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ORIGINAL PAPER

Utilization of natural anthocyanin pigments as photosensitizers for dye-sensitized solar cells

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Abstract Nanocrystalline TiO_2 thin films have been prepared by sol–gel dip coating method. The X-ray diffraction results showed that TiO_2 thin films annealed at 400, 450 and 500 °C are of anatase phase and the peak corresponding to the (1 0 1) plane is present in all the samples. The grain size of TiO_2 thin films was found to increase with increasing annealing temperature. The grain size is found to be 20, 26 and 38 nm for the films annealed at 400, 450 and 500 °C. TiO_2 thin films were sensitized by natural dyes extract from red cabbage and blue pea. It was found that the absorption peak of red cabbage extract is at about 545 nm while that of blue pea extract is at around 576 and 622 nm respectively. The dye sensitized TiO_2 based solar cell sensitized using red cabbage, exhibited a J_{sc} of 4.38 mA/cm^2, V_{oc} of 0.47 V, FF of 0.36 and η of 0.73 % and the solar cell sensitized using blue pea, exhibited a J_{sc} of 4.16 mA/cm^2, V_{oc} of 0.45 V, FF of 0.35 and η of 0.67 %. Natural dyes as sensitizers for dye sensitized solar cells are promising because of their environmental friendliness, low-cost production and designable polychrome modules.

Keywords TiO_2 thin film · Dye sensitized solar cell · AFM · HRTEM · Optical absorption

1 Introduction

Dye-sensitized solar cells have attracted much attention since reported first time by Gratzel and coworkers. The dye-sensitized solar cells is based on nanostructured, mesoporous metal oxide film, sensitized to harvest the visible light by an adsorbed molecular dye. The dye molecules absorb visible light and inject electrons from the excited state into the metal oxide conduction band. The injected electrons travel through the nanostructured film to the current collector and the dye is regenerated by an electron donor in the electrolyte solution. The dye-sensitized solar cell is fully regenerative and the electron donor is again obtained by electron transfer to the electron acceptor at the counter electrode [1]. Attempts are continuously being made to promote the adsorption of dye to harvest more solar light and smoothen the progress of transport of photo excited electrons.

Several organic dyes and organic metal complexes have been employed to sensitize nanocrystalline TiO_2 semiconductors and one of the most efficient sensitizers is the transition metal coordination compound, ruthenium polypiridyl complex. This is because the complex has intense charge-transfer absorption in the whole visible range, a long excitation lifetime and highly efficient metal-to-ligand charge transfer. However, ruthenium-based compounds are relatively expensive, and organic dyes with similar characteristics and even higher absorption coefficients have recently been reported [2]. Organic dyes used in the dye sensitized solar cells often bear a resemblance to the dyes found in natural products [3]. In nature, some fruits,

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flowers, leaves, and so on show various colors and contain several pigments that can be easily extracted and then employed in dye-sensitized solar cells. Unlike artificial dyes, the natural dye is easily available, easy to prepare, low cost, non-toxic, environmentally friendly and fully biodegradable [4]. In most cases, their photo activity is due to the presence of anthocyanin family [5–7]. Anthocyanins from strongly colored fruits, leaves and flowers are capable of attaching to TiO_2 surface and inject electrons into the conduction band of TiO_2 [8, 9]. In this work, we have made an attempt to use natural dyes extracted from red cabbage and blue pea as sensitizers in TiO_2 based dye sensitized solar cells. Blue pea flowers are abundant in tropical countries and rich in anthocyanins. Carbonyl and hydroxyl groups present in the anthocyanin molecule can be bound easily to the surface of a porous TiO_2 film [10]. As reported anthocyanins from various plants give different sensitizing performances. Two anthocyanins having different absorption characteristics would give an even more synergistic effect compared to the mixed anthocyanin–chlorophyll dye as reported by Kumara et al. [11].

2 Experimental

Fresh red cabbage was cut into very small pieces and then soaked in 100 ml of ethanol at room temperature for 24 h and the solid residues were filtered out. Similarly for blue pea flower extract preparation, well cleaned flowers were mixed with 250 ml ethanol and were kept for 24 h at room temperature. Then residual parts were removed by filtration. The filtrate obtained from red cabbage and blue pea 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 ($pH < 1$). Then, the dye solution was stored at 4 °C before use.

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 1.1 ml of titanium isopropoxide with 15 ml of isoproponal at room temperature and stirred for half an hour. Then 0.22 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 prepared sol was deposited on the ITO glass 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. The red cabbage and blue pea dye solution was used for sensitizing TiO_2 electrodes.

The structural properties of the films have been studied using X-ray diffraction method (Rigaku Rint 2000 series). The surface topography of the film has been analyzed using atomic force microscope (nano surf easy scan2). High-resolution transmission electron microscope images have been recorded using transmissioin electron microscope (JEOC, JEM—2100). The transmittance spectra of the films have been recorded using 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 $[I_3^-]/[I^-]$ 1:9 was prepared by dissolving 0.5 M LiI and 0.05 M I_2 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 using platinus chloride as follows: the H_2PtCl_6 solution in isopropanol (2 mg/ml) was deposited onto the ITO glass by spin coating method. TiO_2 film annealed at 500 °C has been used for the fabrication of solar cell. TiO_2 electrode 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_2 electrode, such that the conductive side of the counter electrode faces the TiO_2 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_2 based solar cells have been fabricated with area of nearly 0.25 cm^2, and it was found that the cell efficiency was independent of cell area in this range as reported by Yamazaki et al. [12]. The J–V characteristics of the cell was recorded using a Keithley 4200-SCS meter. A xenon lamp source (Oriel, USA) with an irradiance of 100 mW/cm^2 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_2 films, annealed at 400, 450 and 500 °C. A narrow peak at 25.35° corresponding to (1 0 1) reflection of the anatase phase of TiO_2 has been observed in the diffraction pattern. The grain size has been calculated using Scherrer's formula.

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

where, D is the grain size, K is a constant taken to be 0.94, λ is the wavelength of the X-ray radiation, β is the full width at half maximum and θ is the angle of diffraction. The average grain size was found to be 20, 23 and 26 nm for the films annealed at 400, 450 and 500 °C respectively. Grain size is found to increase with increase in annealing temperature. The annealing temperature facilitates the subsequent crystal growth process, accompanied by the diffusion of titania species forming big sized anatase crystals and causing the merge 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 titania nanocrystals.

The atomic force microscope images of the prepared TiO_2 films annealed at 400, 450 and 500 °C are shown in Fig. 2a–c. The roughness is found to be 19, 27 and 32 nm for the films annealed at 400, 450 and 500 °C respectively. 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. The mesoporous structures of TiO_2 film has been used for dye-sensitized solar cells as discussed below. Figure 3 shows the high-resolution transmission electron microscope images of the TiO_2 thin film annealed at 500 °C. Figures 3a, b shows the presence of close-packed agglomeration of uniform sized nanoparticles which causes the mesoporous structure. This accumulation of nanoparticles creates narrow channels that may serve as electronic injection membranes. The mesoporous structure, which provides a large surface area for adsorbing the dye, has been achieved in the present study, although no polymer was added to make pores. The prepared TiO_2 films showed good mechanical strength, had good adherence to the substrate and could not be easily erased by hand. Figure 3c shows the lattice fringes and the interplanar distance has been calculated using the fringes and is found to be 0.34 nm which corresponds to (1 0 1) lattice plane of anatase phase of nanocrystalline TiO_2 thin films.

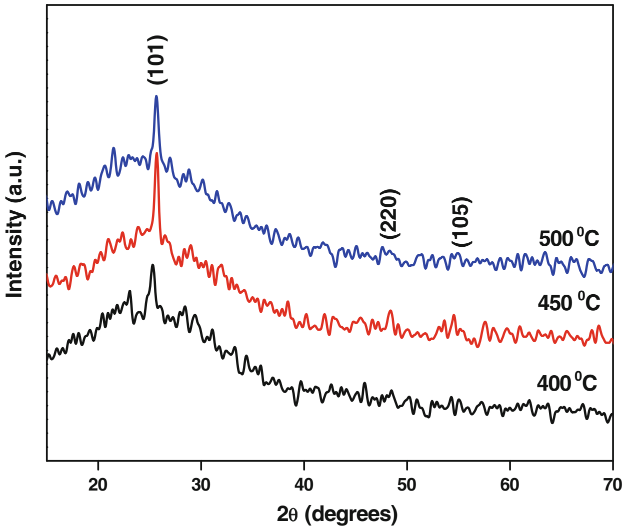


Fig. 1 X-ray diffraction pattern of nanocrystalline TiO_2 thin films

Figure 4 shows the absorption spectra of TiO_2 and red cabbage sensitized TiO_2 thin film. It exhibits a strong absorption band at 545 nm. Red cabbage contains several anthocyanins having different substituents and functional groups. Red cabbage anthocyanins are mostly in the form of glycosides and they have sugar molecules chemically attached to them. Some have acyl functional groups or have acyl functional group in combination with sugar molecules. If the acyl group is attached to an –OH group, it would form an ester linkage. The acyl groups can contribute greatly to color stability. The compounds in red cabbage are essentially cyanidin glucosides and molecules derived from them. They are cyanidin-3-glucoside, cyanidin-3,5-diglucoside, and several others (mainly cyanidin-3-(sinapoyl) diglucoside). The chemical structure of the cyanidin-3-(sinapoyl) diglucoside-5-glucoside present in redcabbage shown in Fig. 5a, b shows the complexation between anthocyanin and TiO_2 molecules. This 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 [13].

Figure 6 shows the absorption spectra of TiO_2 and blue pea sensitized TiO_2 thin film. The visible absorption bands of blue pea correspond to band I of the B-ring of hydroxyl cinnamoyl system of anthocyanin. These spectral characteristics of blue pea suggest that it contains ternatins on the B-ring that are substituted with a series of chains with alternating Dglucosyl and p-coumaryl units [14, 15] and flavonol glycosides [16, 17]. The visible spectrum of blue pea may be attributable to the equilibrium mixtures of red flavylium cations which gives rise to a small shoulder at 543 nm and the two tautomers of neutral blue quinonoidal bases which gives rise to the two absorption bands at 576 and 622 nm. Terahara et al. [14] and Yoshida et al. [18] have suggested that ternatin of blue pea in acid solution forms intramolecular complex with Ti^{4+} ions. The chemical structure of the ternatin present in blue pea is shown in Fig. 7. This has a maximum absorption coefficient that is 17 times higher than that of the N-719 dye, which is generally used in high efficiency dye-sensitized solar cells.

The difference in the absorption characteristics of red cabbage and blue pea extract is due to the presence of different type of anthocyanins and colors of the extracts. The anthocyanin obtained from blue pea is ternatin while those from red cabbage are delphinidin and cyanidin complexes [10]. The red cabbage dye absorbed TiO_2 film

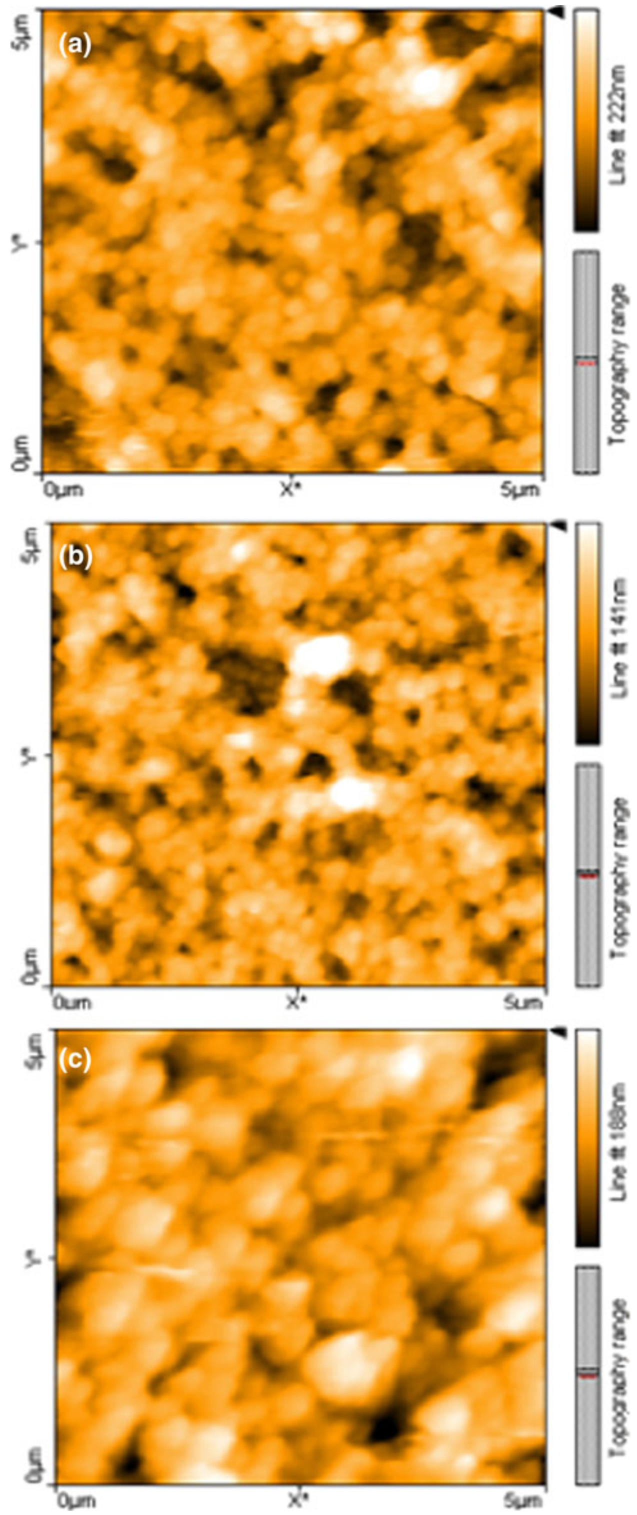


Fig. 2 AFM images of nanocrystalline TiO_2 thin films annealed at (**a**) 400, (**b**) 450 and (**c**) 500 °C

appeared in deep purple colour and the blue pea dye absorbed TiO_2 film appeared in light blue colour. In case of both the dyes the absorption band of the dye adsorbed TiO_2 semiconductor film is found to be shifted to longer wavelength when compared to the absorption spectra of the dye solution as shown in Figs. 4 and 6 [19, 20]. The intensity has been observed to be enhanced due to the interfacial Ti–O coupling between the dye molecule and the TiO_2 molecules. It is generally accepted that the chemical adsorption of these dye takes place due to the

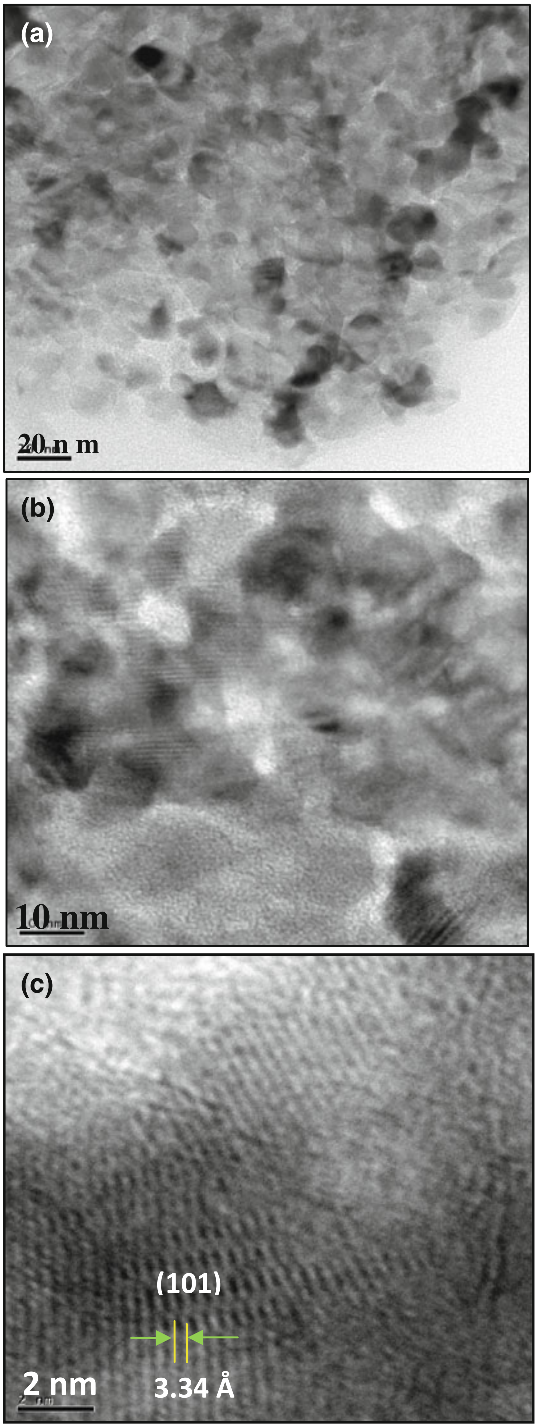


Fig. 3 **a** TEM image **b**, **c** HRTEM images of 500 °C annealed TiO_2 thin film

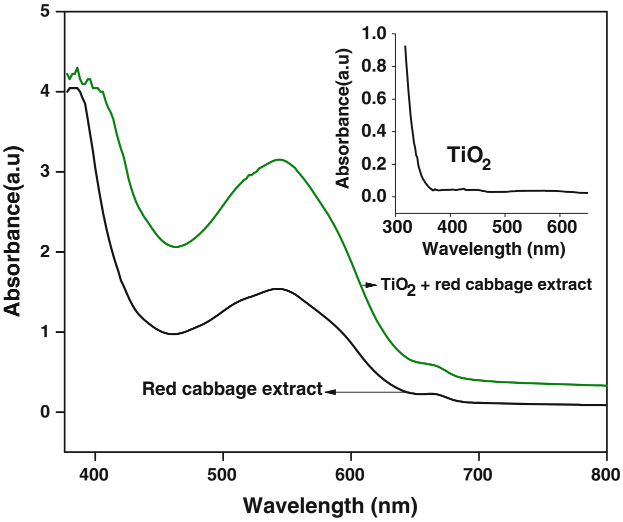


Fig. 4 Absorption spectra of red cabbage and red cabbage sensitized TiO_2

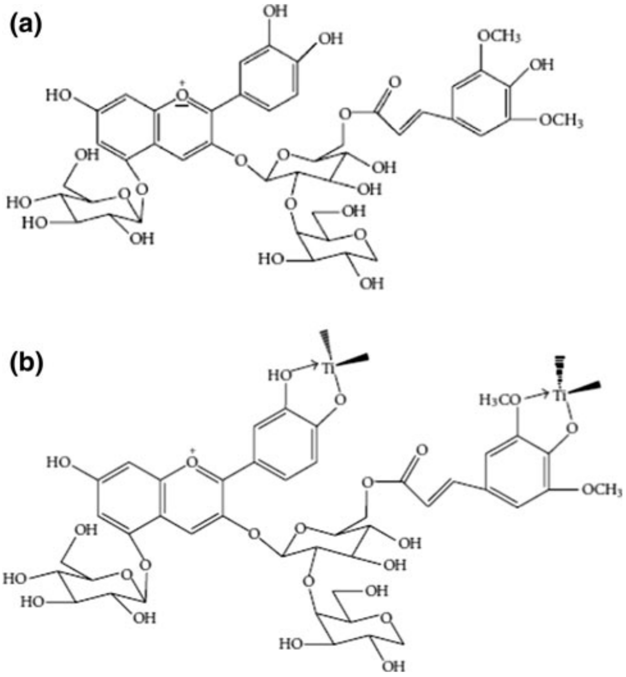


Fig. 5 **a** Chemical structure of cyanidin-3-(sinapoyl) diglucoside-5-glucoside and **b** complexation between anthocyanin and TiO_2 molecules

condensation of alcoholic-bound protons with the hydroxyl groups present on the surface of the nanostructured TiO_2 thin films [21]. This chemical attachment affects the energy levels of the highest occupied molecular level (HOMO) and the lowest unoccupied molecular level (LUMO) of the dye molecule [22], which eventually affects the band gap of these materials and this results in a shift in the absorption band of the absorption spectra.

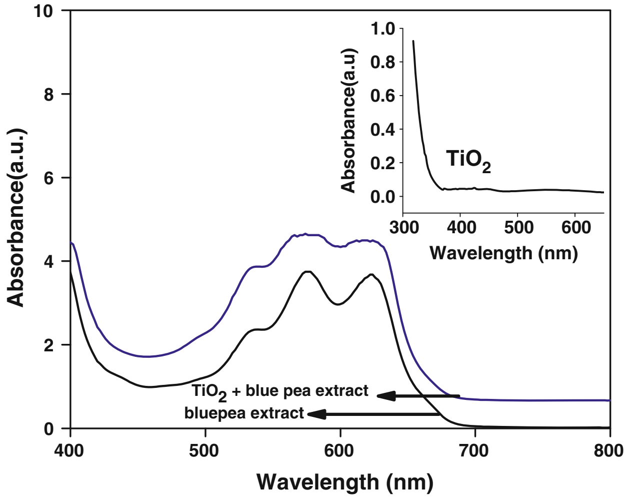
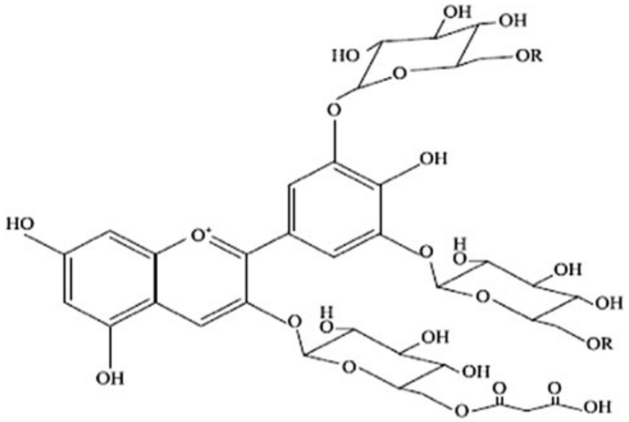


Fig. 6 Absorption spectra of blue pea and blue pea sensitized TiO_2



Ternatin	R
T-A1	-CGCG or –CGCG
T-A2	-CGCG or –CG
T-B1	-CGCG or –CGC
T-B2	-CGC or –CG
T-D1	-CGC or CGC
T-D2	-CGC or -C

where C = p-Coumaric acid and G = glucose

Fig. 7 Chemical structure of ternatin

Figure 8 a–d shows the FTIR spectra of red cabbage, red cabbage sensitized TiO_2, blue pea and blue pea sensitized TiO_2 nanocrystalline thin films. The spectra have been recorded using FTIR 1600 infrared spectrophotometer, operating in the wave number range 800–4,400 cm^{-1}. For the red cabbage extract the bands in the region of 1,641 cm^{-1} represents the amide group and the bands in the regions 2,904, 2,978, 3,078 cm^{-1} represents the C–H bonding and a broad sharp peak is obtained in the region 3,523–3,255 cm^{-1} which corresponds to the hydrogen bonding. The red cabbage sensitized TiO_2 nanocrystalline thin films shows a peak at 1,435 cm^{-1} which corresponds to the absorption band of TiO_2 molecules. Similar peaks were obtained for blue pea extracts also. For blue pea sensitized TiO_2 nanocrystalline thin films the absorption band of TiO_2 occurs at a wavelength of 1,442.76 cm^{-1} [23]. The bands ranging from 2,887 cm^{-1} to 2,974 cm^{-1} correspond to the C–H stretching due to methyl and methylene groups and the bands ranging from 3,200 to 3,400 cm^{-1} correspond to the hydrogen bonding in the dye.

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 cabbage dye extract exhibited a power conversion efficiency of 0.73 % with a short circuit current density (J_{sc}) of 4.38 mA/cm^2, open circuit voltage (V_{oc}) of 0.47 V and fill factor (FF) of 0.36. The solar cell sensitized with blue pea dye extract exhibited a power conversion efficiency of 0.67 % with a short circuit current density (J_{sc}) of 4.16 mA/cm^2, open circuit voltage (V_{oc}) of 0.45 V and fill factor (FF) of 0.35. The photovoltaic properties of the dye sensitized solar cells sensitized by the dye extract from red cabbage and blue pea were compared with that of the reported values and are as shown in Table 1. The reason for better efficiency of red cabbage sensitized solar cell than that of blue pea extract based solar cell is that the molecular structure of cyanidin-3-(sinapoyl) diglucoside-5-glucoside in red cabbage provides two binding sites with Ti^{4+} ions [24]. It is understood that there is an increase in charge density of anthocyanin molecule upon complexation with Ti^{4+} ion and thus, enables electronic coupling for charge injection [25]. Therefore, it can be inferred that the strong electronic coupling for charge injection occurs in cyanidin-3-(sinapoyl) diglucoside-5-glucoside of red cabbage which leads to better performance than that of blue pea.

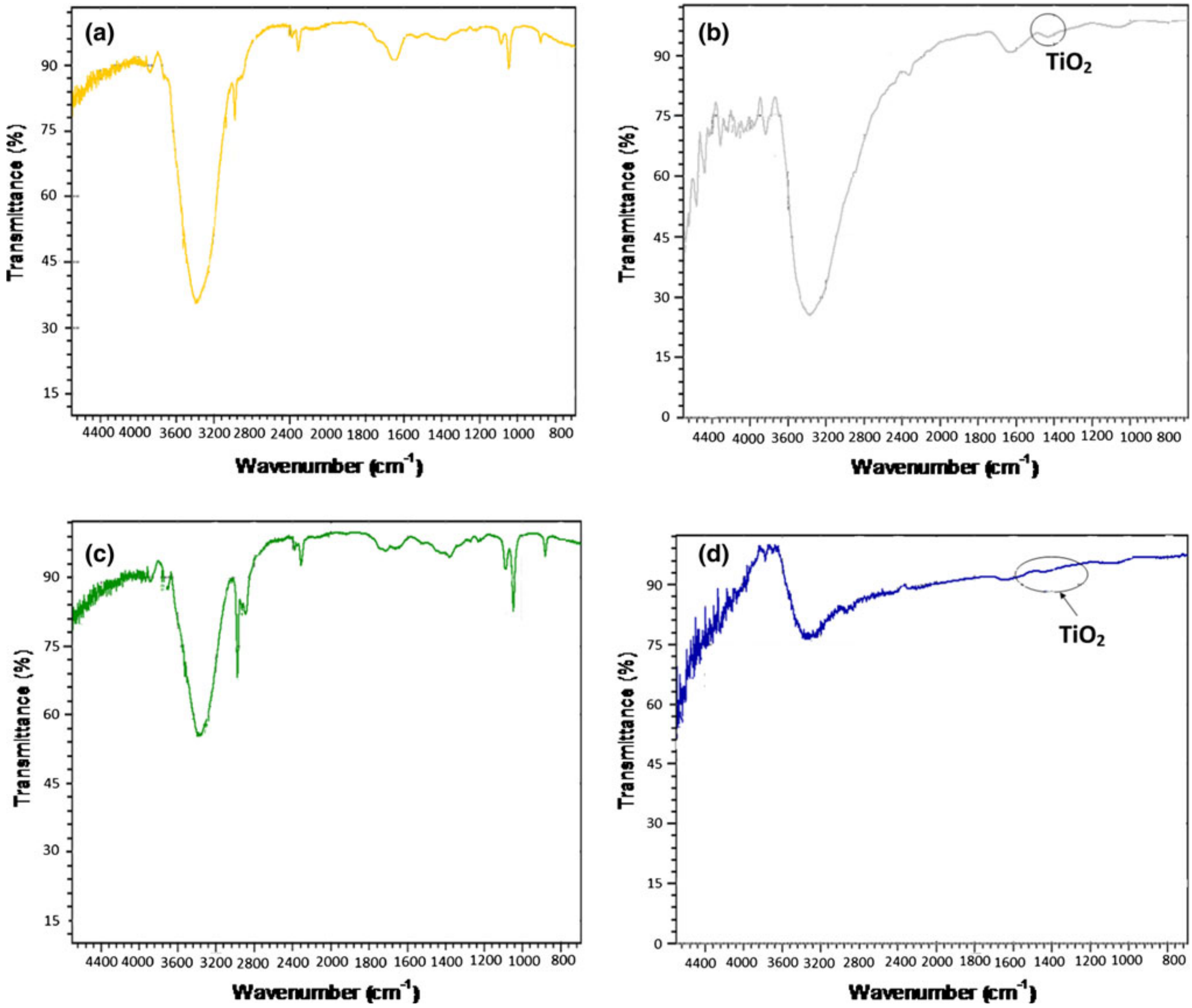


Fig. 8 FTIR spectra of (**a**) red cabbage extract, (**b**) red cabbage sensitized TiO_2,(**c**) blue pea extract and (**d**) blue pea sensitized TiO_2

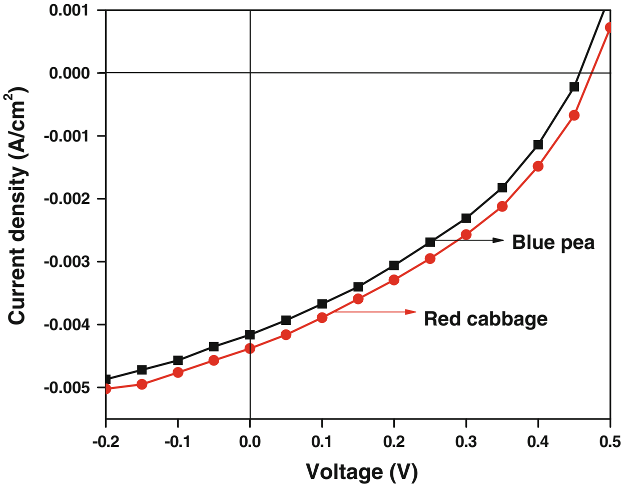


Fig. 9 J–V characteristics of red cabbage and blue pea sensitized TiO_2 solar cells

Table 1 Photoelectrochemical cell parameters of the cells sensitized with natural dye extracts

Dye	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η %	Ref.
Red cabbage	4.38	0.47	0.36	0.73	–
Blue pea	4.16	0.45	0.35	0.67	–
Blue pea	0.37	0.37	0.33	0.05	[11]
Red cabbage	0.35	0.54	0.65	0.13	[10]
Blue pea	0.27	0.49	0.76	0.10	[10]
Red cabbage	0.89	0.60	0.32	0.17	[11]

4 Conclusion

Nanocrystalline TiO_2 thin films have been prepared by sol-gel dip coating method. X-ray diffraction analysis reveals that the TiO_2 nanocrstalline thin films exhibit anatase phase. The dyes extracted from blue pea exhibit absorption band between 576 and 622 nm and red cabbage exhibit absorption at 545 nm respectively and can be used as sensitizers in dye sensitized solar cells. Even though the efficiencies obtained are not comparable with the efficiencies of commercial solar cells, the study shows the potential of natural dye to be used as sensitizers, and may be an initiative for more focused research in this direction.

References

1. Chiba Y, Islam A, Watanabe Y, Komiya R, Koide N, Han LY (2006) Dye-sensitized solar cells with conversion efficiency of 11.1%. Jpn J Appl Phys 45:L638–L640
2. Hao Sancun, Wu Jihuai, Huang Yunfang, Lin Jianming (2006) Natural dyes as photosensitizers for dye-sensitized solar cell. Sol Energy 80:209–214
3. Go′mez-Ortı′z NM, Va′zquez-Maldonado IA, Pe′rez-Espadas AR, Mena-Rejo′n GJ, Azamar-Barrios JA, Oskam G (2010) Dye-sensitized solar cells with natural dyes extracted from achiote seeds. Sol Energy Mater Sol Cells 94:40–44
4. Calogero Giuseppe, Di Marco Gaetano (2008) Red Sicilian orange and purple eggplant fruits as natural sensitizers for dye-sensitized solar cells. Sol Energy Mater Sol Cells 92:1341–1346
5. Cherepy NJ, Smestad GP, Gratzel M, Zhang JZ (1997) Ultrafast electron injection: implications for a photoelectrochemical cell utilizing an anthocyanin dyesensitized TiO_2 nanocrystalline electrode. J Phys Chem B 101:9342–9351
6. Smestad GP (1998) Education and solar conversion: demonstrating electron transfer. Sol Energy Mater Sol Cells 55:157–178
7. Dai Q, Rabani J (2002) Photosensitization of nanocrystalline TiO_2 films by anthocyanin dyes. J Photochem Photobiol A 148:17–24
8. Rossetto M, Vanzani P, Mattivi F, Lunelli M, Scarpa M, Rigo A (2002) Synergystic antioxidant effect of catechin and malvidin 3-glucoside on free radicalinitiated peroxidation of linoleic acid in micelles. Arch Biochem Biophys 408:239–245
9. Markakis P (1982) Anthocyanins as food color. Academic Press, New York
10. Wongchareea Khwanchit, Meeyoo Vissanu, Chavadej Sumaeth (2007) Solar Dye-sensitized solar cell using natural dyes extracted from rosella and blue pea flowers. Sol Energy Mater Sol Cells 91:566–571
11. Kumara GRA, Kanebo S, Okuya M, Onwona-Agyeman B, Konno A, Tennakone K (2006) Shiso leaf pigments for dye-sensitized solid-state solar cell. Sol Energy Mater Sol Cells 90:1220–1226
12. Eiji Yamazaki, Masaki Murayama, Naomi Nishikawa, Noritsugu Hashimoto, Masashi Shoyama, Osamu Kurita (2007) Utilization of natural carotenoids as photosensitizers for dye-sensitized solar cells. Sol Energy 81:512–516
13. Senthil TS, Muthukumarasamy N, Velauthapillai Dhayalan, Agilan S, Thambidurai M, Balasundaraprabhu R (2011) Natural dye (cyanidin 3-O-glucoside) sensitized nanocrystalline TiO_2 solar cell fabricated using liquid electrolyte/quasi-solid-state polymer electrolyte. Renew Energy 36:2484–2488
14. Terahara N, Oda M, Matsui T, Osajima Y, Saito N, Toki K, Honda T (1996) Five new anthocyanins, ternatins A3, B4, B3, B2 and D2, from Clitoria trenatea flowers. J Nat Prod 59(2):139–144
15. Kazuma K, Noda N, Suzuki M (2003) Flavonoid composition related to petal color in different lines of *Clitoria ternatea*. Phytochemistry 64:1133–1139
16. Kazuma K, Noda N, Suzuki M (2003) Malonylated flavonol glycosides from the petals of *Clitoria ternatea*. Phytochemistry 62(2):229–237
17. Bagchi D, Sen CK, Bagchi M, Atalay M (2004) Anti-angiogenic, antioxidant, and anti-carcinogenic properties of a novel anthocyaninrich berry extract formula. Biochemistry 69:75–80
18. Yoshida K, Mori M, Kawachi M, Okuno R, Kameda K, Kondo T (2003) A UV-B resistant polyacylated anthocyanin HBA, from blue petals of morning glory. Tetrahedron Lett 44:7875–7880
19. Ma Hongchao, Yue Lixia, Yu Chunling, Dong Xiaoli, Zhang Xinxin, Xue Mang, Zhang Xiufang, Fu Yinghuan (2012) Synthesis, characterization and photocatalytic activity of Cu-doped Zn/ZnO photocatalyst with carbon modification. J Mater Chem 22:23780–23788
20. Meng Fanke, Hong Zhanglian, Arndt James, Li Ming, Zhi Mingjia, Yang Feng, Wu Nianqiang (2012) Visible light photocatalytic activity of nitrogen-doped $La_2Ti_2O_7$ nanosheets originating from band gap narrowing. Nano Res 5:213–221
21. Fernando JMRC, Senadeera GKR (2008) Natural anthocyanins as photosensitizers for dye-sensitized solar devices. Curr Sci 95:663–666

22. Sheng Meng, Jun Ren, Efthimios Kaxiras (2008) Natural dyes adsorbed on TiO_2 nanowire for photovoltaic applications: enhanced light absorption and ultrafast electron injection. Nano Lett 8(10):3266–3272
23. de Faria Emerson Henrique, Marçal Alex Lemes, Nassar Eduardo José, Ciuffi Katia Jorge, Calefi Paulo Sergio (2007) Sol-Gel TiO_2 thin films sensitized with the mulberry pigment cyanidin. Mater Res 10(4):413–417
24. Buraidah MH, Teo LP, Yusuf SNF, Noor MM, Kufian MZ, Careem MA, Majid SR, Taha RM, and Arof AK TiO_2/Chitosan-NH4I(+I2)-BMII-based dye-sensitized solar cells with anthocyanin dyes extracted from black rice and red cabbage. doi: 10.1155/2011/273683
25. Calogero G, DiMarco G, Caramori S, Cazzanti S, Argazzi R, Bignozzi CA (2009) Natural dye senstizers for photoelectrochemical cells. Energy Environ Sci 2:1162–1172