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PHOTOVOLTAIC PERFORMANCE OF SOLID-STATE DYE-SENSITIZED SOLAR CELLS (SSDSSCS) USING NATURAL DYES EXTRACT

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Abstract

The natural dye solutions were extracted from henna leave, red Dragon fruit flesh and red Spinach leave as photosensitizer for solid-state dye-sensitized solar cells (ssDSSCs). In this work, the ssDSSCs were fabricated using these natural dye extracts and their photovoltaic performance was examined against dye extracting temperature and relative ratio of co-solvents (dimethylformamide (DMF) and ethanol (EtOH)). It is found that the device efficiencies are almost insensitive to the extracting temperature for all dye extracts being studied. The efficiency of red Spinach devices decreased with increasing DMF concentration in ethanol whiles those of Henna and red Dragon fruit devices were almost invariant. Thus co-solvent effect would differ system to system. Among all, the efficiency of red Spinach device (extracted at 45 °C in EtOH) is as high as 0.11 %.

Keywords: *natural dyes, efficiencies, 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 [Gratzel M. et al., (2003) , *J. Photochem. Soc*. 6, 889]. It is a low-cost solar cell belonging to the group of thin film solar cells [O'Regan and Gratzel M. , (1991), *Nature*. 353, 737]. Solar cells are usually divided into three main generations. First generation is single crystal silicon solar cells. They are expensive to produce, and their efficiency hits more than 20%. Second generation is polycrystalline silicon solar cells, amorphous silicon solar cells and polycrystalline non-silicon based solar cells. They have lower efficiency, but are much cheaper to produce, such that the cost per watt is lower than in first generation cells. Third generation solar cells are organic polymer heterojunction solar cells, dye-sensitized solar cells and hybrid solar cells. Most technologies in this generation are not yet commercialized, but there is a lot of research going on in this area. One major advantage of third generation solar cells is the cost-effectiveness for their production [Deibel C. and Dyakonov V. , (2010), *Rep. Prog. Phys*. 73, 39].

DSSC is one of the most promising photovoltaic technologies. Liquid electrolyte-based DSSCs have reached efficiencies as high as 11.1% [Gao F. et al., (2008), *J. Am. Chem. Soc*. 130, 10720]. 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 [Snaith H. J. & Schmidt-Mende L. , (2007), *Adv. Mater* 19, 3187]. One of the most widely-used HTMs is spiro-OMeTAD (2,2’,7,7’ – tetrakis - (N,N-di-p-methoxyphenylamine) -9,9’-spirobifluorene) [Bach U. et al., (1998), *Nature* . 395, 583]. 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 [Snaith H. J. et al., (2007), *Nano Lett*. 7, 3372]. 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 [Schmidt-Mende L. et al., (2005), *Appl. Phys. Lett*. 86,

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013504], 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 μm: 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 [Fabregat-Santiago F. et al., (2009), *J. Am. Chem. Soc*. 131, 558] and the electron diffusion length (L_D) in mesoporous TiO_2 is 6-12 μm, much larger than the optimized 2 μm film thickness.

Since metal oxide nanoparticles [zinc oxide (ZnO) and titanium dioxide (TiO_2)] have been used in DSSC as the photoelectrode sensitized by organic dyes. They have several approaches to improve light-harvesting efficiencies and cell performance: developing photoelectrodes with larger surface areas that could adsorb large amount of dye and synthesizing dyes with broader absorption ranges [Anderson S. et al., (1979), *Nature* . 280, 571].

Experiment

This section details about the preparation of natural dye-sensitizers, fabrication of solid-state dye-sensitized solar cells (ssDSSCs) and device efficiency measurement.

Preparation of Natural Dye-sensitizers

The natural dye solutions were extracted from Henna leave, red Dragon fruit flesh and red Spinach leave. The fresh Henna leaves were dried at 100 °C for 45 min and crushed into fine powder using a mortar and pestle. The powder was 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 Henna dye solutions with different concentrations (0.05-0.35 g/ml) were prepared. In addition, the dyes were extracted at different temperature (45-70 °C). Using the optimal dye concentration, the dye solutions were also prepared in the solvent mixture (various volume ratio of DMF to EtOH). Following the similar procedure of Henna dye synthesis, the red Dragon fruit flesh and red Spinach fresh leave were washed with distilled water, crushed and immersed in the solvent. Fig. 1 shows the preparation of natural dye-sensitizers (Henna leave, red Dragon fruit flesh and red Spinach leave).

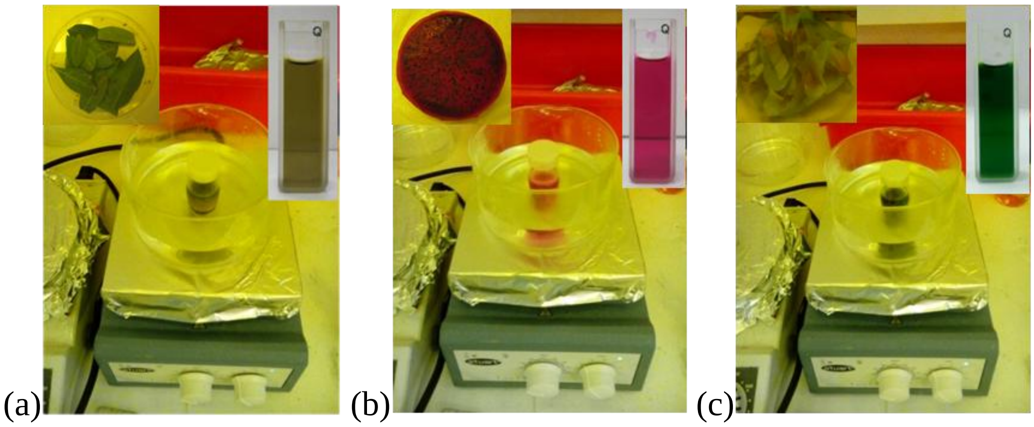

Figure 1 Preparation of natural dye solutions extracted from (a) Henna leaves, (b) Red Dragon fruit flesh and (c) Red Spinach leaves in ethanol

Fabrication of Solid-state Dye-sensitized Solar Cells

(i) Substrate Preparation

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 °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 N_2 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 TiO_2 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 $TiCl_4$ for 30 min at 70°C, rinsed with distilled water and dried at 500°C for 30 min.

(ii) Formation of Mesoporous TiO_2 Photoanode

The mesoporous TiO_2 layer was developed to be used as working electrode in ssDSSC. A 3-μm-thick mesoporous TiO_2 layer composed of 30-nm-sized particles was deposited by screen printing using a commercial TiO_2 paste (Dyesol 18NRT, Dyesol). Mesoporous TiO_2 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 TiO_2 films to cool down naturally to room temperature.

(iii) Infiltration of Dye and Hole-transporting Materials (HTM)

In order to load the dye on the TiO_2 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 TiO_2 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 TiO_2. 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-methoxyphenyamine)-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 µl 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 µl 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.

(iv) Deposition of Gold Electrode

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. 2 shows the active area of the device was defined by metal optical mask with 0.4 cm × 0.5 cm aperture.

Figure 2 Photograph of complete ssDSSC device

Measurement of the Device Efficiency

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 W/m^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 (Oriel) 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. Fig. 3 shows the experimental setup for PCE measurement.

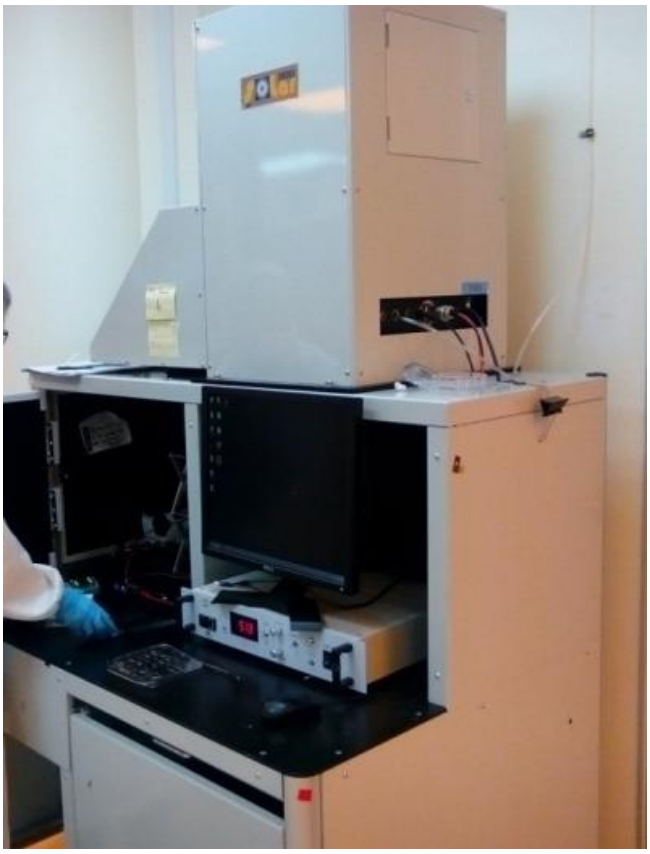

Figure 3 Experimental setup for the measurement of power conversion efficiency (PCE)

Results and Discussion

The section mainly discusses the effect of extracting temperature and solvent on the photovoltaic performance of ssDSSCs using Henna, red Dragon fruit and red Spinach dye extracts is presented.

Photovoltaic Performance of ssDSSCs

We examined the photovoltaic performance of ssDSSCs using Henna, red Dragon fruit and red Spinach dye solutions extracted at different temperatures and dissolved in different solvents.

(i) Varying the Dye Extracting Temperature in Ethanol

Fig. 4 shows J-V characteristics of the ssDSSCs using Henna, and red Dragon fruit and 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 Henna, red Dragon fruit and red Spinach dye solutions extracted in ethanol at different extracting temperatures are listed in Table 1. With Henna dye extracted at RT, 45 °C and 60 °C, the ssDSSC generated similar values of V_{OC}, J_{SC} and FF, and thus PCE. At higher extracting temperature of 70 °C, V_{OC} decreased from 0.46 V to 0.41 V and J_{SC} decreased from 0.15 mA/cm^2 to 0.07 mA/cm^2 while FF increased from 0.41 to 0.47. Overall the PCE decreased from 0.03 % to 0.01 %. In ssDSSC using red Dragon fruit dye and red Spinach dye, we can observe that all the device parameters of ssDSSC were not significantly changed upon varying the extracting temperatures.

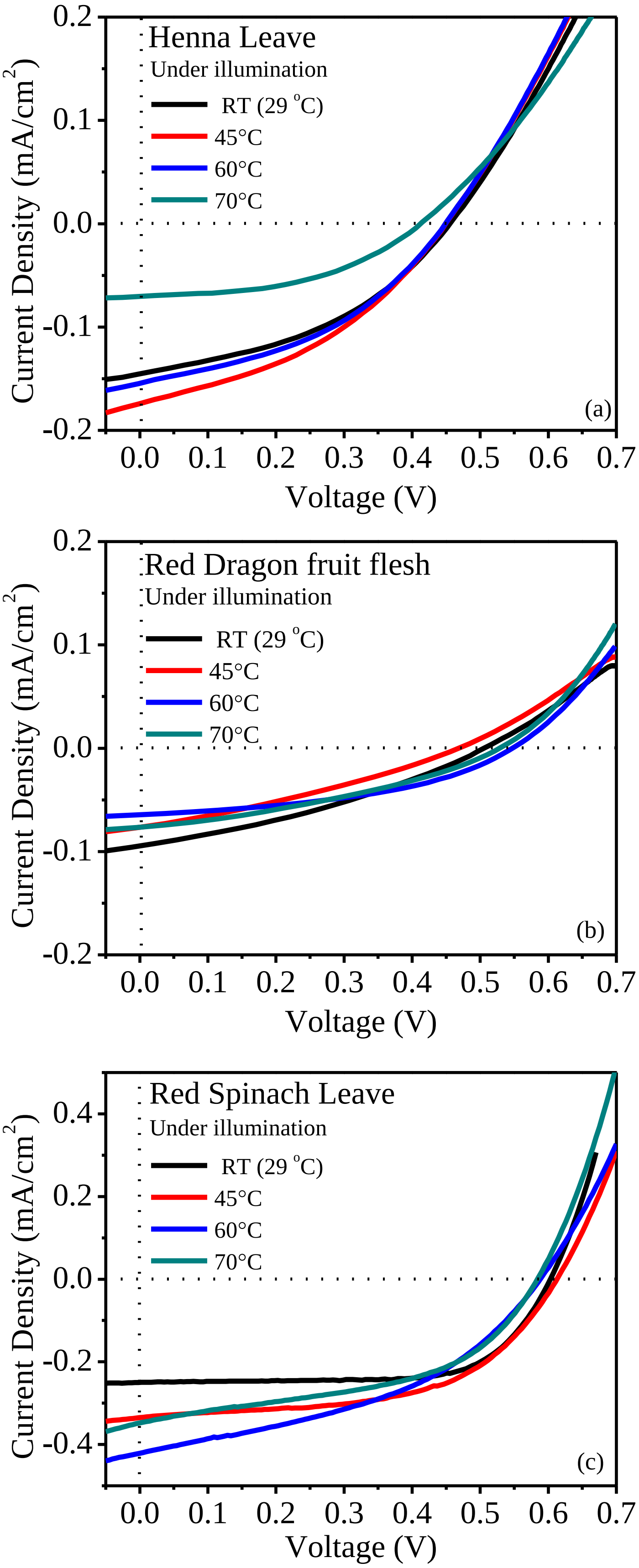

Figure 4 J-V characteristics of the ssDSSCs using (a) Henna, (b) red Dragon fruit and (c) red Spinach dye solutions extracted at RT, 45 °C, 60 °C and 70 °C

Table 1 Device parameters for ssDSSCs using Henna, red Dragon fruit and red Spinach dye solutions in ethanol extracted at different temperatures.

ssDSSC Devices	Extracting Temperature	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)
Henna Dye	RT(29 °C)	0.46	0.15	0.41	0.03
	45 °C	0.45	0.17	0.39	0.03
	60 °C	0.45	0.16	0.41	0.03
	70 °C	0.41	0.07	0.47	0.01
Red Dragon Fruit Dye	RT(29 °C)	0.51	0.09	0.33	0.02
	45 °C	0.47	0.08	0.31	0.01
	60 °C	0.55	0.06	0.43	0.02
	70 °C	0.53	0.08	0.35	0.01
Red Spinach Dye	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

In ssDSSCs with red Dragon fruit dye extract, V_{OC} and J_{SC} are not significantly changed upon varying extracting temperature. FF is higher at extracting temperature of 60 °C. The almost similar PCE values of 0.01-0.02% were obtained. In ssDSSC with red Spinach dye extract, V_{OC} are not significantly changed upon varying extracting temperature. Highest J_{SC} of 0.42 mA/cm^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 ssDSSCs 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 mA/cm^2, and fill factor (FF) of 0.55, under the irradiance of 1000 W/m^2.

(ii) Varying the Concentration of Co-solvents in Solvent-mixture

Fig. 5 shows J-V characteristics of the ssDSSCs using Henna, and red Dragon fruit and red Spinach dye extracts prepared in the solvents with different concentration of DMF in ethanol under AM 1.5 illumination (1000 W/m^2). Device parameters for ssDSSCs using Henna, red Dragon fruit and red Spinach dye solution extracted in different solvents (varying concentration of DMF in EtOH) at room temperature are listed in Table 2.

In ssDSSC using Henna dye in the solvent with varying concentration of DMF in ethanol, V_{OC} remained almost unchanged at around 0.45-0.48 V. However J_{SC} kept changed with maximum J_{SC} of 0.19 mA/cm^2 (DMF : EtOH - 4 : 6) and minimum J_{SC} of 0.08 mA/cm^2 (DMF: EtOH - 2 : 8). The maximum FF is 0.53 for (DMF : EtOH - 8 : 2). Thus PCE of the device (DMF : EtOH - 4 : 6) is 0.04% which is higher than those with other concentrations.

With red Dragon fruit dye extracted in solvent with varying concentration of DMF in ethanol, the ssDSSC generated V_{OC} value of 0.51-0.55 V. At concentration of DMF in ethanol (8 : 2), J_{SC} is maximum (0.16 mA/cm^2) and FF is minimum (0.37) among other concentrations of DMF in ethanol. Since PCE is determined from three device parameters

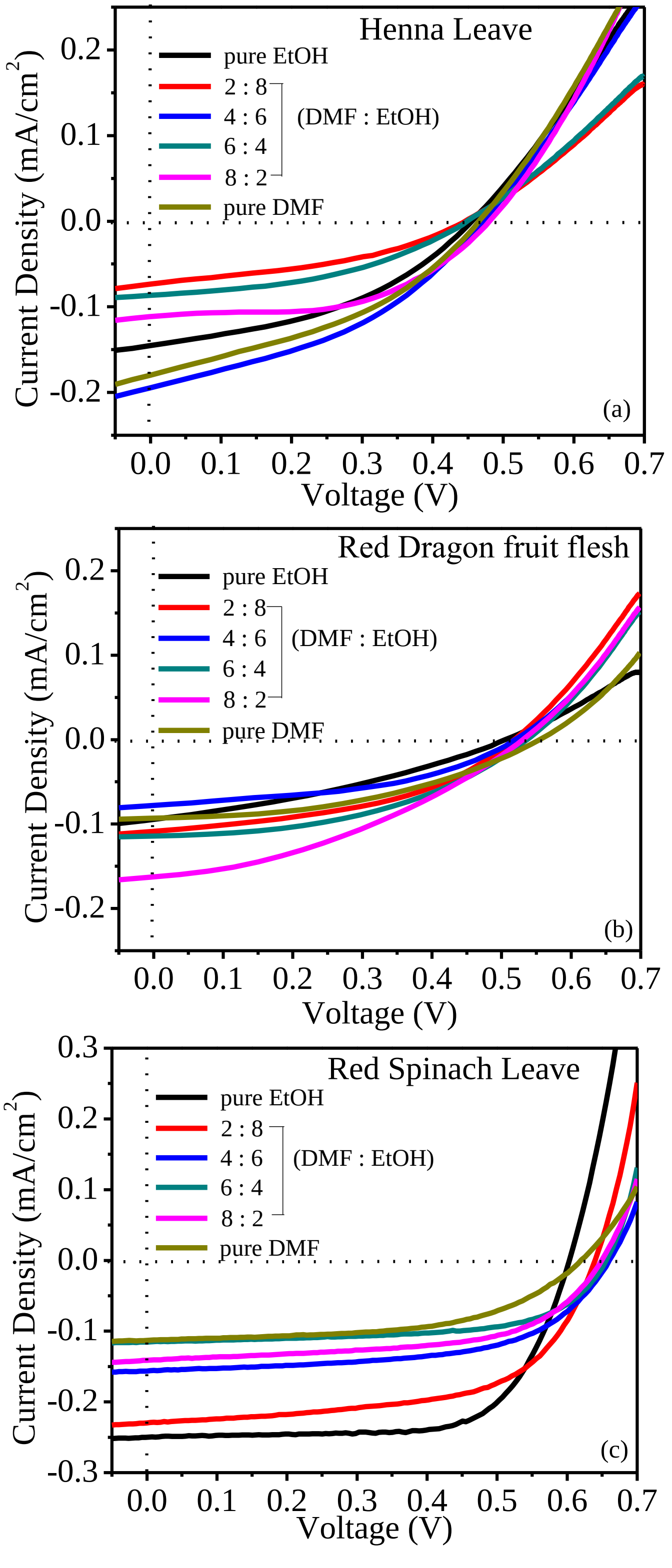

Figure 5 J-V characteristics of the ssDSSCs using (a) Henna, (b) red Dragon fruit and (c) red Spinach dye extracts in different solvents

Table 2 Device parameters for ssDSSCs using Henna, red Dragon fruit and red Spinach dye solution in solvent-mixtures (increasing concentration of DMF in ethanol) at room temperature.

ssDSSC Devices	Solvents	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)
Henna Dye	Pure EtOH	0.46	0.15	0.41	0.03
	(DMF : EtOH - 2: 8)	0.45	0.08	0.38	0.01
	(DMF : EtOH - 4: 6)	0.47	0.19	0.39	0.04
	(DMF : EtOH - 6: 4)	0.45	0.09	0.42	0.02
	(DMF : EtOH - 8: 2)	0.48	0.11	0.53	0.03
	Pure DMF	0.47	0.18	0.38	0.03
Red Dragon Fruit Dye	Pure EtOH	0.51	0.09	0.33	0.02
	(DMF : EtOH - 2: 8)	0.52	0.11	0.43	0.02
	(DMF : EtOH - 4: 6)	0.52	0.08	0.44	0.02
	(DMF : EtOH - 6: 4)	0.54	0.11	0.44	0.03
	(DMF : EtOH - 8: 2)	0.53	0.16	0.37	0.03
	Pure DMF	0.55	0.09	0.42	0.02
Red Spinach Dye	Pure EtOH	0.60	0.25	0.69	0.10
	(DMF : EtOH - 2: 8)	0.64	0.23	0.59	0.09
	(DMF : EtOH - 4: 6)	0.66	0.16	0.58	0.06
	(DMF : EtOH - 6: 4)	0.65	0.12	0.62	0.05
	(DMF : EtOH - 8: 2)	0.65	0.14	0.58	0.05
	Pure DMF	0.62	0.11	0.55	0.04

V_{OC}, J_{SC} and FF, the PCE of red Dragon fruit device is around 0.02-0.03% regardless of varying solvent. Again V_{OC} is not significantly changed upon varying volume ratio in red Spinach device. J_{SC} and FF gradually decreased from 0.25 mA/cm^2 to 0.11 mA/cm^2 and from 0.69 to 0.55 respectively upon increasing DMF concentration. The efficiency of device using red Spinach in pure EtOH is as high as 0.10%.

Summary and Conclusion

In this work, the ssDSSC devices were fabricated using Henna, red Dragon fruit and red Spinach dye extracts. The photovoltaic performance was examined upon varying the dye extracting temperature in ethanol, and the concentration of DMF in ethanol. The highest extracting temperature of 70 °C degraded the device efficiency for Henna dye extracts while the device efficiency is almost insensitive to extracting temperature for red Dragon fruit and red Spinach dye extracts. Upon increasing concentration of DMF in ethanol, the device efficiencies keep fluctuating for Henna extracts, remain unchanged for red Dragon fruit extracts and offer highest efficiency of 0.10% for red Spinach extracts in pure ethanol. Among all, the efficiency of red Spinach device (extracted at 45 °C in ethanol) is as high as 0.11 %.

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