upon increasing concentration of dye solutions, the peak positions of red Spinach dye solutions being studied remained unchanged. However, peak intensities increased with increasing concentration up to 0.50 g/ml and saturated beyond 0.50 g/ml. Thus, the concentration of 0.50 g/ml yielding the maximum absorption intensity was used in preparation of dye solution for ssDSSC.

Fig. 1 (b) shows the absorption spectra of red Spinach dye solutions extracted at different temperatures (RT, 45 °C, 60 °C and 70 °C). The dye solutions with optimal concentration were used (0.50 g/ml). Upon increasing temperature, peak positions for dye solutions remain unchanged. The absorption intensity at 70 °C was significantly lower than 60 °C. Thus, absorption is relatively higher at extracting temperature of 60 °C. Increased absorption intensity at respective optimal higher extracting temperature is due to the

better solubility that would facilitate the penetration of the solvent into the dye molecular structure.

g. 1 (c) shows the absorption spectra of red Spinach extracts in different concentration of DMF in ethanol (10 : 0, 8 : 2, 6 : 4, 4 : 6, 2 : 8, 0 : 10) at room temperature. It is found that the peak position of natural dyes almost kept unchanged upon increasing concentration of DMF. However, peak intensities of natural dyes increased with increasing concentration of DMF. Since, the concentration of DMF in ethanol (10 : 0) provided the maximum absorption intensity for all natural dyes being studied. DMF is a better solvent for natural dyes solubility. The optimum concentrations in ethanol, concentration of DMF in ethanol and extracting temperature for natural dye are listed in Table 1.

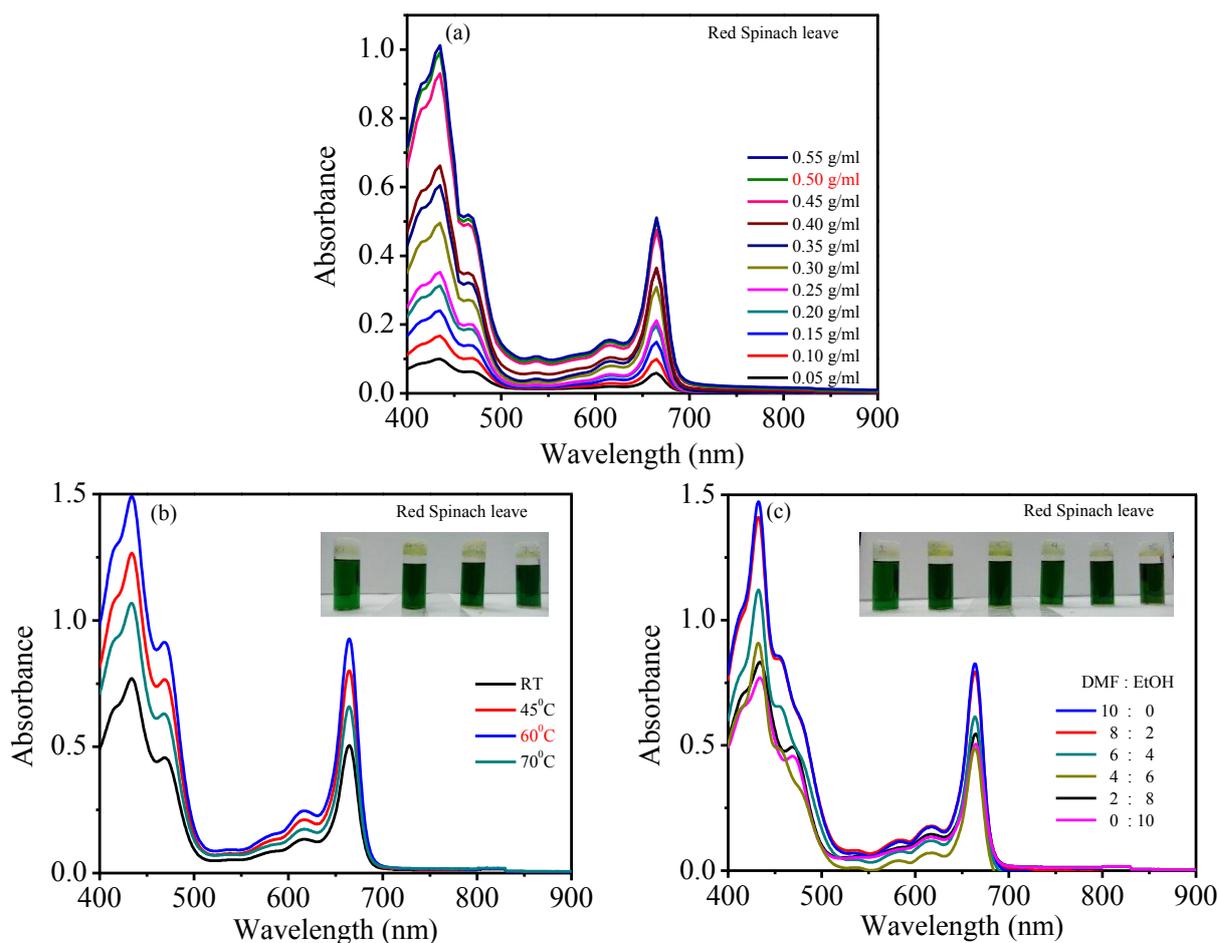


Fig. 1 Absorption spectra of (a) the optimum concentrations in ethanol, (b) extracting temperature and (c) concentration of DMF in ethanol for red Spinach extracts.

Table 1 The optimum concentrations in ethanol, concentration of DMF in ethanol and extracting temperature for natural dye being studied.

Natural dye as sensitizer	Optimum dye concentration in ethanol	Optimum concentration of DMF in EtOH	Optimum extracting temperature
red Spinach	0.50 g/ml	10 : 0	60 °C

Fig. 2 (a) shows J-V characteristics of the ssDSSCs using red Spinach dye extracts prepared at RT, 45 °C, 60 °C and 70 °C under AM 1.5 illumination (1000 Wm^{-2}). Device parameters for ssDSSCs using red Spinach dye solutions extracted in ethanol at different extracting temperatures and in the solvent with different concentration of DMF in ethanol at room temperature are listed in Table 2. In ssDSSC with red Spinach dye extract, V_{OC} are not significantly changed upon varying extracting temperature. Highest J_{SC} of 0.42 mAcm^{-2} was produced at extracting temperature of 60 °C. FF of the device (extracting temperature RT) is 0.69 which is higher than those of the devices (higher extracting temperature 45-70 °C). The PCE values are the same at around 0.10-0.11%. Among the DSSCs with three different extracts, the best performance was observed from the ssDSSCs with red Spinach dye extracted at 45 °C in ethanol, which showed a conversion efficiency (PCE) of 0.11 %, with open circuit voltage (V_{oc}) of 0.61 V, short circuit current density (J_{sc}) of 0.34 mAcm^{-2} , and fill factor (FF) of 0.55, under the irradiance of 1000 Wm^{-2} .

Fig. 2 (b) shows J-V characteristics of the ssDSSCs using red Spinach dye extracts prepared in the solvents with different concentration of DMF in ethanol under AM 1.5 illumination (1000 Wm^{-2}). V_{OC} is not significantly changed upon varying volume ratio in

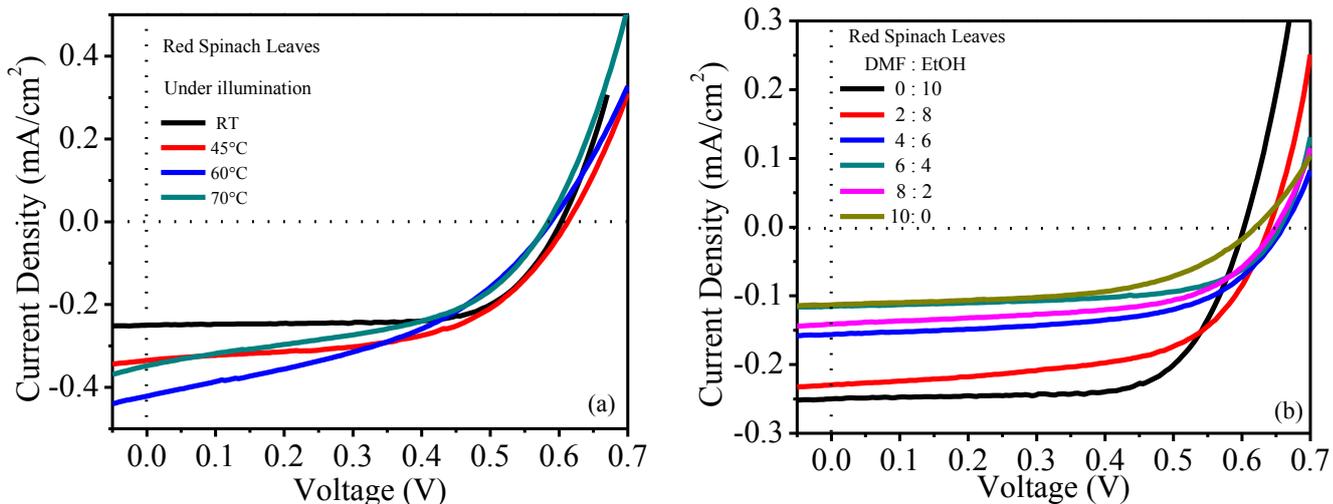


Fig. 2 J-V characteristics of the ssDSSCs using red Spinach dye solutions extracted (a) in ethanol at different extracting temperatures and (b) in the solvent with different concentration of DMF in EtOH at room temperature.

Table 2 Device parameters for ssDSSCs using red Spinach dye solutions extracted in ethanol at different extracting temperatures and in the solvent with different concentration of DMF in EtOH at room temperature.

ssDSSC Devices		V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
Extracting Temperature	RT(29 °C)	0.60	0.25	0.69	0.10
	45 °C	0.61	0.34	0.55	0.11
	60 °C	0.59	0.42	0.42	0.10
	70 °C	0.58	0.34	0.48	0.10
Solvent DMF : EtOH	0 : 10	0.60	0.25	0.69	0.10
	2 : 8	0.64	0.23	0.59	0.09
	4 : 6	0.66	0.16	0.58	0.06
	6 : 4	0.65	0.12	0.62	0.05
	8 : 2	0.65	0.14	0.58	0.05
	10 : 0	0.62	0.11	0.55	0.04

red Spinach device. J_{SC} and FF gradually decreased from 0.25 mAcm^{-2} to 0.11 mAcm^{-2} and from 0.69 to 0.55 respectively upon increasing DMF concentration. The efficiency of device using red Spinach in ethanol-rich solvent is as high as 0.10%.

Summary and Conclusion

As prepared red Spinach dye extracts were used as photosensitizer in solid-state dye-sensitized solar cells (ssDSSCs). The dye concentration maximizing its absorption in ethanol is 0.50 g/ml. A higher absorption at extracting temperature of 60 °C is due to the better solubility of dye molecules at that temperature. In addition, using co-solvent (adding DMF into ethanol) modulated the absorption intensity of dye solutions. Since pure DMF provided the maximum absorption intensity, DMF is a better solvent for the solubility of red spinach dyes. The examination of the photovoltaic performances of ssDSSCs using red Spinach dye solutions extracted at various temperatures and dissolved in co-solvents (DMF and ethanol) showed that the device efficiency was insensitive to the extracting temperature and a relatively higher efficiency of 0.10% was achieved in ssDSSCs using red Spinach extracts in ethanol. Despite higher absorption of red Spinach dye in DMF, the efficiency of ssDSSCs using DMF was lower which can be attributed to poor adhesion of dye towards TiO_2 scaffolds, thus restricting the photon harvesting and electron transport at the dye/ TiO_2 interfaces.

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