

# Dye-sensitized solar cells with natural dyes extracted from rose petals

~~N. Gokilamani · N. Muthukumarasamy ·  
M. Thambidurai · A. Ranjitha · Dhayalan Velauthapillai ·  
T. S. Senthil · R. Balasundaraprabhu~~

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**Abstract** Nanocrystalline TiO<sub>2</sub> dye-sensitized solar cells have been fabricated using TiO<sub>2</sub> photoelectrode sensitized using the extracts of red rose and table rose as natural sensitizers and their characteristics have been studied. The extracts having anthocyanin pigment (pelargonidin, peonidin and cyanidin), which have hydroxyl and carboxylic groups in the molecule can attach effectively to the surface of TiO<sub>2</sub> film. The solar cell constructed using the red rose sensitized TiO<sub>2</sub> photo-electrode exhibited a short-circuit photocurrent of 4.57 mA/cm<sup>2</sup> and a power conversion efficiency of 0.81 % and that of table rose sensitized TiO<sub>2</sub> photo-electrode exhibited a short-circuit photocurrent of 4.23 mA/cm<sup>2</sup> and a power conversion efficiency of 0.67 %. Natural dye sensitized TiO<sub>2</sub> photo electrodes present the prospect to be used as an environment-friendly, low-cost alternative system.

## 1 Introduction

Solar cells have attracted increasing attention over the last few decades as a viable alternative for replacing diminishing fossil fuels [1]. High efficiencies above 20 % have been achieved by monocrystalline silicon solar cells, however their production cost and energy consumption during the fabrication process are quite high [2]. Dye-sensitized solar cells have been extensively studied in recent years because they offer the advantages of low cost, lower toxicity manufacturing processes, straight forward scale-up, low weight, and potential use in flexible panels as compared to conventional p-n junction devices [3]. Among several new energy technologies, dye-sensitized solar cells are one of the most promising new generation systems for photovoltaic technology. Semiconductor nanomaterials like TiO<sub>2</sub> nanoparticles having a particle size less than 100 nm in diameter have become a new generation of advanced materials due to their novel and interesting optical, electrical, and photo-voltaic properties arising from size quantization. Nanoporous TiO<sub>2</sub> electrodes sensitized with ruthenium complexes have exhibited high power conversion efficiencies, but they are not available easily are of high cost. Hence investigation on low cost, readily available dyes as efficient sensitizers for dye-sensitized solar cells has been expedited but still remains a scientific challenge [4, 5]. Dye-sensitized solar cells usually employ ruthenium (II) polypyridyl complexes as sensitizers for wide band gap semiconductors, the energy conversion can also be achieved by natural dyes [6, 7]. Tennakone et al. [8] have investigated the use of tannins and related phenolic substances extracted from black tea, nuts or pomegranate bark, as well as the photosensitization promoted by anthocyanin extracted from flowers [9]. Dai and Rabani [10, 11] have examined the use of anthocyanin extracted

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~~N. Gokilamani (✉) · N. Muthukumarasamy · A. Ranjitha  
Department of Physics, Coimbatore Institute of Technology,  
Coimbatore, India  
e-mail: gokilarajasekar@gmail.com~~

~~M. Thambidurai  
Department of Electrical and Computer Engineering, Global  
Frontier Center for Multiscale Energy Systems, Seoul National  
University, Seoul 151-744, Republic of Korea~~

~~D. Velauthapillai  
Department of Engineering, University College of Bergen,  
Bergen, Norway~~

~~T. S. Senthil  
Department of Chemistry, Yeungnam University, Gyeongsan,  
South Korea~~

~~R. Balasundaraprabhu  
Department of Physics, PSG College of Technology,  
Coimbatore, India~~

from pomegranate seeds and the employment of aqueous mediator for such cells. They have also studied the effect of the mediator solvent in the performance of solar cells sensitized by commercially available anthocyanins [12]. Smestad and Gratzel have pointed out the advantages of the use of natural dyes in experiments for educational purposes [13]. Many researchers have investigated the use of natural dyes in solar cells, such as those obtained from extracts of hibiscus [14], mulberry [15], red cabbage [16] and achote seeds [17]. The function of dye is to absorb light, inject electrons into the TiO<sub>2</sub> conduction band, and then accept electrons from the redox mediator in the electrolyte.

Anthocyanins are natural compounds commonly found in flowers, fruits, and leaves of plants such as the canary bird flower [18], blue pea flowers [19], strawberries [20], blackberries [21], pomegranate fruits [10, 22], and maple leaves [23]. Anthocyanin is a water soluble natural pigment, which can be extracted from red rose. Roses are one of the cut flowers which attract many people, and are often used as ornamental flower for formal and non formal events [24]. There are more than 300 kinds of anthocyanins, and their possible combinations in rose petal which gives the colours like pink, crimson, cerise, magenta and purple to the rose petal. Forty-four taxa of three sections [Cinnamomeae (=Rosa) 26, Chinenses 8 and Gallicanae 10] and eight modern garden roses in the genus *Rosa* were surveyed for their floral anthocyanins. Eleven anthocyanins: 3-glucosides and 3, 5-diglucosides of cyanidin (Cy), pelargonidin (Pg) and peonidin (Pn), 3-rutinosides and 3-rho-coumaroylglucoside-5-glucosides of Cy and Pn, and Cy 3-sophoroside, were isolated from flowers of these taxa and identified by chemical and spectroscopic techniques.

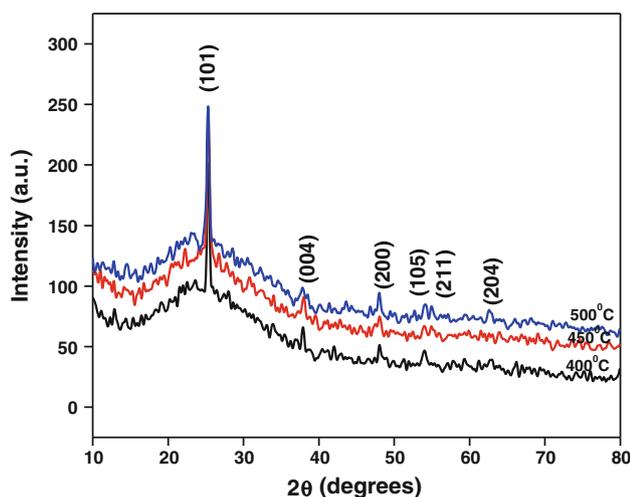


Fig. 1 X-ray diffraction pattern of annealed TiO<sub>2</sub> thin films

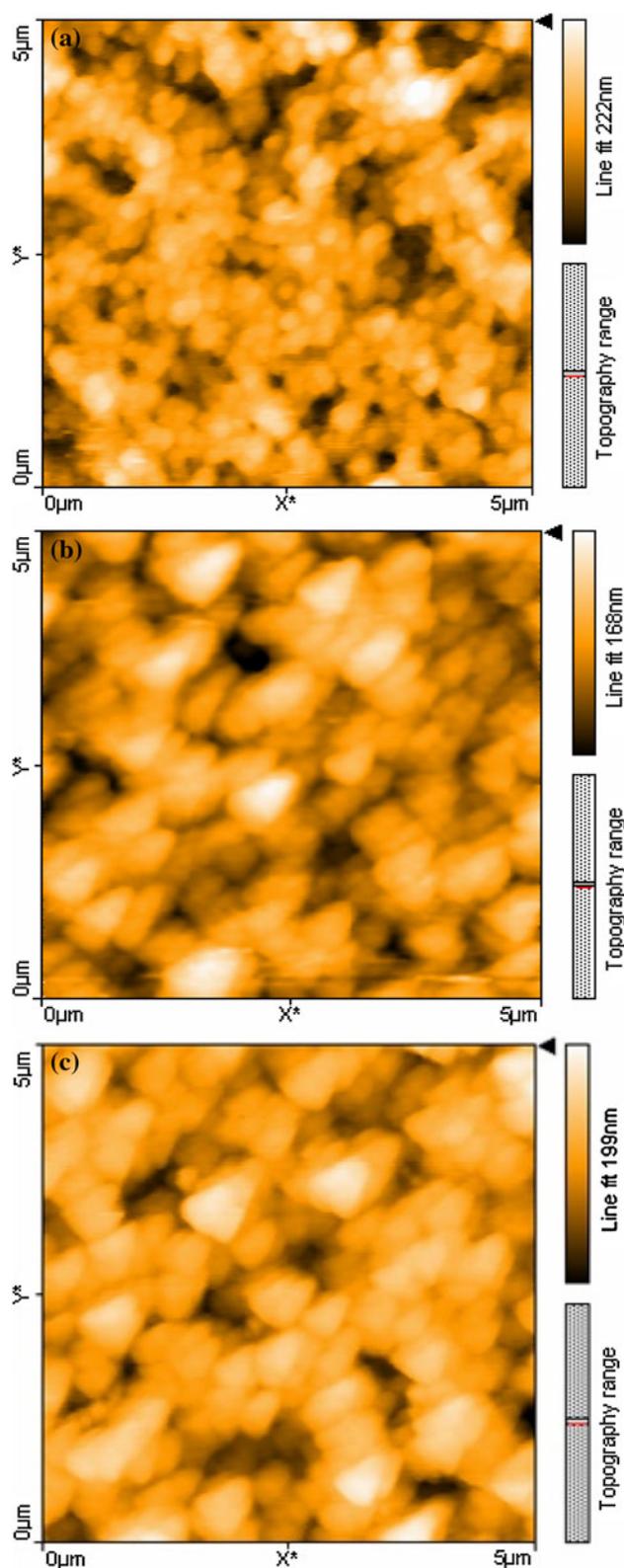


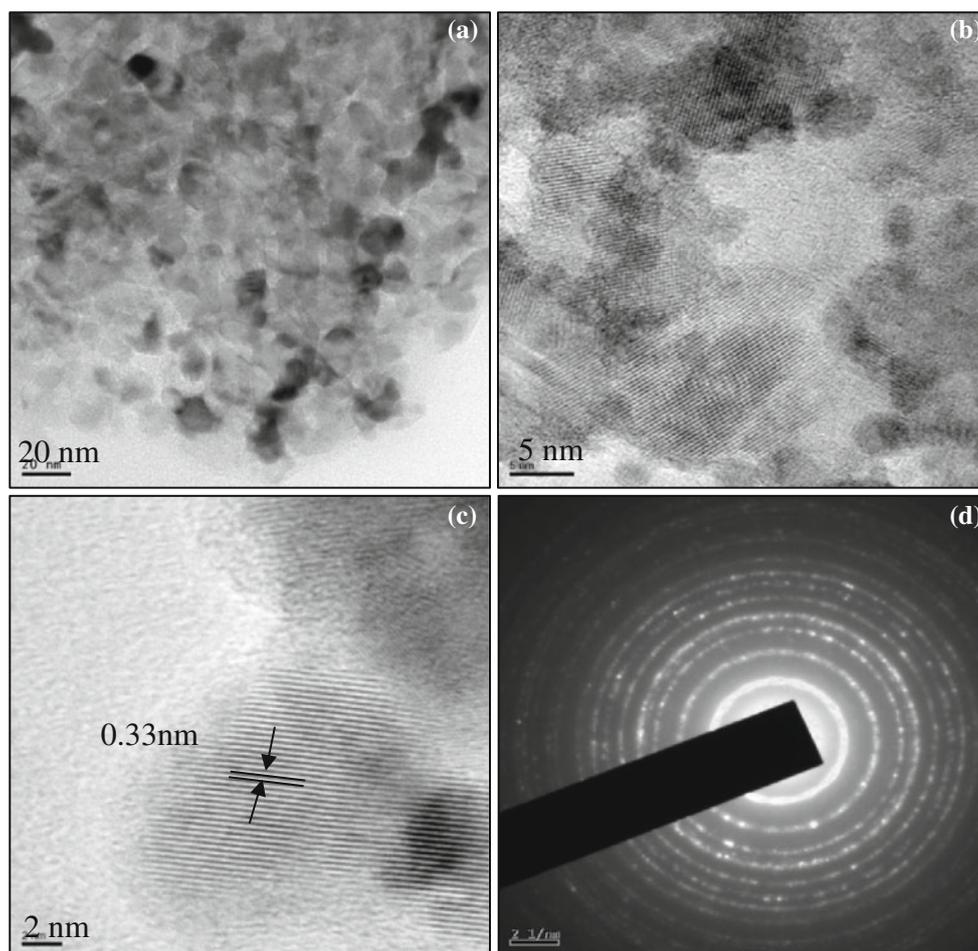
Fig. 2 AFM images of TiO<sub>2</sub> thin film annealed at a 400 °C, b 450 °C and c 500 °C

Investigated sections of wild roses showed that Cy 3, 5-diglucoside was the dominant anthocyanin detected in all three sections [25]. Tennakone et al. [8] studied cyanidin pigments from flowers. Cyanin dyes, extracted from blackberries, have been recently studied by Cherepy et al. using water-free ethylene glycol as solvent for  $I^-/I_3^-$ , and have reported an IPCE = 19 %. Recently, we have observed unusually high photocurrent yield in a system based on a natural cyanidin dye from pomegranate liquid, which is known to be a rich source of anthocyanin pigments. The high photocurrent was observed in an aqueous medium, yet, no desorption of the dye was noticeable. Cyanidin 3, 5-di-O-glucoside was the predominant constituent (375 mg/100 g), representing about 85 % of total content. Anthocyanin molecules with two or three adjacent hydroxyl groups, namely, the delphinidins and cyanidins, show higher yields as well as higher stability compared to the pelargonidins. This is attributed to the double binding involving the formation of a quinonoidal structure in the case of delphinidins and cyanidins. In contrast, the

pelargonidins have isolated hydroxyl groups, which produce only a single bond to the  $TiO_2$  [12]. In the present study  $TiO_2$  thin films have been prepared using dip coating method and  $TiO_2$  based natural dye sensitized solar cells have been fabricated and their characteristics have been studied.

## 2 Experimental

To prepare the photo-anode of dye sensitized solar cells, the ITO conducting glass sheet (Asahi Glass; Indium-doped  $SnO_2$ , sheet resistance: 15 U/square) was first cleaned in a detergent solution using an ultrasonic bath for 15 min, rinsed with double distilled water and then dried. The matrix sol was prepared by mixing 1.5 ml of titanium (IV) isopropoxide with 15 ml of isoproponal at room temperature and stirred for half an hour. Then 0.365 ml of glacial acetic acid is added drop wise and stirred vigorously for 2 h to obtain a homogeneous mixture of  $TiO_2$  sol. The



**Fig. 3** HRTEM micrograph of  $TiO_2$  nanocrystalline thin films annealed at 500 °C

prepared sol was deposited on the ITO glass plate by sol-gel dip coating method. The film was dried at 80 °C for 30 min in air and then annealed at 400, 450 and 500 °C in a muffle furnace. For table rose dye extract preparation, well cleaned flowers were mixed with 250 ml ethanol and were kept for 12 h at room temperature. Similarly for red rose extract preparation, the flowers were cut into small pieces. After removing the pollen grains they were soaked in ethanol (250 ml) and kept for 12 h. 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 fraction was separated and few drops of concentrated HCl was added so that the solution became deep red in colour (pH < 1). This was directly used as dye solution for sensitizing TiO<sub>2</sub> electrodes. The red rose and table rose dye were used for sensitizing TiO<sub>2</sub> electrodes.

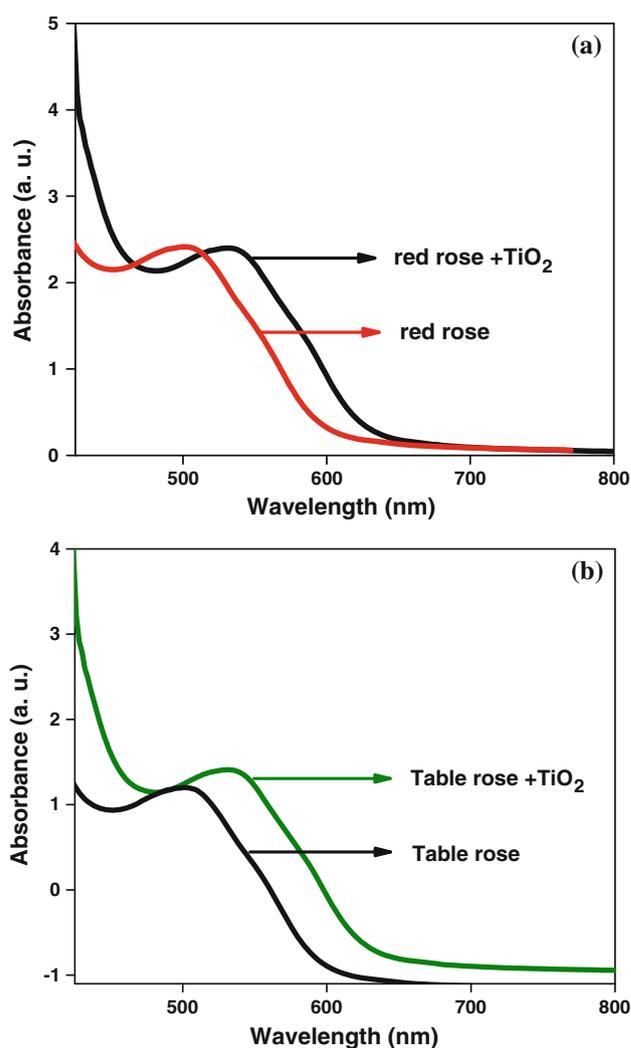
Crystallinity and phase analysis of the films were carried out using X-ray diffraction method (Rigaku Rint 2000 series) and transmission electron microscope (JEOL, JEM—2100). The surface topography of the film was analyzed by atomic force microscopy (Nanosurf easyscan) and transmission spectra has been recorded using UV-VIS-NIR spectrophotometer (Jasco V-570). Lithium iodide, iodine and acetonitrile purchased from Sigma Aldrich have been used as received for the preparation of electrolyte. The redox electrolyte with [I<sub>3</sub><sup>-</sup>]/[I<sup>-</sup>] 1:9 was prepared by dissolving 0.5 M LiI and 0.05 M I<sub>2</sub> in acetonitrile solvent. Since LiI is extremely hygroscopic, electrolytes were prepared in a dry room maintained at dew point of 60 °C. The counter electrode was prepared by using platinum chloride as follows: the H<sub>2</sub>PtCl<sub>6</sub> solution in isopropanol (2 mg/ml) was deposited onto the ITO glass by spin coating method. TiO<sub>2</sub> electrode annealed at 500 °C was immersed in the extracted dye solution at room temperature for 24 h in the dark. The electrode was then rinsed with ethanol to remove the excess dye present in the electrode and then the electrode was dried. The counter electrode was placed on the top of the TiO<sub>2</sub> electrode, such that the conductive side of the counter electrode faced the TiO<sub>2</sub> film with a spacer separating the two electrodes. The two electrodes were clamped firmly together using a binder clip. Now the prepared liquid electrolyte solution was injected into the space between the clamped electrodes. The electrolyte enters into the cell by capillary action. This resulted in the formation of sandwich type cell. Natural dye sensitized TiO<sub>2</sub> based solar cells have been fabricated with area of 0.25 cm<sup>2</sup>, and it was found that the cell efficiency was independent of cell area in this range as reported by Yamazaki et al. [7]. The J–V characteristics of the cell was recorded using a Keithley 4200-SCS meter. A xenon lamp source (Oriol, USA) with an irradiance of 100 mW/cm<sup>2</sup> was used to illuminate the solar cell (equivalent to AM1.5 irradiation).

### 3 Results and discussion

Figure 1 shows the diffraction pattern of the sol-gel prepared TiO<sub>2</sub> films, annealed at 400, 450 and 500 °C. A narrow peak at 25.35° corresponding to (101) reflection of the anatase phase of TiO<sub>2</sub> has been observed in the diffraction pattern. The crystal size has been calculated using Scherrer's formula [26].

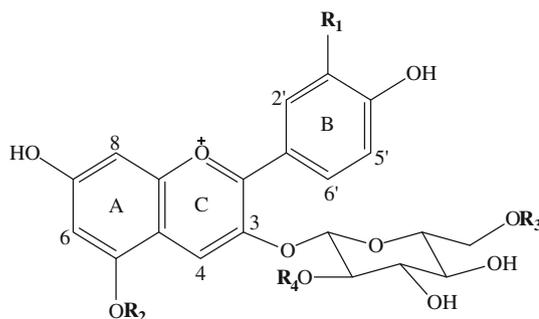
$$D = \frac{K\lambda}{\beta \cos\theta}$$

where, D is the grain size, K is a constant taken to be 0.94,  $\lambda$  (1.54 Å) is the wavelength of the X-ray radiation,  $\beta$  is the full width at half maximum and  $\theta$  is the angle of diffraction. The average grain size is found to be 18, 22 and 25 nm for the films annealed at 400, 450 and 500 °C. Grain size is found to increase with increase in annealing temperature. The annealing temperature facilitates the



**Fig. 4** Absorption spectra of **a** red rose and **b** table rose sensitized TiO<sub>2</sub> thin films (Color figure online)

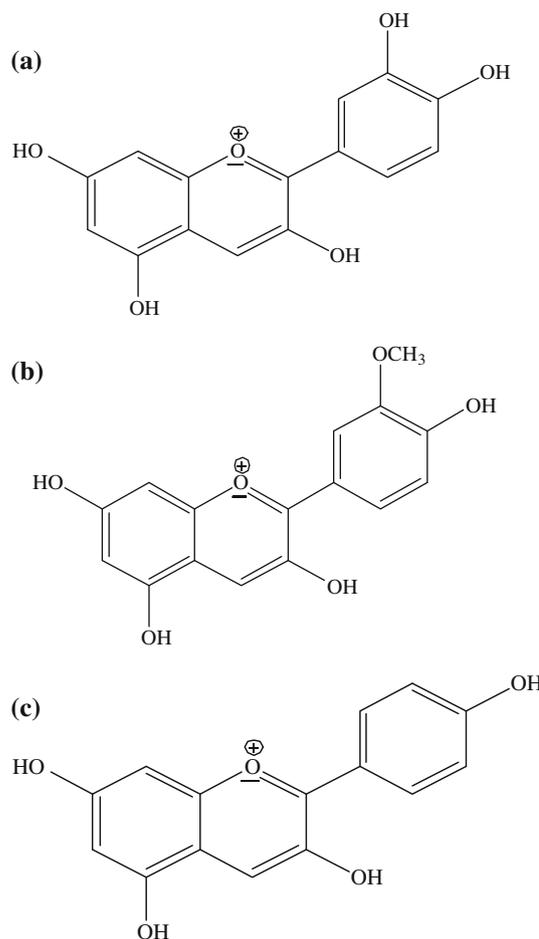
**Fig. 5** The eleven types of anthocyanins



- 1 pelargonidin 3-glucoside,  $R_{1,2,3,4} = H$
  - 2 cyanidin 3-glucoside,  $R_{2,3,4} = H, R_1 = OH$
  - 3 peonidin 3-glucoside,  $R_{2,3,4} = H, R_1 = OCH_3$
  - 4 pelargonidin 3,5-diglucoside,  $R_{1,3,4} = H, R_2 = \text{glucosyl}$
  - 5 cyanidin 3,5-diglucoside,  $R_{3,4} = H, R_1 = OH, R_2 = \text{glucosyl}$
  - 6 peonidin 3,5-diglucoside,  $R_{3,4} = H, R_1 = OCH_3, R_2 = \text{glucosyl}$
- (Additional *Rosa* anthocyanins)
- 7 cyanidin 3-rutinoside,  $R_{2,4} = H, R_1 = OH, R_3 = \text{rhamnosyl}$
  - 8 peonidin 3-rutinoside,  $R_{2,4} = H, R_1 = OCH_3, R_3 = \text{rhamnosyl}$
  - 9 cyanidin 3-sophoroside,  $R_{2,3} = H, R_1 = OH, R_4 = \text{glucosyl}$
  - 10 cyanidin 3-*p*-coumarylglucoside-5-glucoside,  $R_4 = H, R_1 = OH, R_2 = \text{glucosyl}, R_3 = \textit{p}$ -coumaryl
  - 11 peonidin 3-*p*-coumarylglucoside-5-glucoside,  $R_4 = H, R_1 = OCH_3, R_2 = \text{glucosyl}, R_3 = \textit{p}$ -coumaryl

subsequent crystal growth process, accompanied by the diffusion of titania species forming big sized anatase crystals and causing the merging of some adjacent mesopores. At the same time, the spatial confinement by mesopore arrays controls the formation and growth of anatase phase, leading to a more or less uniform distribution of  $TiO_2$  nanocrystals.

The atomic force microscope images of the prepared  $TiO_2$  films annealed at 400, 450 and 500 °C is shown in Fig. 2a–c. The particles are found to be of uniform size, dense and compact. The image indicates the nature of surface topography and it was found that as annealing temperature increases the roughness increases from 28 to 32 nm. The mesoporous structure of  $TiO_2$  film annealed at 500 °C was clearly observed from the AFM image. It can be seen that the particles are distributed homogeneously with a high degree of porosity consistent with a high surface area structure. High-resolution transmission electron microscopy was used to investigate the exact microstructure of  $TiO_2$  nanocrystalline films annealed at 500 °C. Figure 3a shows the closely-packed agglomeration of the uniform nanoparticles in the mesoporous structure, which displays the even monodispersity of mesopores. This accumulation of nanoparticles creates narrow channels that may serve as electronic injection membranes. It can be seen from Fig. 3b that the size of the nanoparticles is extremely uniform with a diameter of nearly 25 nm. This is in good agreement with the particle size calculated by the Scherrers formula. Figure 3c shows lattice fringes and the interplanar distance is measured to be 0.33 nm which



**Fig. 6** Chemical structure of **a** cyanidin, **b** pelargonidin and **c** peonidin

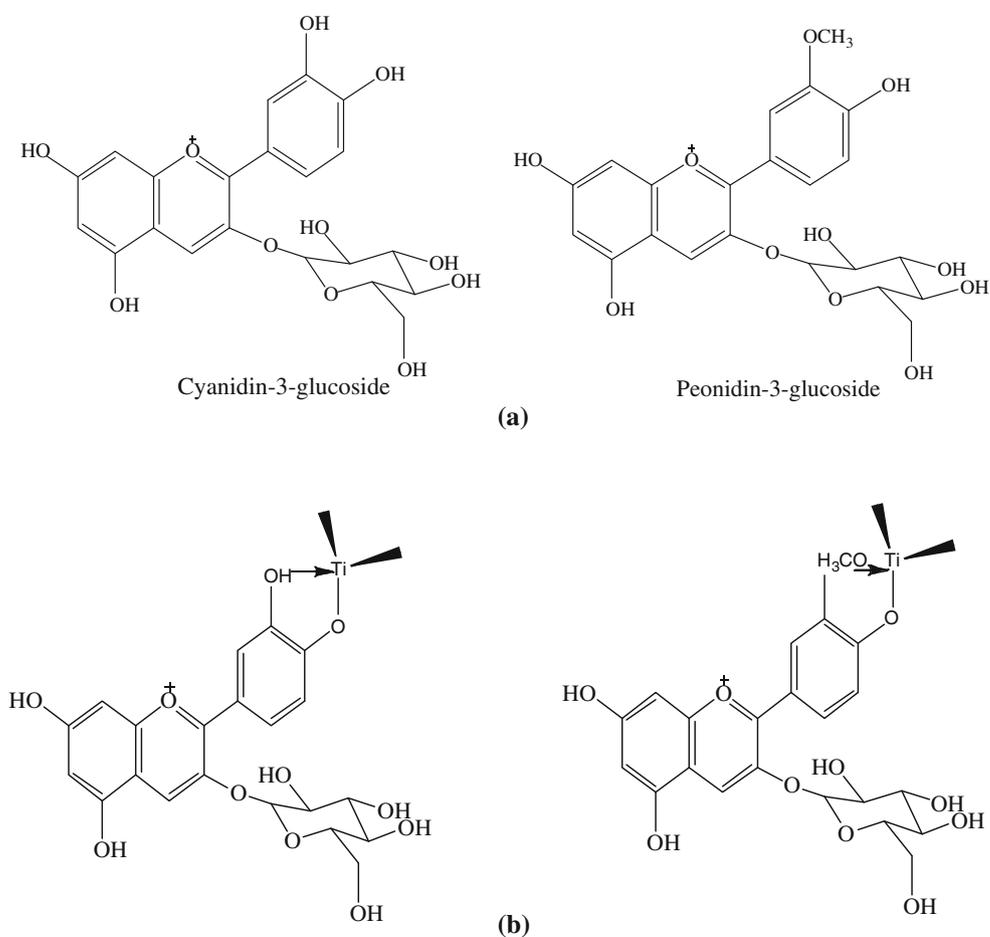
corresponds to the (101) lattice plane of anatase phase of nanocrystalline  $\text{TiO}_2$  thin film. Selective area electron diffraction pattern is used to learn about the crystal properties of a particular region. Figure 3d shows the selective area electron diffraction pattern of the nanocrystalline  $\text{TiO}_2$  thin film and the presence of rings with discrete spots suggest that the  $\text{TiO}_2$  nanocrystalline film is made of small particles of uniform size.

Figure 4a, b shows the absorption spectra of red rose and table rose extracts and the red rose and table rose sensitized  $\text{TiO}_2$  thin films. The maximum absorption for red rose is at 535 nm and that for table rose is at 530 nm. It is seen that the red rose has a maximum absorption coefficient that is about 15 times higher than that of the N-719 dye, which is generally used in high efficiency dye-sensitized solar cells. The absorption band of the dye adsorbed  $\text{TiO}_2$  semiconductor films is shifted to longer wavelength when compared to the absorption spectra of the dye solution as shown in Figs. 4a, b. The intensity of light absorption has been enhanced due to the interfacial Ti–O coupling between the anthocyanin molecule and the  $\text{TiO}_2$  molecule. Flower colour investigation carried out on roses so far have detected that eleven anthocyanins are present in them (Fig. 5) and

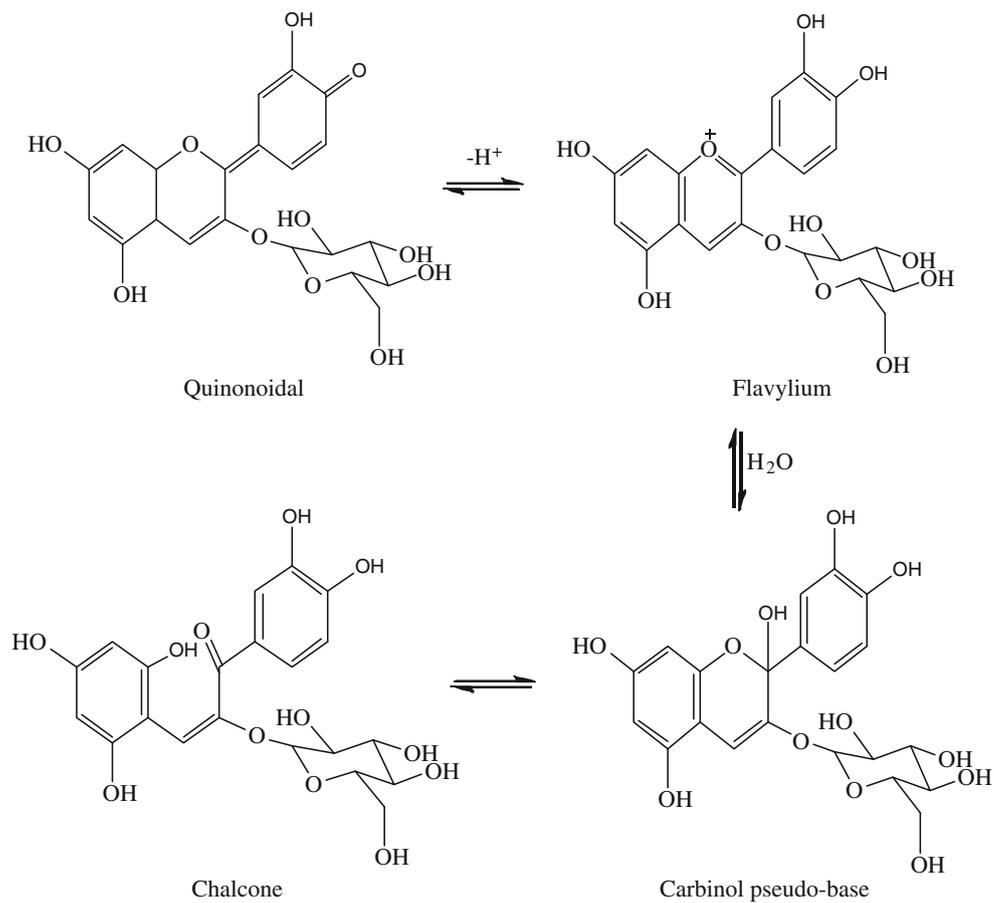
the most important are pelargonidin 3,5-di-*O*-glucoside, peonidin 3,5-di-*O*-glucoside and cyanidin 3,5-di-*O*-glucoside representing about 85 % of total content [25]. The chemical structure of anthocyanin mainly present in roses is illustrated in Fig. 6. Figure 7a, b shows that the complexation occurs between anthocyanin molecule and  $\text{TiO}_2$ . It can be seen that  $\text{TiO}_2$  particles can form bonding with hydroxyl group in cyanidin-3-glucoside and both hydroxyl and methoxy groups in peonidin-3-glucoside.

Anthocyanins are glycosylated polyhydroxyl derivatives of 2-phenylbenzopyrylium salts and are better known as flavylium salts. They are made up of three six-membered rings, that is, an aromatic ring bonded to heterocyclic aromatic ring that contains oxygen and carbon which is also bonded to another aromatic ring. It is said that anthocyanins can exist in various chemical forms, that is, quinonoidal base, flavylium cation, carbinol or pseudobase, and chalcone. Figure 8 depicts the different molecular structures of cyanidin-3-glucoside. Anthocyanins are mainly present as flavylium cations which are red in colour whereas quinonoidal base is blue in colour. Anthocyanins can exist in four chemical forms, that is, flavylium cation, anhydrous quinonoidal base, carbinol base, and chalcone.

**Fig. 7** Chemical structure of **a** cyanidin-3-glucoside and peonidin-3-glucoside **b** the binding between anthocyanin molecule and  $\text{TiO}_2$



**Fig. 8** Various chemical structure forms of cyanidin-3-glucoside

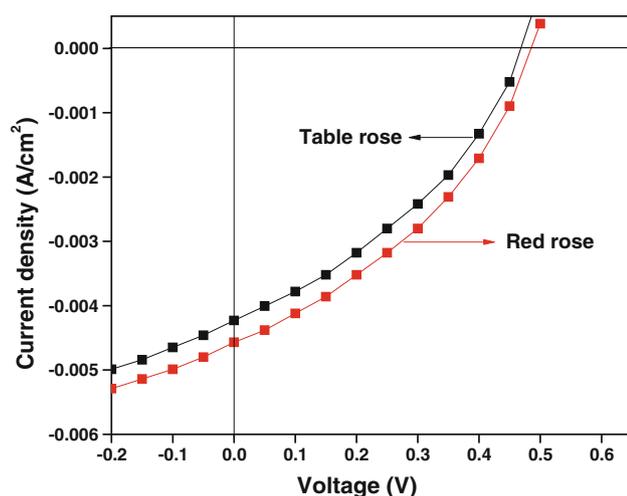


Carbinol base has no colour whereas the colour of chalcone is pale yellow. The equilibrium between the quinonoidal bases and carbinol has to take place via the flavylium cation. According to the literature [27], it is known that the flavylium cation is the stable form of anthocyanin. The oxonium ion in flavylium form is said to assist in the absorption of photons in the visible range [28]. Consequently, it can be said that the flavylium ion is the predominant ion present in red rose that can form bonding with  $Ti^{4+}$  ions more effectively [29].

It is generally accepted that the chemical adsorption of these dyes takes place due to the condensation of alcoholic-bound protons with the hydroxyl groups present on the surface of the nanostructured  $TiO_2$  thin films. The attachment of the dye to  $TiO_2$  surface stabilizes the excited state, and shifts toward the lower energy of the absorption maximum. Anthocyanin compounds exhibit a broad band in the visible region of the spectrum, ascribed to charge transfer transitions. After dye absorption, the absorption band is broadened and its maximum is red-shifted [18]. This may be due to the chemical adsorption of dye to the  $TiO_2$  surface. The effects were observed for both extracts of red and table roses.

The dye obtained from red and table roses are capable of promoting light harvesting and the electron injection into the semiconductor conduction band. The anthocyanins obtained by such extracts are capable of being chemically adsorbed to the semiconductor surface, sensitizing it to the visible region of the spectrum. The energy of the excited state of these dyes is also appropriate to promote the electron injection into the semiconductor conduction band, consequently, converting the sunlight into electrical output. The use of other natural sources as dye sensitizers demonstrate that only selected extracts promotes the energy conversion.

The J–V characteristics of  $TiO_2$  nanocrystalline thin films sensitized with natural dyes is shown in Fig. 9. The solar cell sensitized with red rose dye extract exhibit a power conversion efficiency of 0.81 %, with a short circuit current density ( $J_{sc}$ ) of 4.57  $mA/cm^2$ , open circuit voltage ( $V_{oc}$ ) of 0.485 V and fill factor (FF) of 0.36. The solar cell sensitized with table rose dye extract exhibited a power conversion efficiency of 0.67 % with a short circuit current density ( $J_{sc}$ ) of 4.23  $mA/cm^2$ , open circuit voltage ( $V_{oc}$ ) of 0.46 V and fill factor (FF) of 0.35. Based on investigation on the structure and properties of dye molecules, it was



**Fig. 9** J–V characteristics of dye sensitized TiO<sub>2</sub> based solar cells

found that the red rose extract possesses better photosensitization effect than that of table rose extract. This is due to the better interaction between the carbonyl and hydroxyl groups of anthocyanin molecule in red rose extract and the TiO<sub>2</sub> film than that of table rose extract. Huizhi Zhou et al. [30] have prepared extracts from different types of roses and have fabricated dye sensitized solar cells resulting in a power conversion efficiency of 0.26, 0.38, and 0.27 % for yellow, red and Chinese roses respectively. The obtained power conversion efficiency for table rose and red rose extracts of 0.67 and 0.81 % is the best efficiency reported so far for TiO<sub>2</sub> nanocrystalline thin film based rose dye sensitized solar cells.

#### 4 Conclusion

The nanocrystalline TiO<sub>2</sub> thin films have been prepared by sol–gel dip coating method. X-ray diffraction analysis reveals that the TiO<sub>2</sub> nanocrystalline thin films exhibit anatase phase. The dyes extracted from red rose and table rose strongly absorb visible light and have been found to be suitable for the use as sensitizer in solar cells. The efficiency of the fabricated dye sensitized solar cell using red rose extract is 0.81 % and table rose extract is 0.67 %. The use of natural dyes in dye sensitized solar cells is of low cost, environmentally friendly, renewable and clean source of energy.

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