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Research Article

Performance of Natural Dye Extracted from Annatto, Black Plum, Turmeric, Red Spinach, and Cactus as Photosensitizers in TiO_2NP/TiNT Composites for Solar Cell Applications

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This paper is aimed at how to select, extract, and characterize natural dyes and to use them as sensitizers in dye-sensitized solar cells (DSSCs). Dyes obtained from fresh sources of annatto fruits, black plums, cactus fruits, turmeric roots, and red spinach leaves were used as sensitizers. The dye pigments were analyzed using UV-Vis spectrophotometer and FT-IR for the characterization of their spectral properties. The combination from Titanium dioxide paste with the powdered nanotubes was used as photoanodes for DSSCs. The photovoltaic properties of the DSSCs such as efficiency, fill factor, open-circuit voltage, and short circuit current were studied using a standard illumination of air-mass 1.5 global (AM 1.5 G) having an irradiance of $100\,\mathrm{mW/cm^2}$. The highest power conversion efficiencies (η) of 0.7% was achieved for the DSSCs fabricated using dye extracted from annatto fruits and 0.4% each for dyes extracted from black plum fruits and cactus fruits, respectively. The widespread accessibility of these fruits, roots, and leaves and ease of extraction of dyes from these ordinarily available natural resources render them unique and low-cost candidates for solar cell fabrication.

1. Introduction

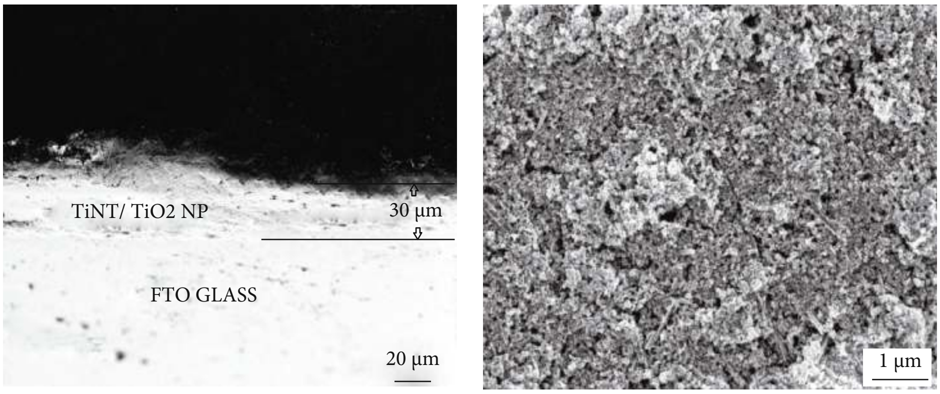
The emergence of dye-sensitized solar cells (DSSCs) was pioneered by O'Regan and Grätzel in 1991 [1]. The dye as a sensitizer in a DSSC plays a key role in absorbing sunlight and transforming solar energy into electric energy. DSSCs belong to the third generation in the photovoltaic devices, and they also hold a good relation for the low-cost conversion of solar energy to electricity due to the rather simpler materials and lower cost of fabrication [2]. The essential need for the innovative selection of materials for the photosensitizing applications led to the production and improvement in DSSCs [3–5]. These cells are based on the coating of the glass with a suitable nanostructured, mesoporous metal oxide films anchored to the visible light with the aid of adsorbed molecular dye. The injection of the electrons forms the excited states of the dye to the conduction band of the metal oxides. The passing electrons travel along the current-carrying collector, while the dye gets regenerated by the electron donor within the electrolyte solution. Usually, the dyes are generated from plant leaves, fruits, and other naturally occurring products. Several papers have been reported in this regard [6–16]. Although metal complex-based DSSCs have provided a relatively high efficiency, their limited resources and costly production remain to be a major disadvantage. Recently, organic dyes with related characteristics that of Ru-based compound having higher absorption coefficients have been reported [17–20]. Organic dyes used in the DSSC often show similarity to natural dyes that are found in plant leaves, fruits, and other natural products. Employing natural dyes as sensitizers DSSC is emerging as a prevalent area of research due to their low cost, nontoxicity, and far-reaching biodegradation. Thus far, numerous natural dyes have been employed as sensitizers in DSSC [21–26]. In the recent past,

(a) Annatto seeds (b) Black plum fruits

(c) Turmeric roots (d) Red spinach leave

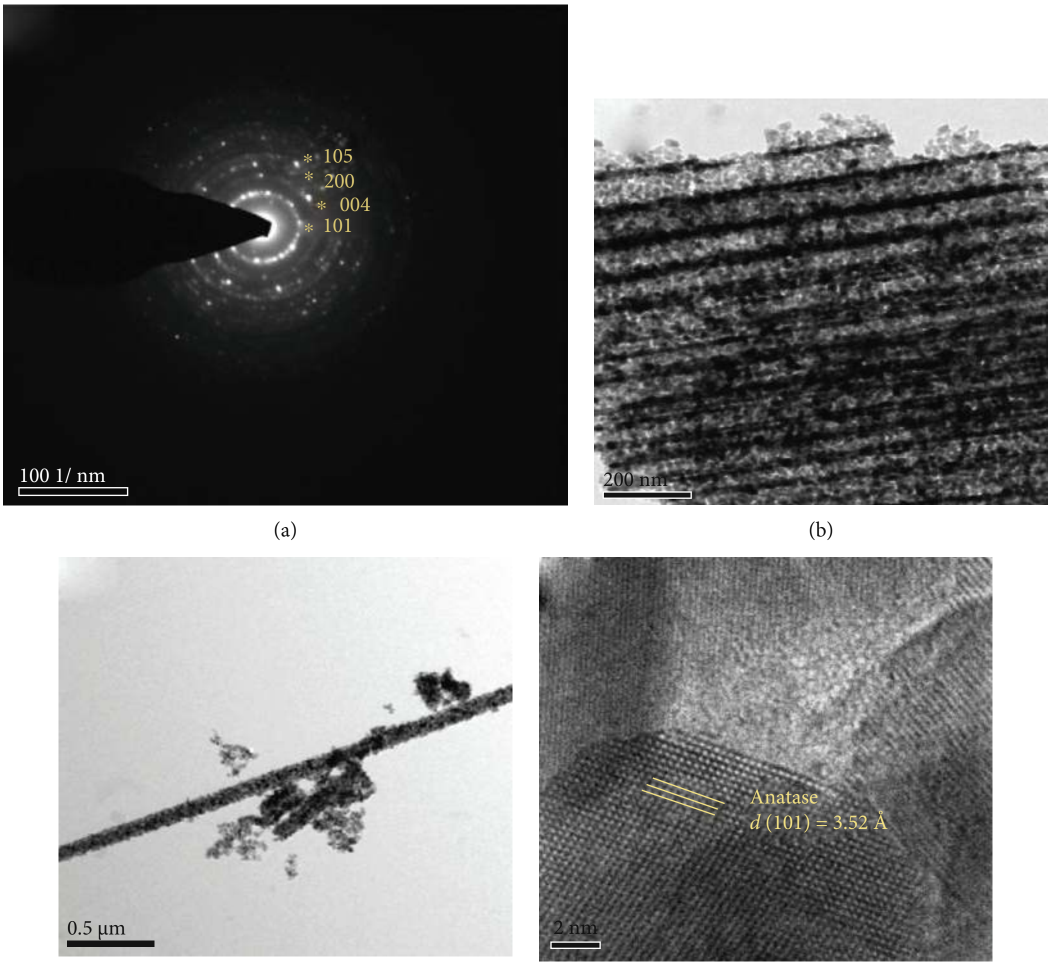
(e) Cactus fruits (f) The extracted dyes

Figure 1: Photographs of selected natural products for dye extraction.



(a) Vertical view (~30 μm) (b) Top view

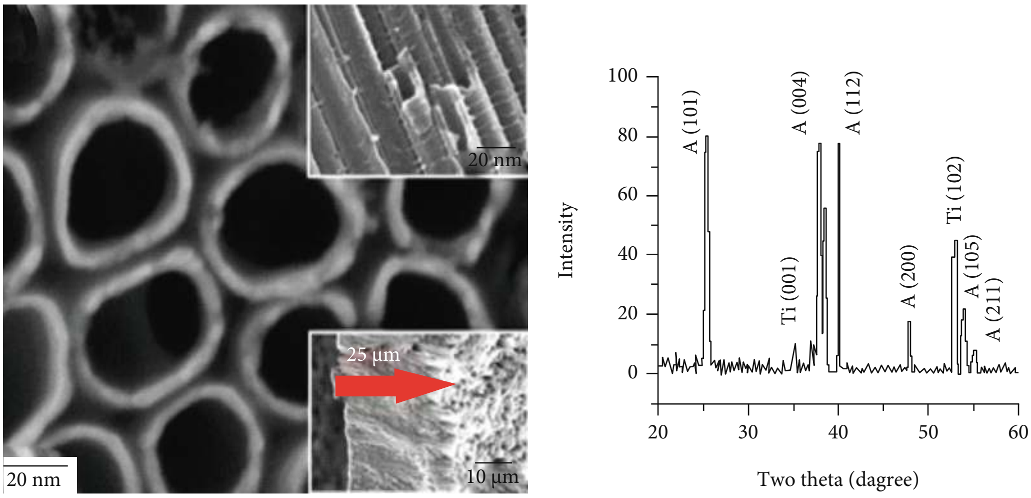
Figure 2: FESEM images of TiNT/TiO$_2$ NP on FTO glass.



(a) (b)

(c) (d)

FIGURE 3: HRTEM images of the synthesized TiNT: (a) the SAED pattern showing the crystal lattices, (b and c) the nanotube bundle, and (d) the crystal lattice.



(a) (b)

FIGURE 4: (a) The FESEM image of the TiO_2NT and (b) the XRD pattern of the TiO_2NT.

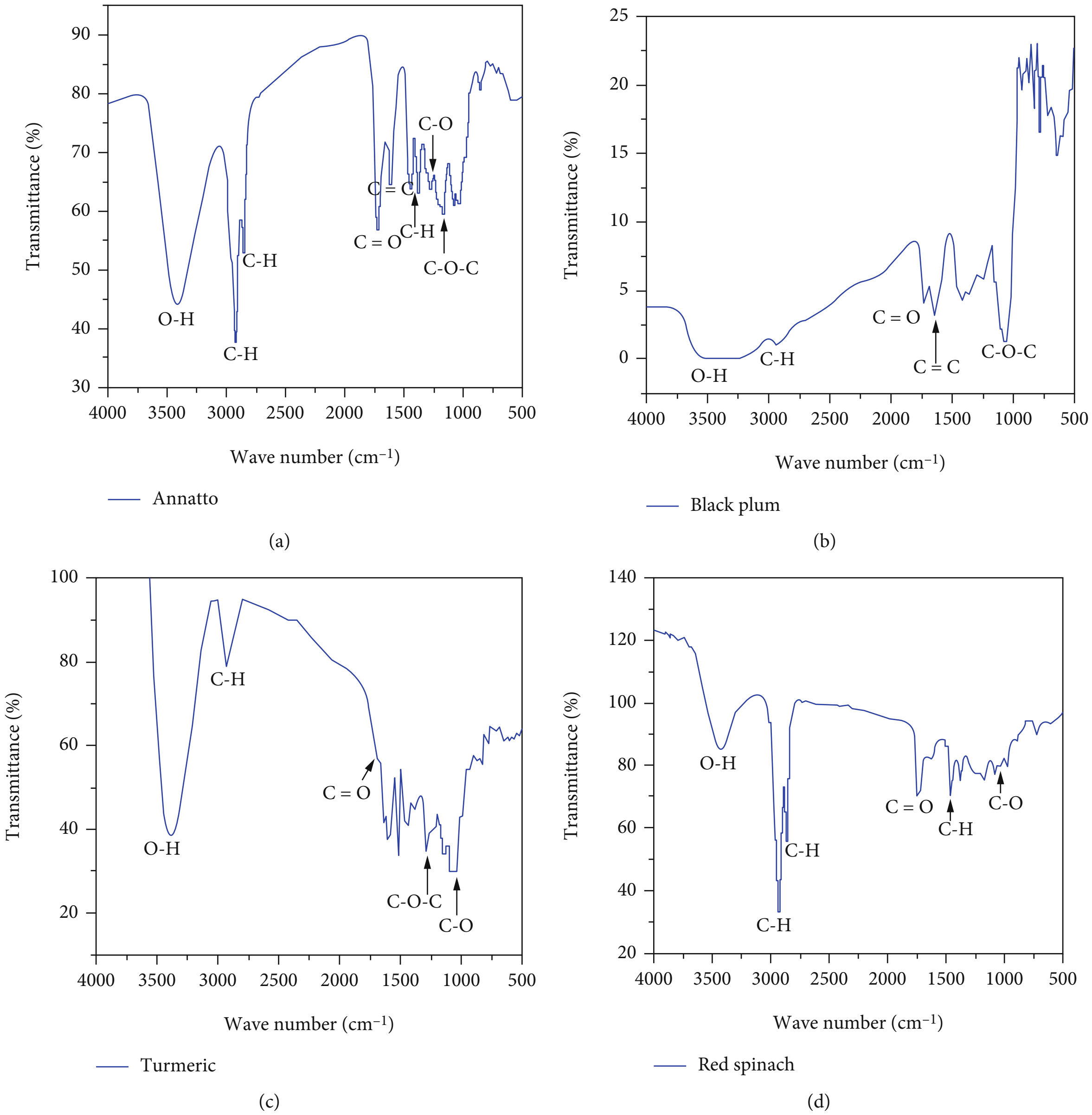
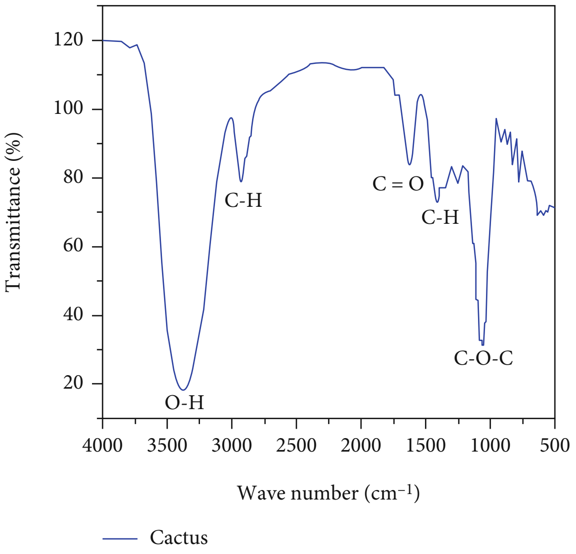


Figure 5: Continued.



(e)

Figure 5: FT-IR spectra of (a) annatto dye, (b) black plum dye, (c) turmeric dye, (d) red spinach dye, and (e) cactus dye.

several steps have been taken to optimize the structure of these natural dyes to improve the efficiency of DSSC, and the outcomes are promising.

This paper summarizes the work of five different types of natural dyes extracted from various fruits, leaves, and roots which are found common in the southern part of India. UV-Vis absorption and FT-IR spectroscopy studies were carried out on the extracted dyes. The photovoltaic properties of natural DSSCs were also investigated.

2. Material and Methods

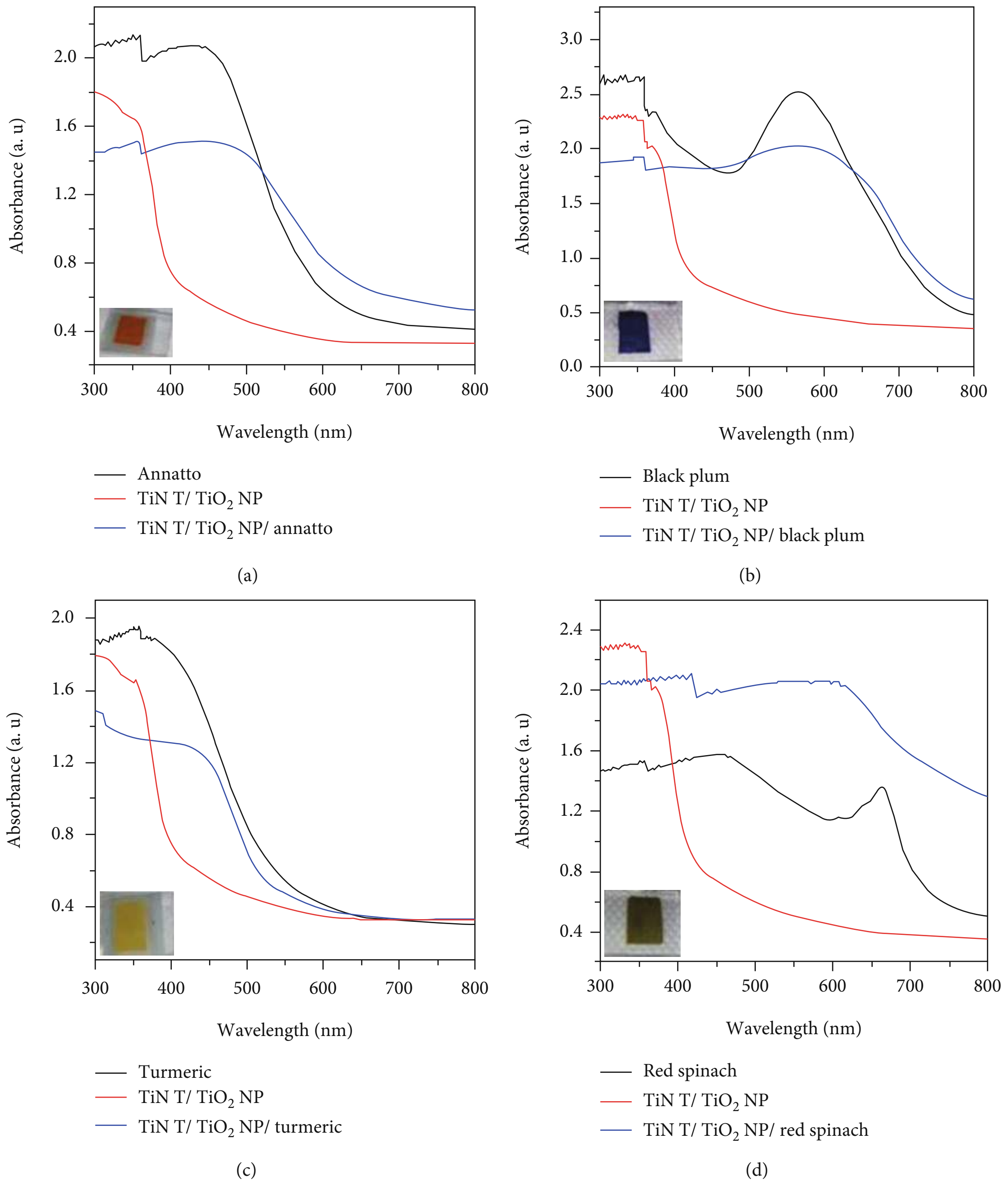
2.1. Preparation of TiO_2 Nanotubes. TiO_2 nanotubes were synthesized by the anodization method where ethylene glycol (EG) electrolyte is used in the presence of NH_4F. Ti foils (0.5 mm thickness, 99.4% purity, Sigma Aldrich) were successively cleaned before anodization in acetone, ethanol, and deionized (DI) water. Anodization was performed in a two-electrode arrangement with titanium foil as the cathode and platinum foil as the anode [25–27]. Keithley 2400 was used as the voltage source to drive the anodization. The electrolyte consisted of 0.3 wt% NH_4F and 2 vol% H_2O in ethylene glycol. The anodization was conducted at 60 V for 12 h at room temperature. After the prescribed duration, the anodized samples were annealed at 450°C for 2 h in air. The annealed samples were characterized using FESEM and EDAX to study the surface morphology and chemical composition of the synthesized materials. XRD and HRTEM analyses were carried out to evaluate the crystalline nature of the samples. Later, the annealed freestanding tube arrays were crushed into powder and mixed well with the TiO_2 NP paste (Dysol Ltd.) to form the photoanode. The detailed preparation method is illustrated in our previous article [28].

2.2. Preparation of Natural Dye Sensitizers. The annatto seeds were collected from fresh fruits and vacuum dried at 60°C. After drying, these seeds were dipped in absolute ethanol at room temperature in the dark for 24 h, and then, the solution was filtered to remove the seeds and other solid particles. The filtered solution was then used as sensitizer. The dye attained from black plums is as follows; fresh fruits were collected and the black skins of the fruits were carefully separated and dried in vacuum. After drying, the product was immersed in ethanol for 24 h to extract the dye. The solids were then filtered out from the dye solution. Similarly, fresh cactus fruits were collected, washed, and crushed well in ethanol solution and kept for 24 h to extract the dye. Once the ethanol solution became deep red in color, the solids were removed from the solution by filtration.

To obtain turmeric dye, fresh turmeric roots were cut into small pieces and dipped in ethanol for 24 h and filtered out to obtain dark yellow turmeric dye. The dye from red spinach leaves was extracted with acetone. The leaves were dried sufficiently well in a dark room. The dried leaves were crushed and soaked in acetone for 24 h, and a fine green colored dye was obtained. The red color disappeared once the leaves got dried.

Figure 1 demonstrates the five different natural dyes which were used as the sensitizers. These natural dyes were used to sensitize the photoanodes prepared from the composite of TiO_2 nanoparticle/TiO_2 nanotube paste (TiO_2 NP/TiNT). Later, DSSCs were assembled, and the photoelectrical properties were inspected.

2.3. Fabrication of Natural Dye-Sensitized Solar Cells. The natural dye-sensitized solar cell (n-DSSC) was fabricated using TiO_2 NP/TiNT composite photoanodes with platinum sputtered FTO (Dyesol Ltd.) as counter electrode. The commercially available iodine/triiodide electrolyte (Dyesol Ltd.) was used as electrolyte solution in the preparation of n-DSSC. The sintered photoanodes after cooling into the normal temperature was immersed in to the solution containing natural dye for 24 h. Once the dye was completely absorbed by the photoanodes, it was sandwiched with the platinum



(a)

(b)

(c)

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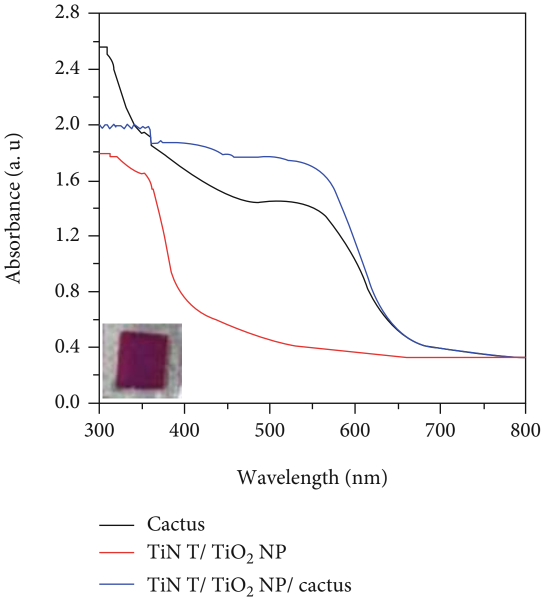
Figure 6: Continued.



(e)

Figure 6: UV-Vis absorption spectra of dye extracts and corresponding photoanodes: (a) annatto, TiNT/TiO_2 NP, and TiNT/TiO_2 NP/annatto dye; (b) black plum, TiNT/TiO_2 NP, and TiNT/TiO_2 NP/black plum dye; (c) turmeric, TiNT/TiO_2 NP, and TiNT/TiO_2 NP/turmeric dye; (d) red spinach dye, TiNT/TiO_2 NP, and TiNT/TiO_2 NP/red spinach dye; and (e) cactus dye, TiNT/TiO_2 NP, and TiNT/TiO_2 NP/cactus dye. (Inset: photographs of corresponding dye sensitized photoanodes).

counter electrode with iodine/triiodide electrolyte between them. As soon as the electrolyte was injected, it was sealed properly to avoid any outflow of the electrolyte.

3. Result and Discussion

3.1. Characteristics of TiO_2 Nanotube-Array Electrode. Figure 2(a) shows the FESEM image of the TiO_2 NT array film after anodization of Ti foil. The nanotubes are well defined after the ultrasonic treatment of the synthesized samples. As compared with the planar film, the nanotubular assembly provides a high specific surface area for the absorption of a sufficient amount of dyes on the electrode surface followed by the crystallization obtained by the annealing of TiO_2 onto the DSSCs [29]. HRTEM images of the synthesized TiO_2NT are depicted in Figures 3(b)–3(d) and the SAED pattern in Figure 3(a). Figure 4(a) shows the FESEM image of the as formed TiO_2NT, and Figure 4(b) shows the XRD patterns of TiO_2 nanotubes annealed at 450°C. It is evidenced that TiO_2 transforms from amorphous phases to crystalline anatase phases after the annealing at 450°C.

3.2. Spectroscopic Characterization of Natural Photosensitizers

3.2.1. Annatto Dye (Bixa orellana). Annatto or *Bixa orellana* is a small tree from the family of *Bixaceae* that contains pigment bixin. From the annatto seeds, a dark-red extract is obtained, which is widely used for food colouring and flavouring. The pericarp of the seeds contains a high concentration of carotenoids and is composed of up to 80% of the carotenoid cis-bixin and the remaining 20% include trans- and cis-norbixin [30]. Cis-bixin ($C_{25}H_{30}O_4$) is insoluble in water and consists of a chain of alternating double conjugated bonds, with a carboxylic acid group at one end of the chain and a methyl ester group at the other. Norbixin ($C_{24}H_{28}O_4$) is a water soluble carotenoid with only difference is the presence of a carboxylic acid moiety in the position of the methyl ester group in bixin [30].

Figure 5(a) shows the FT-IR spectrum of annatto dye. The following assignments were made in the spectrum; at 3410 cm^{-1}, the O-H stretching vibration is observed. The C-H stretches due to methyl and methylene groups are observed at 2915 cm^{-1} and 2850 cm^{-1}, respectively. At around 1722 cm^{-1}, the carboxylic C=O group, and at 1608 cm^{-1}, the alkene C=C stretch are seen. The peaks positioned at 1438 cm^{-1} and 1378 cm^{-1} represent the C-H bending of the methyl groups, and the peak at 1287 cm^{-1} is attributed to the C-O vibrations. The peaks at 1254 cm^{-1} and 1159 cm^{-1} represent the symmetric and asymmetric vibrations of the C-O-C ester group [30, 31].

Figure 6(a) demonstrates the UV-Vis absorption spectrum of annatto dye. From the spectrum, it is observed that the annatto dye shows a wide absorption peak in the visible region (360-40 nm). With TiNT/TiO_2 NP composite, there is a widening of the peak from 360-570 nm and thereby confirms the integration of the dye into the TiNT/TiO_2 NP composite film.

3.2.2. Black Plum Fruits (Syzygium cumini). Black plum fruits (*Syzygium cumini*) are commonly found in India. The black plum fruits are deep violet or bluish in color, having various medicinal properties. The anthocyanin compounds that are present in the fruit are responsible

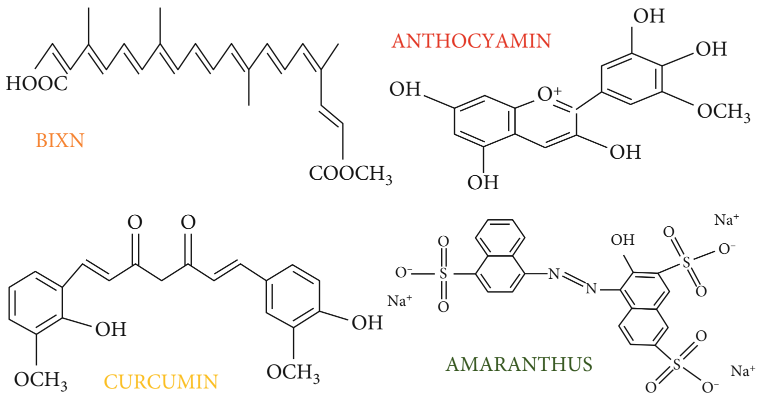


FIGURE 7: Chemical structures of the bixin, anthocyamin, curcumin, and amaranthus dyes.

TABLE 1: $J-V$ characteristic of DSSC fabricated using TiNT/TiO_2 NP photoanodes with natural dye sensitizers in comparison with the literature survey.

Natural dye	λ_{max} (nm)	V_o (V)	J_{sc} (mA/cm)^2	FF	η (%)	Ref.
Mulberry	543	0.86	0.42	0.43		[37]
Myrtus cauliflora Mart (Jaboticaba)	520	7.20	0.59	0.54	—	[38]
Red cabbage	537	0.50	0.37	0.54	0.13	[39]
Hylocereus polyrhizus (dragon fruit)	535	0.20	0.22	0.30	0.22	[40]
Bixa orellana L (annatto seeds)	474	1.1	0.57	0.59	0.37	[41]
Spinach	437	0.47	0.55	0.51	0.13	[32]
Cherries	500	0.46	0.30	38.3	0.18	[9]
Fructus lycii	447,425	0.53	0.68	46.6	0.17	[42]
Raspberries	540	0.26	0.42	64.8	1.50	[43]
Turmeric	507.2		1.857	0.503	0.473	[44]
Annatto	455	0.63	6.19	18.9	0.74	This work
Black plum	550	0.51	5.43	14.68	0.40	This work
Turmeric	425	0.62	4.59	7.99	0.22	This work
Red spinach	430 and 665	0.51	3.56	9.21	0.16	This work
Cactus	550	0.58	5.68	13.48	0.44	This work

for the violet or bluish color of the dye. The FT-IR spectroscopy studies confirmed the presence of anthocyanin pigment extracted in the black plum fruits. Figure 5(b) displays the FT-IR spectrum of the black plum fruit. The peak at 3520 cm^{-1} corresponds to the -OH stretching vibration. The peaks at 2933 cm^{-1} are assigned to the -CH stretching modes [32]. The spectral region between 1550 to 1700 cm^{-1} allows infrared absorption of C=C. Consequently, the peak at 1627 cm^{-1} corresponding to the double bond (C=C) stretching vibration could be correlated with the stretching of aromatic C=C in anthocyanin. The peaks at 1730 cm^{-1} are assigned to the C=O stretching vibration [32, 33].

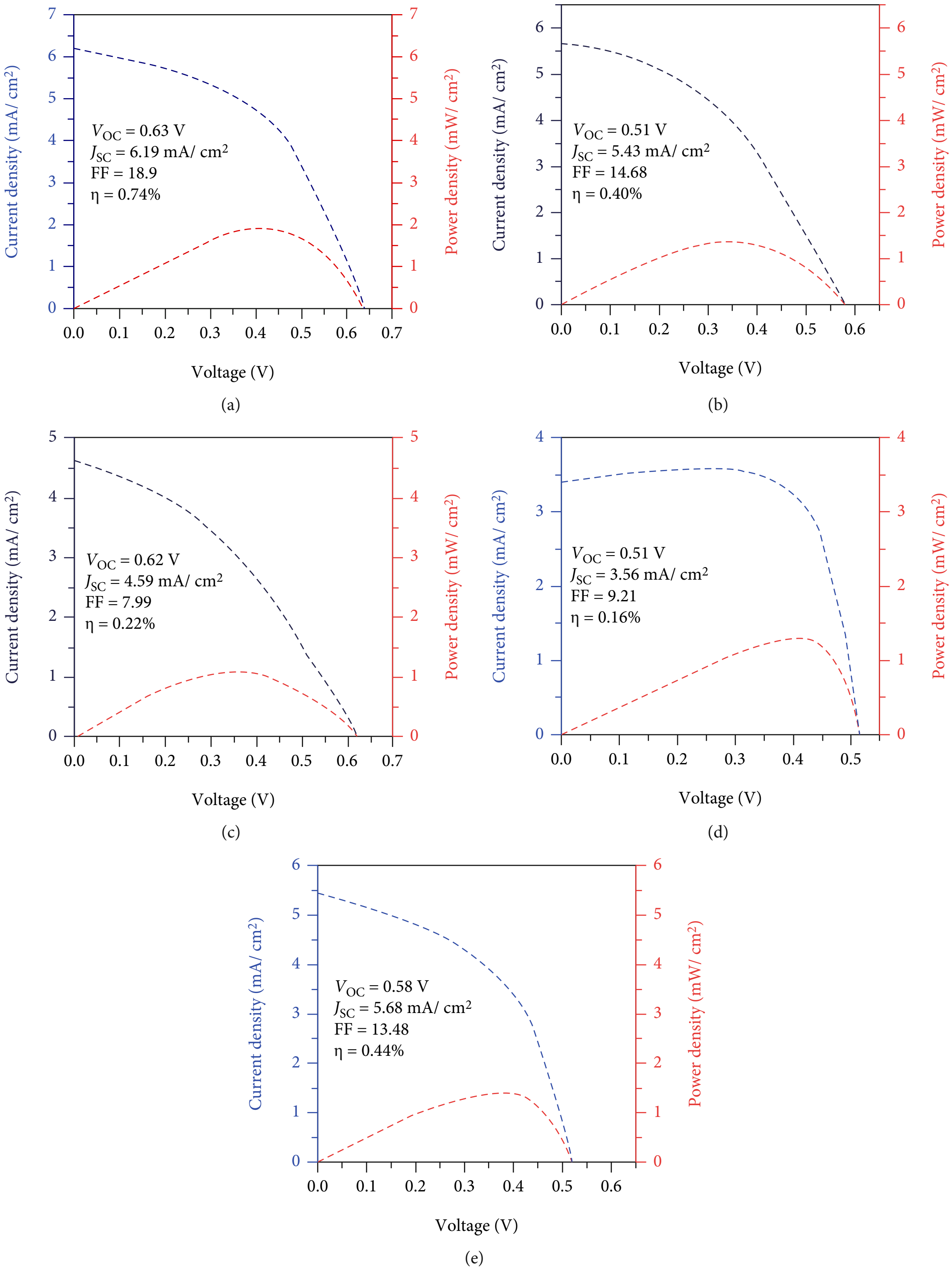
Figure 6(b) explains the UV-Vis absorption spectrum of black plum dye and the dye-sensitized TiNT/TiO_2 NP photoanode. A maximum absorption is observed at 570 nm for the dye. After immersing the photoanode in the black plum dye, the photoanode films turn to blue in color (inset of Figure 6). The absorption band of the adsorbed dye was broader than the absorption band of the fresh dye solution.

3.2.3. *Turmeric Dye (Curcuma longa).*

Turmeric rhizome root contains up to 5% essential oils and up to 3% curcumin a polyphenol. Curcumin is the active ingredient of turmeric. It exists at least in two tautomeric forms, keto and enol. The keto form is preferred in solid phase and the enol form in solution [34]. The extract of turmeric root yields a deep orange-yellow dye.

FT-IR spectrum of turmeric dye recorded in the waveband 4000-500 cm^{-1} is illustrated in Figure 5(c). The -OH stretching frequency appears at 3368 cm^{-1}. The asymmetrical C-O-C stretching frequency of aryl alkyl ethers appears at 1287 cm^{-1}. The band at 1688 cm^{-1} corresponds to the symmetrical C=O stretching of the keto group. The sharp band at 1087 cm^{-1} is assigned to the C-O-C stretch of alkyl aryl ether. The sharp band at 1039 cm^{-1} is assigned to the C-O stretch of the phenyl alkyl ether that confirms the molecular structure of curcumin extracted from turmeric [34].

Figure 6(c) reveals the UV-Vis absorption spectrum of pure curcumin and curcumin sensitized TiO_2 photoelectrode. As perceived from the curves of the absorption



(a)

(b)

(c)

(d)

(e)

FIGURE 8: *J* – *V* curves of natural DSSC: (a) annatto, (b) black plum, (c) turmeric, (d) red spinach, and (b) cactus.

spectrum, the maximum absorption peak of curcumin is at the wavelength 425 nm.

It also shows a broad peak at the wavelength range from 400 nm to 450 nm. Owing to adsorption on the TiO_2 of all pigments, the absorption band shifts to higher energy in the visible range. The broad range also indicates that the dye is stained well on the TiO_2 nanoparticles. This broadening can lead to the capacity of dye to harvest photons in a broader spectrum of solar energy, which eventually produces a higher photocurrent [34].

3.2.4. Red Spinach (Amaranthus dubius). Red spinach is a normally available vegetable in many parts of India. Its leaves are usually round thick and red in color. It also has a bright red color central stem. The leaves and stem of red spinach contain a red liquid. To extract dye from red spinach, the leaves were initially dried, crushed, and then soaked in acetone and fine green-colored dye was obtained. The red color disappeared once the leaves got dried. Figure 5(d) shows the FT-IR spectrum of red spinach dye in the spectral range within the waveband of 4000-500 cm^{-1}.

The dye extracted from red spinach exhibits the following bands corresponding to different functional groups. The peak at 3416 cm^{-1} corresponds to the -OH stretching vibration. The CH_3 and CH_2 vibrations are observed at 2930 cm^{-1} and 2817 cm^{-1}, respectively [35]. Moreover, C=O vibration at 1721 cm^{-1} and C-O vibration at 1045 cm^{-1} are also observed. The UV-Vis absorption spectrum of red spinach dye is shown in Figure 6(d). It has approximate absorption maxima at 430 and 662 nm, which were attributed to the presence of chlorophyll pigment in the extract.

3.2.5. Cactus Fruit Dye (Opunitia ficus). The fruit of the cactus, known by the name prickly pear, is in oval shape with a reddish-purple color. The reddish color is due to the presence of anthocyanin compounds. The properties of cactus fruit dye have been investigated by FT-IR and UV-Vis spectroscopic techniques.

The FT-IR spectrum of cactus dye was recorded in the spectral range of waveband 4000 cm^{-1} to 500 cm^{-1} (Figure 5(e)). From the spectrum, the broad absorption range between 3200 and 3400 cm^{-1} indicates that the chemical has an intermolecular H-bond, and the sharp peak between 1600 and 1700 cm^{-1} shows that C=O stretching vibration is conjugate. The sharp peak around 1030-1060 cm^{-1} is due to the C-O- C stretching vibration of esters acetates [35, 36].

The results prove that the due from cactus fruit contains anthocyanin which is one of the core compositions for natural dye. Chemically, cactus dye contains intermolecular H-bonds, conjugate C=O stretching, and existing ester acetates, C-O-C asymmetric stretching vibrations, all of which are caused by the anthocyanin component [36]. The carbonyl and hydroxyl groups in cactus fruit dye can be bound with the surface of TiO_2 and thus result in photoelectric effects.

The absorption spectrum of cactus fruit was obtained in the wavelength range between 300 nm and 800 nm using UV-Vis spectroscopy. In Figure 6(e), the cactus dye is found to have an absorption peak at 535 nm and show a good absorption level between 450 and 600 nm. The structures of the dye based on the natural sources are depicted in Figure 7.

3.3. Photoelectrochemical Performance of DSSCs Sensitized with Natural Dyes. In the presence of white light emitted(100 mW cm^{-2}) from the solar simulator, the DSSC with the natural dyes was studied. The performance of DSSC using natural dye sensitizers was evaluated by short circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and energy conversion efficiency (η). The $J-V$ characteristics of the DSSC sensitized with natural dyes are listed in Table 1. Figures 8(a)–8(f) show the photocurrent photovoltage ($J-V$) characteristics of the DSSCs, and the fill factors of these DSSC are found to be very low. The V_{oc} varies from 0.51 to 0.63 V, and the J_{sc} changes from 3.56 to 6.19 mA cm^{-2}. Specifically, a high V_{oc} (0.63 V) and J_{sc} (6.19 mA cm^{-2}) were obtained from the DSSC sensitized by the annatto dye, where the efficiency of the DSSC reached up to 0.7%.

4. Conclusion

An investigation on the use of natural dyes as photosensitizers for DSSC fabrication was taken up in this study. Natural dye-based solar cells appear to be limited by low V_{oc} and J_{sc}. Though the studies cornered with the natural dyes are still below the necessary requirements, the obtained results are highly encouraging and could also pave way for new natural dyes or modification to the present ones. The environmental friendliness and low-cost production make it a promising candidate for natural dyes as sensitizers.

Data Availability

The data supporting this work is available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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