

Betalain pigments as natural photosensitizers for dye-sensitized solar cells: the effect of dye pH on the photoelectric parameters

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Abstract Dye-sensitized solar cells (DSSC) were fabricated using red *bougainvillea glabra* flower dye extracts as natural dye sensitizers at three dye pH values of 1.23, 3.0, and 5.7. Water was used as dye-extracting solvent. DSSCs from dye extract of pH 3.0 had the highest photocurrent density J_{sc} of 3.72 mA/cm² and fill factor FF of 0.59. While the DSSCs from dye sensitizer pHs of 1.23 and 5.7 had J_{sc} of 1.13 and 2.27 mA/cm², and fill factors of 0.43 and 0.61, respectively. The maximum powers P_{max} of the DSSCs were 0.50, 1.64, and 0.94 mW/cm² for dye sensitizer pH of 1.2, 3.0, and 5.7, respectively.

Keywords Dye-sensitized solar cell · Dye sensitizer · *Bougainvillea glabra* · PH

Introduction

Dye-sensitized solar cell (DSSC) developed by Gratzel et al. [1] has attracted considerable attention due to its environmental friendliness and relative low cost of production [2]. Sensitizer dye in DSSC plays a key role in harvesting sunlight and transforming solar energy into

electric energy and thus of paramount importance to photovoltaic cell performance and efficiency [3]. It attaches to the surface of a wide band-gap mesoporous semiconductor serving as electron transporter [4]. Ruthenium-based dye sensitizers are very expensive and hard to prepare, which restricts their large-scale applications in solar cells, stimulating the search for alternatives such as natural dyes.

Anthocyanins from natural pigments and carotenoids have been used as natural dye sensitizers in DSSC and have shown low to modest solar energy conversion efficiencies [2, 5–7]. These natural dyes are easy to prepare, cheap, non-toxic, environmentally friendly, and easily biodegradable.

Betalain is another interesting class of pigments, whose purified extracts from commercial sources have been subjected to photoelectrochemical study [8]. Betalains consisting of the yellow betaxanthins and red–violet betacyanins are a group of water-soluble nitrogen-containing alkaloid pigments characteristic of certain members of plant sub-order *chenopodineae* within *caryophyllales* and some higher fungi [9]. They absorb visible radiation over the range 476–600 nm, they are immonium derivatives of betalamic acid (the chromophore of all betalains) and divided into two structural groups: the red–violet betacyanins that have a maximum absorptivity at $\lambda \approx 535$ nm and the yellow–orange betaxanthins with maximum absorptivity at $\lambda \approx 480$ nm [10–13]. Betalains are characterized by high molar extinction coefficients in the visible region and pH-dependent redox properties [14, 15]. They are relatively stable over pH range 3–7, however, at pH less than 3.5 the absorption maximum shifts toward lower wavelength [16]. Acidic conditions are known to induce recondensation of betalamic acid with amine group of the addition residue [17] and favors betalain-sensitized photo-electrodes with high optical densities capable of

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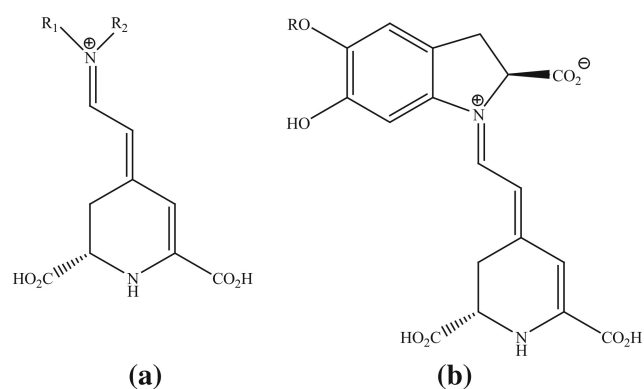


Fig. 1 General structures of the main betalain **a** betaxanthin ($R_1 = H$ and $R_2 =$ amine or amino acid group), **b** betacyanin ($R = \beta$ -D-glucose)

complete absorption in the visible range of 400–600 nm [6]. Solar energy conversion efficiency being a function of photocurrent density J_{sc} , open-circuit voltage V_{oc} , and fill factor FF [18], suggest their improvement is essential to raising conversion efficiency.

This work reports the use of water extracts of red *Bougainvillea glabra* flower a source of betalain as natural dye sensitizer and the influence of sensitizer dye pH on the photoelectric parameters of the DSSCs.

Bougainvillea is a member of the *Nyctaginaceae* family comprising of 18 shrubby species which though indigenous of South America are distributed widely in the world, with flowers ranging from white, yellow, orange, and various shades of red to purple and violet color [12–14]. The Betalain pigment in *Bougainvillea* is different from that in other sources due to the presence of saccharide type present in the betanidin (an aglycone of most betacyanins) which is produced 90 % from betacyanins, and the remaining 10 % comes from indicaxanthin a common betaxanthin [15]. *Bougainvillea glabra* has been found to have eleven violet–red pigments having maximum absorbance in wavelength range of 522–551 nm and is known to have two epimeric betacyanins; bougainvillein-r-1 and isobougainvillein-r-1 [15].

The general structure of Betalain is shown in Fig. 1 [10]; it contains carboxylic functional group which facilitates TiO_2 surface binding.

Experimental

The red *Bougainvillea glabra* flower dye pigments were extracted by crushing 20 g of the flower in a porcelain mortar with a pestle and adding 50 ml of water to the crushed sample. This was filtered to get the raw dye extracts of the flower which was divided into three and used as sensitizing dye at three different pHs. The first, the as-extracted dye had

a pH of 5.70, the pH of the second was adjusted to 3.0 by adding 4 drops of 20 % HCl to it, and the third after adding 8 drop of HCl had a pH value 1.23.

The transparent conducting oxide was fluorine-doped tin oxide (FTO) with a sheet resistance of $15 \Omega/cm^2$ (SOLARONIX). The TiO_2 film was prepared by blending commercial TiO_2 powder (Degussa, P25) of Ca. 0.2 g, nitric solution (0.1 M) of 0.4 ml, polyethylene glycol (MW 10,000) of ca. 0.08 g, and one drop of a non-ionic surfactant, Triton x-100. The mixture was well blended using an ultrasonic bath for 1 h. Squeegee was used to screen-print the resulting TiO_2 paste on the conducting layer/FTO glass substrate. It was left for 30 min so that the paste could settle to reduce the irregularity of the surface. The substrates were then left to dry. This screen-printing procedure was repeated to obtain the TiO_2 working electrode of appropriate thickness of 9 μm .

Prior to sensitisation, the TiO_2 photo-anodes were pre-heated at 150 $^\circ C$ for 30 min, allowed to cool. It was then subjected to $TiCl_4$ treatment by immersing in 40 mM of $TiCl_4$ solution for 30 min at a temperature of 70 $^\circ C$ and subsequently sintered at 450 $^\circ C$ for 45 min. After cooling to 80 $^\circ C$, the TiO_2 electrodes were immersed into the three dye solutions of pH 1.23, 3.0, and 5.7 for 16 h. The photo-electrode were then rinsed with 99 % ethanol solution, to remove excess dye and thereafter left to dry. The counter electrode was made from platinum catalyst T/SP product by SOLARONIX which was screen-printed using a polyester mesh of 90 and dried. The substrates were sintered for 1 h at 45 $^\circ C$. The DSSC was assembled from the various components following the procedure reported elsewhere [19].

Characterization

The absorption spectra of the dyes were determined using an AVASPEC 2048 UV–Visible spectrophotometer, while the morphology and composition characterization of the nanoporous TiO_2 film was carried out using Carl Zeiss EVO MA-10 scanning electron microscope (SEM), with EDX model ISIS 300 Oxford. Simulated Solar irradiation was provided by a Solar Simulator, Model 4200-SCS Semiconductor Characterization System under the irradiation of AM 1.5 ($100 mWcm^{-2}$), and the Current–Voltage curves were recorded by a digital Keithley multimeter Model 2400 coupled to a computer.

Results and discussion

Figure 2 shows the UV–Vis optical absorption spectra of the *bougainvillea* flower dye extracts at three different pHs.

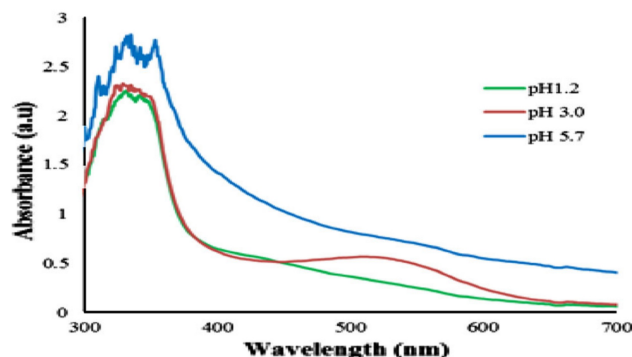


Fig. 2 Absorption spectrum of the dye extract from *red bougainvillea glabra* flower for pH_{1.2}, pH_{3.0}, and pH_{5.7}

Absorption spectra of a dye reflect optical transition probability between the ground state, the excited state and the solar energy range absorbed by the dye. The three dyes' extracts show absorption peaks centered between 310 and 340 nm in the UV-range, with maximum peaks at 330 nm for pH 5.7 and 327 nm for pH 3.0 and 1.2. The dye extracts at pH 1.23 and 3.0 have about the same absorption intensity in short wavelength range, with dye extract at a pH of 5.7 having the highest intensity in this range. The lowest absorption intensity in the long wavelength is observed for dye pH of 1.2, indicating a highly suppressed absorbance as a result of degradation of betanin in very strong acidic environment [20]. Dye extract at a pH of 3 displays broad absorption peak in the 480–560 nm range resulting from $\pi - \pi^*$ transitions due to the mixed contributions of the yellow–orange betaxanthins (480 nm) and of the red–purple betacyanin (540 nm) [6]. At a pH of 5.7, the extract has a highest but flattened absorption spectrum in the long-range wavelength indicating a suppressed absorption peak at this pH and a wider range of red, orange, yellow, and blue light can be absorbed. Absorbance peaks around 300 and 535 nm are characteristic absorptions for red–violet betalain group, betacyanin [14].

The betaxanthin and betanin concentration in the dye extracts in μM are estimated from the absorbance A at 482 and 536 nm from the absorbance spectra using [10],

$$[B_{\text{betax}}] = 23.8A_{482} - 7.7A_{536}$$

$$[B_{\text{betan}}] = 15.38A_{536}$$

$[B_{\text{betax}}]$ is the betaxanthin concentration and $[B_{\text{betan}}]$ the betanin concentration. The betaxanthin concentrations were 7.39, 8.79, and 15.17 μM for pH of 1.23, 3.0, and 5.7, respectively, while the betanin concentration at a pH of 1.2, 3.0 and 5.7 were 4.35, 8.15, and 11.26 μM , respectively.

Figure 3 shows the scanning electron micrograph of the TiO₂ (anatase) film. The TiO₂ film has thickness of 9 μm and a mean particle size of 20 nm. It shows a mesoporous

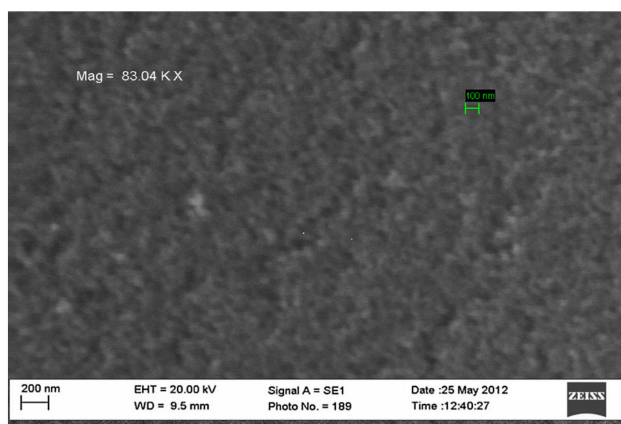


Fig. 3 SEM micrograph of a nanoporous TiO₂ (anatase) film

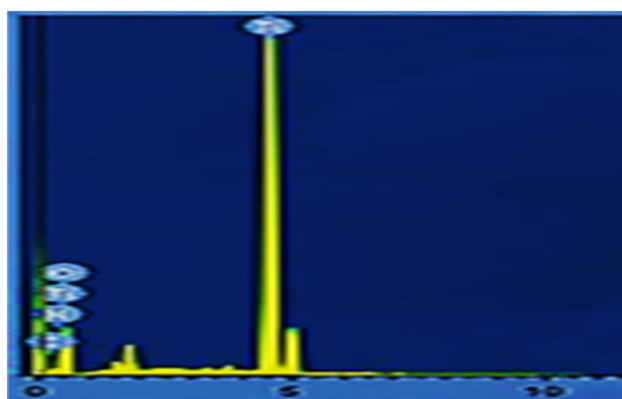


Fig. 4 Elemental composition of TiO₂ compound

surface of the spherical nanoparticles of TiO₂ that forms nanopores across the surface. The EDX analysis of the TiO₂ electrode in Fig. 4 shows the presence of Titanium, Oxygen, Nitrogen, and Carbon. The presence of chlorine in the compound was due to TiCl₄ which was applied at a final treatment of the porous TiO₂ electrodes in the anatase TiO₂ compound contained.

The current–voltage curve of a solar cell yields important photoelectric parameters such as short-circuit current density J_{sc} , the open-circuit voltage V_{oc} , the current I_{mp} , and voltage V_{mp} at the maximum power point P_{max} . The photoelectric characteristics of the DSSCs were inspected under the simulated sunlight source (AM1.5).

The combined J–V and P–V curves of the DSSCs at different pHs are shown in Fig. 5. The open-circuit voltage V_{oc} of 0.44 V is obtained for dye pH of 1.2 and 3.0, respectively, while at a pH of 5.7 the V_{oc} is 0.41. The DSSC prepared from a dye pH of 3.0 has the highest photocurrent density J_{sc} of 3.72 mA/cm^2 and fill factor of 0.59. At a dye sensitizer pH of 1.2, the DSSC has the lowest Photocurrent density of 1.13 mA/cm^2 and lowest fill factor of 0.43 due to betanin degradation in very strong

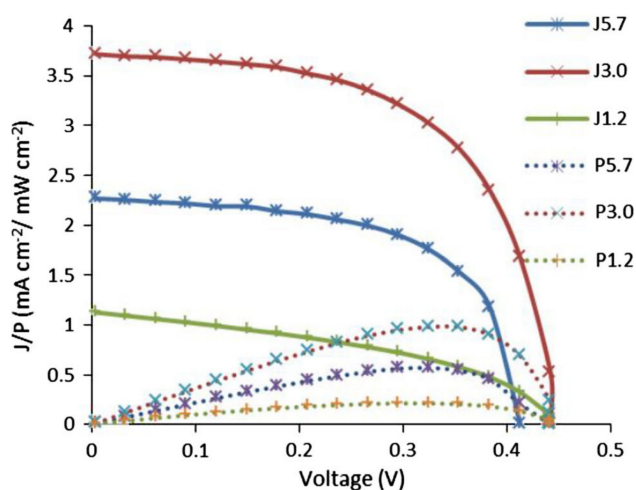


Fig. 5 Combine J–V and P–V curves of the cells for dye sensitizers at pH of 1.2, 3.0, and 5.7

Table 1 Photoelectric parameters of the cells sensitized with natural extracts

Dye pH	J_{sc} (mA/cm ²)	V_{oc} (V)	P_{max} (mW/cm ²)	FF	η
1.2	1.13	0.44	0.50	0.43	0.21
3.0	3.72	0.44	1.64	0.59	0.98
5.7	2.27	0.412	0.94	0.61	0.57

acidic environment [17, 20] with resultant inefficient light harvesting by the dye and inefficient charge injection into the TiO₂ nanoparticles; also possible cell deterioration by acid leaching is expected as the pH goes lower.

The reduction in photoelectrical property observed at pH 5.7 compared to pH 3 results because at high pH betanin is poorly adsorbed onto titania due to its inhibition by indicaxanthin (a common betaxanthin in red *bougainvillea*) competing with betanin for adsorption sites, but at lower pH protonation of the betalainic carboxylic acid group from its anionic form occurs promoting its adsorption onto the TiO₂ [14].

The photoelectric parameters are listed in Table 1.

The obtained photoelectric parameters using *bougainvillea glabra* flower dye extract as sensitizer dye at pHs of 1.2, 3.0, and 5.7 are comparable to J_{sc} of 1.881–2.344 mA/cm² though with lower V_{oc} of 0.23–0.26 V from betalain pigments extracted from bracts of *bougainvillea glabra* and *bougainvillea spectabilis* at a pH of 5.7 [14].

Also although J_{sc} of up to 9.5 mA/cm² have been reported at a dye pH of 1.0 from other sources of betalain, corresponding V_{oc} was just between 0.23–0.3 V [6]. The obtained photoelectric parameters at dye pHs of 1.23 and 5.7 are much lower than that of black dye. The black dye has a certified J_{sc} of 20.5 mA/cm² and a V_{oc} of 0.72 V and is superior to all charge-transfer sensitizers on the basis of

photovoltaic performance under AM 1.5 [21]. The J_{sc} 3.72 mA/cm² at dye sensitizer pH of 3.0 is encouraging.

Conclusion

Betalain raw extracts of red *bougainvillea glabra* flower were used as natural dye sensitizers for DSSCs at different dye sensitizer pH values. At a pH of 1.23, the DSSC had the lowest parameters as a result of betalain degradation in very acidic environment and leaching of the dye from the TiO₂ surface. The DSSC from dye sensitizer pH of 3.0 offered the highest J_{sc} of 3.72 mA/cm², a FF of 0.59, and highest P_{max} of 1.64 mW/cm². The poor absorption of betanin onto the titania at high pH lead to decreased photoelectrical parameter of the cell at pH of 5.7. The obtained photoelectric parameters are much lower than that of black dye which is superior to all charge-transfer sensitizers on the basis of photovoltaic performance under AM 1.5 presently, with a certified J_{sc} of 20.5 mA/cm² and a V_{oc} of 0.72 V [21]. Nevertheless, natural *bougainvillea glabra* flower betalain raw extracts present promising low-cost, non-toxic, and environmentally friendly alternative photosensitizers in DSSCs.

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