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Received 16 January 2008; revised accepted 30 July 2008

Natural anthocyanins as photosensitizers for dye-sensitized solar devices

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Different natural pigments containing anthocyanins extracted from tropical flowers were studied as possible sensitizers for TiO₂ by assembling dye-sensitized solar cells (DSCs). Photocurrent densities ranging from 1.1 to 5.4 mA cm⁻² were obtained with photovoltages ranging from 390 to 410 mV. The overall efficiency and fill factor of these cells varied from 0.2 to 1.1 and 53 to 64 respectively. Among the flower pigments studied, the extract from *Hibiscus surattensis*-HST (cultivated species/colour of the flower: magenta) gave the best photosensitized effect, which can be used as an environment-friendly, low-cost alternative system, especially for educational purposes.

Keywords: Dyes, natural pigments, solar cells, tropical flowers.

DYE-sensitized solar cells (DSCs) have attracted much attention as low-cost photovoltaic cells and have become a rapidly expanding field with potential applications, especially after the discovery of an efficient photovoltaic cell by O'Regan and Grätzel^{1,2}. In this context, although highly efficient cells have been shown to operate with power conversions up to 10% using nanoporous TiO₂ electrodes sensitized with ruthenium complexes, there remains the need for alternative photosensitizers for use with TiO₂-based photovoltaic devices, especially due to the high cost of ruthenium complexes and the long-term unavailability of these noble metals. Therefore, investigation of low cost, readily available dyes as efficient sensitizers for DSCs still remains a scientific challenge^{3–13}. In this context, application of naturally occurring pigments such as anthocyanins, carotenoids and chlorophylls for DSCs has several advantages over rare metal complexes and other organic dyes, such as readily availability, easy extraction into cheap organic solvents, can be applied without further purification, is environment-friendly and considerably reduces the cost of the devices. Numerous efforts have been done by several research groups all over the world to utilize these natural dyes as sensitizers in these devices^{12–16}. In this context, among the natural dyes, anthocyanins are a group of naturally occurring phenolic compounds responsible for the colour of many flowers, fruits (particularly in berries) and vegetables^{17,18}. They are glycosylated polyhydroxy or polymethoxy derivatives of 2-phenylbenzopyrylium or flavylum salts, which consist of three six-membered rings (Figure 1) and usually the glycosylation occurs at 3, 5 and 7 positions. These important floral pigments give rise to a wide range of flower colours, from orange to blue¹⁸. The most common anthocyanidins found in flowers are pelargonidin (orange), cyanidin (orange-red), peonidin (orange-red), delphinidin (blue-red), petunidin (blue-red) and malvidin (blue-red; Figure 1)^{17–19}.

In this study we have extracted anthocyanine pigments from several locally available flowers and especially from one of the endemic plants, *Rhododendron arboreum zeylanicum*-RAZ (locally called maha rathmal; colour of the flower: red). The other pigments included *Sesbania grandiflora* Scarlet – SGS (locally called as rathu kathuru murunga; colour of the flower: red), *Hibiscus rosasinensis* – HRS (locally called pokuru wada; colour of the flower: deep red), *Hibiscus surattensis* – HST (cultivated species; colour of the flower: magenta), *Nerium oleander* – NRO (locally called kaneru; colour of the flower: red), *Ixora macrothyrsa* – IMT (locally called rath mal; colour of the flower: orange-red). We studied their photo-responses as sensitizers for DSCs.

Petals of flowers chosen were cut into small pieces and extracted into ethanol (Fluka, 96% (v/v)), keeping them overnight. Then residual parts were removed by filtration and the filtrate was washed with hexane several times to remove any oil or chlorophyll present. The ethanol frac-

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tion was separated and few drops of conc. HCl were added so that the solution became deep red in colour ($\text{pH} < 1$). Possible reaction with HCl is shown in Figure 1 *b*, as reported in the literature¹⁵. This was directly used as dye solution for the preparation of photovoltaic devices. Elucidation of exact structures was not done, since the aim of the present study was to use them as available in the flowers without any isolation.

TiO_2 paste purchased from Solaronix (nanoxide-T, colloidal anatase particles size: ~ 13 nm, ~ 120 m²/g (BET), Switzerland) was coated by Doctor Blade method on pre-cleaned fluorine-doped conducting tin oxide (FTO) glasses (Nippon sheet glass $10\text{--}12$ Ω sq⁻¹). The electrodes were pre-heated ($\sim 50^\circ\text{C}$) using a hair-drier and then sintered at 450°C for 40 min, and then allowed to cool to room temperature. The thickness of the TiO_2 electrodes was found to be $\sim 4\text{--}5$ μm (Dektak profilometer; Veeco, Dektak 3).

The TiO_2 electrodes were dipped in each dye solution for 12 h. The electrodes were then removed and rinsed with ethanol and dried using an airflow. DSCs were constructed by introducing the redox electrolyte containing tetrabutylammonium iodide (TBAI; 0.5 M)/ I_2 (0.05 M), in a mixture of acetonitrile and ethylene carbonate (6:4, v/v) between the dyed TiO_2 electrode and platinum counter electrode.

UV-visible absorption measurements of extracted pigments in acidified ethanol solution and of absorbed TiO_2 surfaces were carried out with a Shimadzu dual wavelength/double beam spectrophotometer (model UV-3000).

Current-voltage (I - V) characteristics of the cells were examined with a standard solar irradiation of 100 mW cm⁻²

(Xe-lamp with an Oriol AM 1.5 filter) as the light source. An Eko pyranometer was used to measure light intensity and a fully computerized set-up consists of a multimeter (Keithley 2000) coupled to a potentiostat (Hokuto Denko, HA 301) via a computer used for data acquisition. The power conversion efficiency (η) was calculated according to the following equation: $\eta = (FF \times J_{\text{sc}} \times V_{\text{oc}})/I$, where J_{sc} is the short-circuit photocurrent density (A cm⁻²), V_{oc} is the open-circuit voltage (volts), I is the intensity of the incident light (W cm⁻²) and FF is the fill factor defined as $FF = J_{\text{m}}V_{\text{m}}/J_{\text{sc}}V_{\text{oc}}$, where J_{m} and V_{m} are the optimum

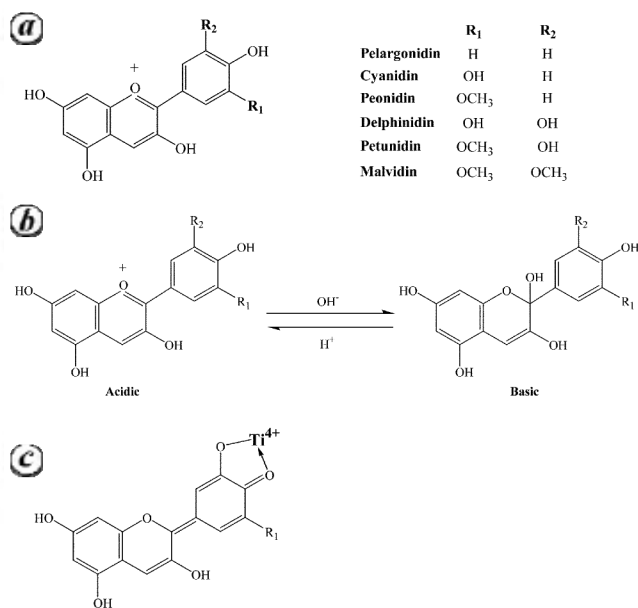


Figure 1. *a*, Basic chemical structures of the most abundant anthocyanidins. *b*, Two chemical structures of anthocyanidins in acidic and basic media. *c*, Chelation mechanism of anthocyanidins with TiO_2 .

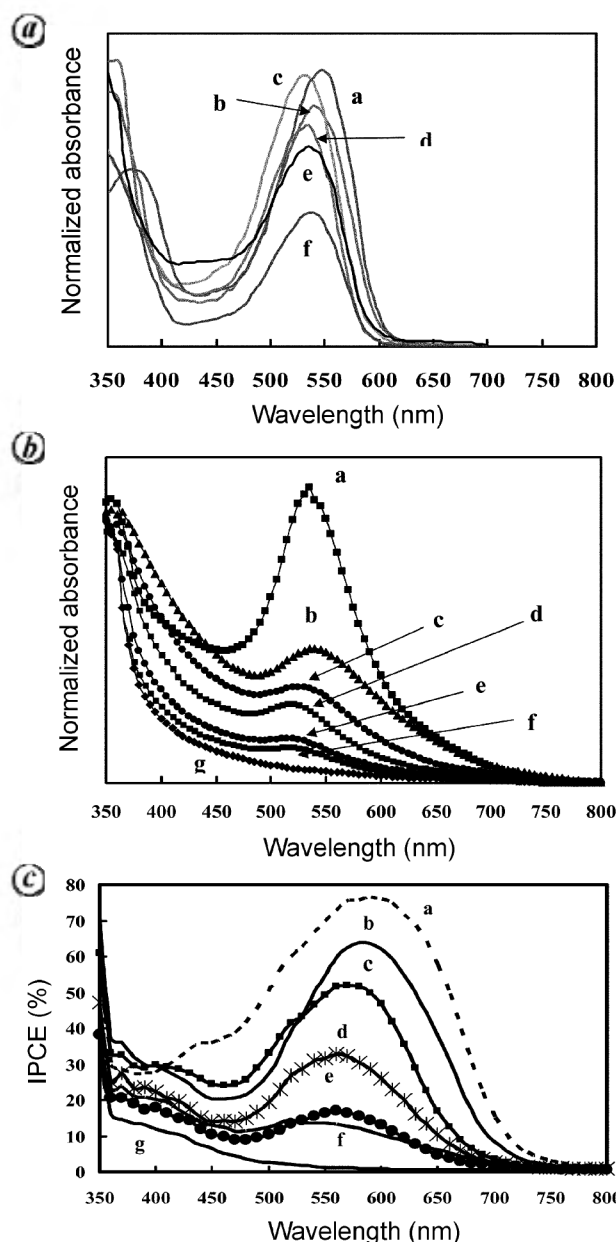


Figure 2. Absorption spectra of (a) pigments in acidified ethanol solutions and (b) pigmented TiO_2 electrodes. *c*, Incident photon to current conversion efficiency (IPCE) curves of pigment-sensitized photovoltaic devices. (a) HST, (b) SGS, (c) HRS, (d) NRO, (e) IMT, (f) RAZ and (g) naked TiO_2 .

Table 1. Absorption data and photovoltaic performances of extracted flower pigments

Pigment	In acidified ethanol ^a	Photovoltaic performance				
		J_{sc} (mA cm ⁻²)	V_{oc} (mV)	Fill factor (%)	Efficiency (%)	Maximum IPCE % (wavelength/nm) ^b
HST	545.0	5.45	392.1	53.5	1.14	76 (590)
SGS	544.0	4.40	406.7	56.9	1.02	64 (580)
HRS	534.0	4.04	400.3	63.3	1.02	52 (570)
NRO	539.0	2.46	408.8	59.1	0.59	33 (560)
IMT	537.0	1.31	403.1	56.8	0.30	17 (560)
RAZ	538.0	1.15	402.0	63.7	0.29	14 (520)

^aMaximum absorption wavelength.^bValues in parenthesis denote the corresponding wavelength to maximum IPCE.

IPCE, Incident photon to current conversion efficiency; J_{sc} , Short-circuit current density; V_{oc} , Open-circuit voltage; SGS, *Sesbania grandiflora* Scarlet; HRS, *Hibiscus rosasinensis*; HST, *Hibiscus surattensis*; NRO, *Nerium oleander*; IMT, *Ixora macrothyrsa*; RAZ, *Rhododendron arboretum* Zeylanicum.

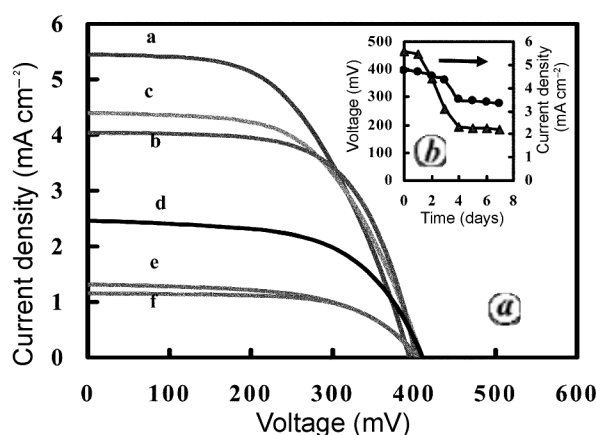


Figure 3. *a*, Current–voltage (I – V) characteristics of photovoltaic devices sensitized with (a) HST, (b) HRS, (c) SGS, (d) NRO, (e) IMT and (f) RAZ pigments. *b*, Variation of short-circuit current density and open-circuit voltage of cell sensitized with HST with time.

photocurrent and voltage that can be extracted from the maximum power point of the I – V characteristics^{1,2,20,21}. The effectiveness of the cell to convert light of various wavelengths into electrical current was measured as the incident photon to current conversion efficiency (IPCE), defined as the number of electrons generated by light per number of photons incident on the cell, i.e. $IPCE\% = 1240J_{sc}/\lambda W_i$, where J_{sc} is the short-circuit current density (A cm⁻²), λ is the excitation wavelength (nm) and W_i the photon flux (W m⁻²)^{1,2,20,21}, using a Nikon monochromator auto-scanner ASC-1101 coupled to a Keithly multimeter via a computer. The measured photocurrent spectra were corrected for the spectral response of the lamp and monochromator by normalization to the response of a calibrated silicon photodiode (Hamamatsu, model S 1227 1010BQ), whose sensitivity spectrum was known. No correction was made for reflection off the surface of the sample.

The dyes/pigments extracted from the above flowers were soluble in ethanol and resulted in deep coloured solutions. Figure 2 *a* shows the absorption spectra of the extracts in ethanol, while Figure 2 *b* shows the absorbance

of the pigmented TiO₂ electrodes. It is generally accepted that the chemical adsorption of these dyes takes place due to condensation of alcoholic-bound protons with the hydroxyl groups in the surface of nanostructured TiO₂ (Figure 1 *c*)^{14,15}. Therefore, this chemical attachment affects the energy levels of the highest occupied molecular level (HOMO) and the lowest unoccupied molecular level (LUMO) of these pigments, which eventually affects the band gap of these materials and a shift in the absorption peak of the absorption spectra. The absorption maxima of natural extracts in ethanol and of the respective photo anode are listed in Table 1. As is evident from Table 1, the shift in the absorption maxima in our samples could be considered as an evidence for the attachment of these molecules to the surface of TiO₂, as depicted in Figure 1 *c*.

In an acidic solution, the oxonium ion results in an extended conjugation of double bonds through three rings of the aglycone moiety, which helps in the absorption of photons in the visible spectra. Addition of a base disrupts the conjugation of double bonds between the second and third rings and results in absorption of photons in the UV range, rather than in the visible range. The change in pH on increasing the number of conjugated double bonds in the molecule, lowers the energy level of the electronic transition between the ground state and the excited states and in turn results in the absorption of photons at greater wavelength (Figure 1 *b*). Considering the absorption maxima and results of Nielsen *et al.*¹⁸, it would be possible to presume that all these flowers contain cyanidin, peonidin, pelargonidin, malvidin, delphinidin, quercetin and flavonol co-pigments. Further, since the red-coloured varieties would contain lower content of delphinidin-derived pigments, but a more variable amount of flavonol-glycosides, the extracts obtained from SGS, HRS, NRO and RAZ flowers should contain the above pigments. The orange-red coloured IMT would contain a large amount of cyanidin 3,5-*O*-diglucoside and relatively lesser amount of flavonol-glycosides. Accordingly, the content of delphinidin-derived anthocyanins and flavonol-glycosides should be high in the magenta-coloured HST¹⁸.

Figure 2c depicts the photo-action spectra of solar cells sensitized with the above pigments. The calculated maximum IPCE values are given in Table 1, with the respective wavelengths. The maximum IPCE of 76 was obtained for cells sensitized with extracts from HST at 590 nm (curve a). The peak around 350 nm is related with the direct band-gap photo-electron excitation of TiO₂ (curve g). However, as can be seen from Figure 2b and c, the close relationship between the action spectra and the optical absorption spectra reveals that the junctions between the pigments and the semiconductor are responsible for the photocurrent generation.

Figure 3a shows the photocurrent–voltage characteristics of solar cells sensitized with extracted pigments under irradiation with simulated sunlight at 100 mW cm^{−2} intensity (AM 1.5). The effective area of the devices for irradiation was 0.25 cm². The overall results are summarized in Table 1. The highest short-circuit photocurrent density of 5.45 mA cm^{−2} was obtained from the device sensitized with pigment HST, with an open-circuit voltage of 392 mV, fill factor of 54% and efficiency 1.14%. One of the reasons for this could be due to the higher amount of dye adsorbed onto the TiO₂ film in HST. It should be noted that even though the degree of absorbance of SGS to TiO₂ is the least, cells fabricated with SGS showed the second highest photocurrent density (Figure 3a; Table 1), possibly due to the higher number in λ maximum in the absorption than the other pigments, which could absorb higher energies from the solar spectrum. Figure 3b shows the preliminary data obtained for the stability of cells prepared with HST under continued illumination with a 15W Osram Day Light lamp at intensity of 325 Wm^{−2} for one week (current–voltage curves were obtained under 1 sun conditions). Even though these cells showed a decline in both the open-circuit voltage and the short-circuit current density in the initial stages, they showed a reasonably good stability. However, the long-term stability of these cells should be performed systematically with perfect sealing to avoid contact with the moisture. Cells sensitized with other flower pigments showed poor stability compared to those sensitized with HST.

Natural dyes were extracted from different easily available flower species and their photo responses were studied for possible application as sensitizers in DSCs. This simple and low-cost technique could be useful for educational purposes, specially in undergraduate courses²¹. Among the flower species investigated, HST gave significantly high photocurrent voltages, with reasonable efficiency. This could be due to better interaction between the dye molecules and the surface of TiO₂.

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Received 10 August 2007; revised accepted 25 July 2008