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EFFECT OF EXTRACTING SOLVENTS ON THE STABILITY AND PERFORMANCES OF DYE-SENSITIZED SOLAR CELL PREPARED USING EXTRACT FROM *LAWSONIA INERMIS*

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Abstract

Reddish-brown anthocyanins from Henna leaves (*Lawsonia inermis*) extracted in ethanol (**A**) and mixture of Ethanol and water in the ratio 4:1 by volume (**B**) were employed as TiO_2 dye-sensitizers. Solar cells sensitized by extracts **A** achieved up to J_{sc} 1.870 $mAcm^{-2}$, V_{oc} 0.61V, FF 0.58 and η 0.66%, while for extract **B** sensitized cells the values determined were J_{sc} 1.35 $mAcm^{-2}$, V_{oc} 0.59V, FF 0.65 and η 0.52%. Long period stability in efficiency of the cells investigated revealed a drastic degradation of 13.64% in the efficiency of cell prepared using **A**

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and a fairly stability in efficiency in that of **B** cell. The results obtained with extracts **A** and **B** confirmed that Ethanol could be considered not suitable as solvent for the extraction of natural dye used as sensitizer in dye-sensitized solar cell operations. This study also represents an environmental friendly alternative for dye-sensitized solar cells with low cost production and an excellent system for educational purposes.

1. Introduction

Energy can affect all kinds of development in this world like environment, livelihoods, population levels, health, access to water, agricultural productivity, by and large economic and social developments.

Utilizing energy from the sun allows all parts of the world to use this energy. Solar power from solar cells is not only environmentally safe, but also used as an energy that will exist for billions of years. To date, many of the solar energy systems are significantly more expensive than the traditional options available to customers (for example; engines, gas heater, grid electricity). The cost, performance and convenience of these systems must be improved if solar energy is going to compete in energy markets against more traditional alternatives.

Dye-sensitized TiO_2 solar cell (DSSC) has become an attractive and cheap device for the conversion of solar light into electrical energy since its prototype was first reported by O'Regan and Grätzel in 1991 [1]. DSSC is assembled with a cathode of TiO_2 porous film on a conductive glass substrate anchored a monolayer of dyes, an anode of conductive glass coated with platinum, and a electrolyte of certain organic solvent containing a redox couple, such as iodide/triiodide.

However, effort has been intensified towards dyes used as sensitizers, since it plays a key role in the harvesting of sunlight and transferring of solar energy into electric energy. The best studied example is that of Ru-bipyridyl dye bound via carboxylate bonds to analytase (TiO_2) crystallites. This complex is found to have intense charge transfer absorption in the whole visible range, long excited lifetime, highly efficient metal-to-ligand charge transfer (MLCT) [2] and with a power conversion efficiency of about 11%-12% [3]. On the contrary, for the weak binding energy with TiO_2 film and the low charge transfer absorption in the whole visible range, natural dyes sensitizers perform poorly in DSSC. Naturally, various parts of the shoot and root system of plants show various color from red to purple and contain various natural dyes which can be extracted by simple procedures.

Among the natural dyes, anthocyanins are a group of natural occurring phenolic compounds responsible for the color of many flowers, fruit and vegetables. The most common anthocyanidins found in flowers are pelargonidin (orange), cyanidin (orange- red), peonidin (orange-red), deliphinidin (blue-red), petunidin (blue-red) and malvidin (blue-red) as shown in Figure 3.

Useful natural dye extracts utilized as photosensitizers in DSSC have been reported [6-12] but shown low overall solar energy conversion efficiencies below 2%. Here, we reported the results of a series of experiments carried out on raw extracts of *Lawsonia inermis* as this plant is relatively abundant in the tropical rain forest countries and because of its richness in anthocyanin, it is commonly used by the Hausa/Fulani tribes in some African countries as skin ornament in a manner similar to the making of tattoo in the western countries.

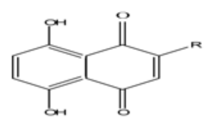

Figure 1. Hydroxynaphthoquinone from *Lawsonia inermis* colour, reddish brown (English; Henna plant).

2. Experimental

2.1. Preparations of natural dye-sensitizers

Leaves harvested from *Lawsonia inermis* during sunshine were dried in an open but dark place in the laboratory for several days until their weight became invariant. It was then crushed into tiny bits and extracted into ethanol-fluka, 96% (v/v) (**A**), and a mixture of ethanol and water (**B**), respectively, keeping them overnight.

The residual part was removed by filtration and filtrate was washed with hexane severally to remove oil droplets and chlorophyll that may be present. It was then hydrolysed with few drops of HCl so that the extract became deeper in colour. The extracts were used directly as prepared for the construction of the DSSCs at room temperature.

2.2. Preparation of DSSCs

TiO_2 -paste purchased from solaronix (nanoxide -T, colloidal anatase particles size ~ 13nm, ~ $120\, m^2 / g$ (SA) was coated by screen printing method on precleaned fluorine doped Tin-Oxide (FTO) conducting glasses (Nippon glass sheet 10-$12\,\Omega m^{-2}$). Finally, the glass sheet was sintered at $450\,°C$ for 30 minutes and furnace-step cooled to room temperature to melt together the TiO_2 nanocrystals and to ensure its good mechanical cohesion on the glass surface.

The TiO_2 electrode thickness was determined by Dekar profiliometer to be $8.15\,nm$. The impregnation of the electrode was achieved by the immersion of the electrode (face-up) in the natural dye extract for 4-6 hours, this turned the TiO_2 thick-film from white to fairly reddish-brown color. Impurities/excess dye were washed away with anhydrous ethanol, dried in moisture free air and stored in a dark anhydrous condition.

DSSC of $1\,cm^2$ active area were assembled by filling a liquid electrolyte (0.5M KI + 0.05M I_2 in solvent of ethylene glycol + acetonitrite with a volume ratio of 4:1) between the TiO_2 photoanode and platinum counter electrode prepared by spraying method).

The two electrodes were clipped together and a cyanoacrylate adhesive was used as sealant to prevent the electrolyte from leaking.

2.3. Characterization and measurements

The crystalline phases of the TiO_2 film were identified by X-ray diffraction (sciece RAD-2R) using graphite monochromatized CuK_α radiation $(\lambda = 0.154\,nm)$.

UV-visible absorption measurements of the extracts **A** and **B** were carried out with Avante UV-VIS spectrophotometer.

Current-voltage (*I-V*) characteristics of DSSCs were examined under a standard solar radiation of $1000\,W/m^2$ using overhead Veeco-viewpoint solar simulator, a four point Keithley multimeter coupled with a Lab-tracer software was used for data acquisition at room temperature.

Based on the *I-V* curve power conversion efficiency (η) was calculated according to the equation

$$\eta = FF \times J_{sc} \times V_{oc} / I, \tag{1}$$

where J_{sc} is the short-circuit voltage (volts), I is the intensity of the incident light

$(\mathrm{W/m^2})$, V_{oc} is the open circuit voltage (volts), FF is the fill factor defined as

$$\mathrm{FF} = J_m V_m / J_{sc} V_{oc}\ , \tag{2}$$

where J_m and V_m are the optimum photocurrent and voltage that can be extracted from the maximum power point of the *I-V* characteristics [4, 8, 9].

3. Results and Discussion

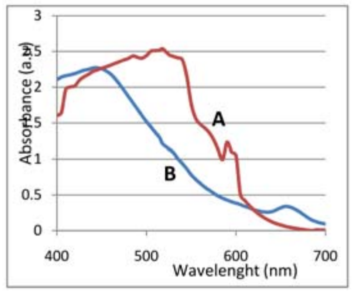

Figure 2. Absorption spectra of *Lawsonia inermis* extracts in ethanol (**A**) and a mixture of ethanol and water in the ratio 4:1 by volume (**B**).

Figure 2 shows the UV-VIS absorption spectral of *Lawsonia inermis* extracts in ethanol (**A**) and a mixture of ethanol and water in the ratio 4:1 by volume (**B**). The dyes extracted from the *Lawsonia inermis* was soluble in ethanol as well as in the mixture of ethanol and water (4:1) and result into deep reddish brown colored solution.

Generally, anthocyanins and their derivates show a broad absorption band in the range of visible light ascribed to charge transfer transition from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) [13]. Absorption spectra of anthocyanidins (anthocyanins without the glycoside group) are mainly dependent on the substitute groups, R1 and R2, [12], i.e.,

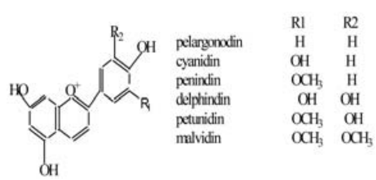

Figure 3. Anthocyanidins structure and the substitute groups R1 and R2.

It can be seen that the extract **A** exhibits a maximum at 518 nm while **B** at

445 nm shows an absorption maximum. The bands were also broadened with a shoulder at 590 nm and 655 nm, respectively.

However, further spectra studies depicted that in the DSSCs sensitized by extracts **A** and **B**, the anthocyanins promote an efficient light harvesting and electron injection with maximum efficiency at 531 nm and 458 nm, respectively. The shift in the absorption maxima in the samples could be considered as an evidence for the attachment of these molecules to the surface of TiO_2.

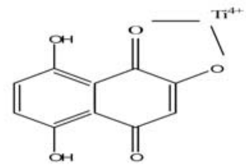

Figure 4. Chelation mechanism of hydroxynaphthoquinone with TiO_2 particle.

Table 1 shows the photocurrent - voltage characteristics of solar cells sensitized with extracts **A** and **B** under irradiation with simulated sunlight at 1000 W/m^2 intensity (AM 1.5).

3.2. Effects of solvent on DSSC's stability

Table 1 shows that the efficiency of DSSC prepared using extract obtained from sample **A** (in which ethanol was used as solvent) is higher than that of sample **B** which involved mixture of water and ethanol (1:4) as extracting solvent reported at 0.66% and 0.52%, respectively.

Table 1. Photovoltaic performances of *Lawsonia inermis* extracts in different solvents

Solvents	J_{sc} (mAcm^{-2})	V_{oc} (V)	FF	η%
A	1.87	0.61	0.58	0.66
B	1.35	0.59	0.65	0.52

This might be attributed to the fact that anthocyanin is more soluble in ethanol (**A**) than in mixture of ethanol and water (**B**), it could be due to the higher amount of dye chemoadsorbed onto the TiO_2 in sample **A** than in **B**, it may be possibly due to the higher number in λ maximum in the absorption in **A** than in **B**, which could absorb higher energies from the solar spectrum.

The long period stability of these cells was investigated systematically with perfect sealing to avoid contact with moisture. Unfortunately, cell sensitized with sample **A** showed poor stability compared with those sensitized with sample **B**. The efficiency of the ethanol system was observed drastically diminished to 0.57% after being exposed to the simulated sunlight for 4 hours while a very small decrease in the efficiency for the case of sample **B** (0.49%) was noticed.

It was reported that this effect could be due to photocatalytic decomposition of anthocyanin by TiO_2 in the presence of ethanol [12, 14], this is observed in the color of the photoanode which become pale after the long time exposure to simulated sunlight. Hence, the DSSC prepared from sample **A** is unable to function properly just after a short operating period.

4. Conclusion

We have shown that DSSC of reasonably high efficiency can be developed using *Lawsonia inermis* extracts using different solvents. The results for extracts using ethanol were slightly better than that of extract obtained using a mixture of ethanol and water (4:1 in volume) in cell operation.

However, efficiency obtained under long time irradiation period confirmed a reduction in value of efficiency for DSSC prepared with ethanol compared with that constructed using a mixture of water and ethanol. Therefore in terms of long period stability in efficiency of DSSC, ethanol could be considered not suitable as solvent for the extraction of natural dye used as sensitized in DSSCs.

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References

[1] B. O'Regan and M. Grätzel, A low cost, high efficiency solar cell based on dye-sensitized colloidal TiO_2 films, Nature 353 (1991), 737-740.

[2] Andre Sarto, Melina Kayoko Itokazu, Neyde Yukie and Murakani Iha, Metal complex sensitizing in dye-sensitized solar cell, Coordination Chemistry Review 284 (2004), 1343-1361.

[3] Michael Grätzel, Solar energy conversion by dye-sensitized photovoltaic cells, Iorg. Chem. 44 (2005), 6841-6851.

[4] K. Tennakone, A. R. Kumarasinghe, G. R. R. A. Kamara, K. G. U. Wijayantha and P. M. Sirimanne, Nanoporous TiO_2 photoanode sensitization with flower pigment cyanidin, J. Photochem. Photobiol. A: Chem. 108 (1997), 193-195.

[5] K. Sakata, N. Saito and T. Honda, Ab initio study of molecular structure and exited state in anthocyanins, Tetrahedron 62 (2006), 3721-3731.

[6] Giuseppe Calogero, Gaetano Di Marco, Silvia Cuzzanti, Stefano Caramori, Robert Argazzi, Aldo De Carlo and Carlo Alberto Bignozzi, Efficient dye-sensitized solar cells using red turnip and purple wild Sicilian pear fruit, Int. J . Mol. Sci. 11 (2010), 254-257.

[7] J. H. Hao Swu, Y. Huang and J. Lin, Natural dye as photosensitizer for dye-sensitized solar cells, Sol. Energy 80 (2006), 209-214.

[8] E. Yamazaki, M. Murayama, N. Nishikwa, N. Hashimoto, M. Shoyama and O. Kurita, Utilization of natural carotenoids as photosensitizers for dye-sensitized solar cells, Sol. Energy 81 (2007), 512-516.

[9] G. Calogero and G. Di Marco, Red Sicilian orange and purple eggplant fruits as natural dye from calafate and jabotica, Solar Energy Materials and Solar Cells 92 (2008), 1341-1346.

[10] Sancun Hao, Jihuai Wu, Yunfang Huang and Jianming Lin, Natural dyes as photosensitizers for DSSC, Solar Energy 80 (2006), 209-214.

[11] G. P. Smestad, Education and solar conversion: demonstrating electron transfer, Solar Energy Materials and Solar Cells 55 (1998), 157-178.

[12] J. M. R. C. Fernando and G. K. R. Senadeera, Natural anthocyanins as photosensitizers for dye-sensitized solar devices, Current Science 95(5) (2008), 663-666.

[13] N. J. Cherepy, G. P. Smestad, M. Grätzel and G. J. Zhang, Ultrafast electron injection: implications for a photoelectrochemical cell utilizing an anthocyanin dye-sensitized TiO_2 nanocrystalline electrode, J. Phys. Chem. B 101 (1997), 9342-9351.

[14] Khwanchit Wongcharee, Vissanu Meeyoo and Sumaeth Chavadej, Dye-sensitized solar cell using natural dyes extracted from rosella and blue pea flowers, Solar Energy Materials and Solar Cells 91(7) (2007), 566-571.