

# Dye-Sensitized Solar Cells Employing Extracts from Four Cassia Flowers as Natural Sensitizers: Studies on Dye Ingredient Effect on Photovoltaic Performance

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Natural dyes extracted from four different flowers, namely, Cassia surattensis, Cassia tora, Cassia alata and Cassia occidentalis were used as sensitizers for  $TiO_2$ -based dye-sensitized solar cells (DSSC). The dye extracts from flowers were obtained by a simple extraction technique and used without any further purification. Optical characteristics of dye extracts were studied. Fouriertransform infrared (FTIR) spectra were used to identify the constituents of extracted dyes. The photovoltaic performance of DSSC employing dye-capped  $TiO_2$  photoanodes was measured. The sensitization performance related to anchoring groups present and interaction between dyes with  $TiO_2$  surface is demonstrated. An attempt has been made to rationalize the observations by light absorption of the dye extracts and their adsorption on TiO<sub>2</sub>. The shortcircuit current density  $(I_{SC})$  values ranged from 0.06 mA/cm<sup>2</sup> to 0.20 mA/cm<sup>2</sup>; open circuit voltage  $(V_{OC})$  from 0.292 V to 0.833 V; fill factor (FF) from 0.7 to 0.9; efficiencies ( $\eta$ ) from 0.013% to 0.15% and incident photon-to-current conversion efficiency from 13% to 20%, were obtained for DSSC using these natural dye extracts. Cassia occidentalis showed the highest current density of 0.20 mA/cm<sup>2</sup> and power conversion efficiency of 0.15%, which was due to better interaction between the carbonyl and hydroxyl group of the anthocyanin molecule of C. occidentalis and surface of  $TiO_2$  film. The red and blue shift of absorption wavelength of C. surattensis and the blue shift of absorption wavelength of the C. tora, C. alata and C. occidentalis extract in ethanol solution compared to that on  $TiO_2$  film has been used for the interpretation of obtained results.

Key words: Renewable energy, DSSC, natural dye,  $TiO_2$  thin film, adsorption

## **INTRODUCTION**

The last century witnessed an unbelievable number of technology advances that have changed our lifestyle significantly. The immense use and growing dependence on electrical and electronic equipments have escalated the energy/power requirements on a global scale with decreasing reserves; there is an urgent need to find alternate energy resource to meet increasing demand. The harnessing of solar energy in this context becomes a very attractive plan. Dye-sensitized solar cells (DSSC) which are based on the sensitization of wide band-gap semiconductors are simple and cheap devices capable of converting the visible light into electricity through a regenerative photoelectrochemical process. In DSSC, the dye molecules play key role in light harvesting, and as these dye molecules sensitize wide band-gap semiconductors

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to visible radiation, are referred to as "sensitizers".<sup>1</sup> The concept of DSSC was first proposed by Gratzel et al. in the year 1991 by blending nanostructured TiO<sub>2</sub> with dyes which were effective in charge injection.<sup>2</sup> The first DSSC developed was found to absorb visible light up to nearly 800 nm which led to the extension of solar cells to a new third-generation device and an energy conversion efficiency exceeding 7% was achieved. Subsequently, by employing nanostructured semiconductor electrodes, the conversion efficiency reached 11.4%.<sup>3,4</sup> Recently, Mathew et al., by using mesoporous semiconductor electrodes and porphyrin sensitizers, obtained an unprecedented conversion efficiency of 13%.<sup>5</sup>

The absorption of light in DSSC is achieved through sensitizer(s) embedded in the  $TiO_2$  architecture. The sensitizer is mostly comprised of inorganic metal complexes and organic dves.<sup>6</sup> Transition-metal coordination compounds (specifically ruthenium polypyridyl complexes) are the most successful sensitizers for application in DSSC, as they get anchored to nanocrystalline TiO<sub>2</sub> surfaces through carboxylic acid groups.<sup>7,8</sup> Moreover, in addition to effective anchorage of the dye to the TiO<sub>2</sub> surface, these dyes also have advantageous characteristics such as excellent stability, intense absorption in the visible range of the solar spectrum, increased excited lifetime of the electron, excellent electron injection and efficient metal-to-ligand charge transfer. $^{9-11}$  The metal-to-ligand charge transfer takes place at a much faster rate than the back reaction, where the electron recombines with the oxidized dye molecule rather than flowing through the circuit and performing work.<sup>12</sup>

Though, the Ru-based dyes are capable of yielding conversion efficiencies greater than 10–11%, their preparation usually requires multi-step procedures and time-consuming methods.<sup>8</sup> Additionally, ruthenium polypyridyl complexes have high cost, longterm unavailability and contain a heavy metal, which is undesirable from an environmental concern; therefore, emphasis is on widening of research on low-cost, eco-friendly and easily available efficient sensitizers. As an alternative, natural dyes can be used for the same purpose with an acceptable efficiency. Natural pigments offer advantages of great abundance, simplicity of preparation, low cost, non-toxicity and environmental friendliness. Moreover, they can serve as renewable reservoirs to materials for many applications.

Organic dyes such as cyanine, phthalocyanine, coumarine, xanthene etc. are found to be poor sensitizers because of weak binding with the  $\text{TiO}_2$ surface and low charge-transfer absorption in the whole visible region.<sup>13</sup> Another drawback of organic dyes is the formation of aggregates on the semiconductor surface, which leads to self-quenching and reduces electron injection into  $\text{TiO}_2$ . The organic dyes used in DSSC often bear a similarity to the dyes that are present in natural products like flowers, fruits, leaves, tree barks, roots etc.<sup>5,9</sup> Maurya, Singh, Neetu, Gupta, Srivastava, and Bahadur

Therefore, natural dyes are feasible alternatives to organic-based DSSC.

Keeping aside the fact that their application is far below the industrial requirements, the pigments present in the different parts of plant have been extensively analyzed as sensitizers over the last two decades. Naturally accessible fruits, flowers, leaves, bacteria etc. evince various colors from red to purple and contain various natural dyes which have been extracted by simple procedures and employed in  $DSSC.^{14-18}$  The additional advantage of employing these natural dyes as photosensitizers in DSSC is their large absorption coefficients in the visible region<sup>17,18</sup> and the fact that the synthesis route for natural dye-based DSSC is economic as it does not involve noble metal(s) like Ru.<sup>19</sup> The plant materials possess natural pigments such as anthocyanin, chlorophyll, carotenoid and betalain that are easily extracted from natural products in comparison to synthetic dyes.<sup>20</sup> So far, various natural dyes have been utilized as sensitizers in DSSC and it is demonstrated that the DSSC with different pigments can produce varied photosensitizing effects, mitigating the fact that only preferred pigments convert sunlight into electricity. In natural pigments, betalain pigment showed the best performance due to the better interaction between betalain and TiO<sub>2</sub>.<sup>21</sup>

Wongcharee et al.<sup>22</sup> fabricated DSSC using natural dyes extracted from rosella, blue pea flowers and a mixture of these extracts; the extracts exhibited efficiencies of 0.37%, 0.05%, and 0.15%, respectively. Calogero et al.<sup>23</sup> used extract from bougainvillea, red turnip and the purple wild sicilian prickly pear fruit juice as sensitizers. DSSC fabricated with red turnip resulted in a remarkable current density of 9.5 mÅ/cm<sup>2</sup> and an efficiency of 1.70%, whereas the wild sicilian prickly pear fruit extract showed a conversion efficiency of 1.26% with a current density 9.4 mA/cm<sup>2</sup>. Shanmugam et al. have fabricated and characterized DSSC based on ivy gourd fruits and red frangipani flowers as sensitizers and reported an efficiency of 0.301% with red frangipani flowers.<sup>24</sup> Anthocyanin pigments obtained from natural products have been successfully used as sensitizers as they consist of hydroxyl and keto groups that can easily bind with the  $TiO_2$  surface.<sup>20</sup> Mounir Alhamed et al. have fabricated and characterized DSSC based on the anthocyanin dyes as well as their combinations and reported that the combination of the extracted natural dyes exhibited better photovoltaic performance with an efficiency of 3.04%.<sup>25</sup> Kumara et al.<sup>26</sup> have fabricated and characterized DSSC based on pigments of shiso plants, a well-known vegetable in Japan. The fabrication of DSSC with two anthocyanin pigments of the shiso plant, referred to as shisonin and malonylshisonin, were used and a promising efficiency of 1.30% with a current density value of 4.80 mA/cm<sup>2</sup> and an open-circuit voltage of 0.53 V was demonstrated.

In the present study, an attempt has been made to extract natural pigments from four flowers, namely C. surattensis, C. tora, C. alata and C. occidentalis belonging to the same genus, fabeaceae family. Interestingly, the use of these natural dyes as sensitizers in DSSC has not attracted significant research attention. These extracted natural pigments have a long intense wavelength absorption range from 400 nm to 500 nm in the visible region. The extracted dyes were used without any purification in order to monitor the performance of the dye with minimal chemical procedure and simple extraction technique. We studied their photo-response as sensitizers for TiO<sub>2</sub>-based DSSC.

# **EXPERIMENTAL SECTION**

#### Materials

All experiments were performed in the open at ambient temperature and pressure. The solvents were purified by standard procedures. Ethanol (A.R. grade, 99.9%, Merck) was used for extracting natural dyes from plants. Titanium paste (HT), platinum catalyst (T/SP) and the sealant (SX1170-60, 50- $\mu$ m thick) were obtained from Solaronix SA. LiI (99.9%, Aldrich), I<sub>2</sub> (G.R. grade, 99.8%, BDH) was added as a redox couple in cell electrolyte, and acetonitrile (ACN; Merck, India) was used as the medium of the electrolyte solution. Conductive glass (TCO 22-15, 2-mm-thick glass with 15- $\Omega$ /sq surface resistivity, SnO<sub>2</sub>:F coating) obtained from Solaronix SA was used as substrate for preparing TiO<sub>2</sub> thin film and platinum counter electrodes.

#### Instruments

All the instruments used were same as that given in our previous work.<sup>15</sup> A bipotentiostat (AFRDE 4E, Pine Instrument Company, PA, USA), along with an e-Corder (Model 201, eDAQ, Australia) was used for all current-potential measurements. A 150-W xenon arc lamp with a lamp housing (model no. 66057) and power supply (model no. 68752), all from Oriel Corporation, USA, was used as the light source, and the semiconductor electrode was illuminated after passing the light beam through a 6-inch-long water column [to filter infrared (IR)] and condensing it with the help of fused silica lenses (Oriel Corporation, USA). For selective excitation of dye (not  $TiO_2$ ), the ultraviolet (UV) part of this IR-filtered light was cut off by using a long pass filter (model no. 51280, Oriel Corporation, USA). For IPCE measurements a monochromator (Oriel model no. 77250) fitted with a grating (model no. 7798) was used in combination with a multimeter (Philips model no. 2525). The light intensities were measured with a photometer (Tektronix model no. J 16 with J6502 sensor). The absorption spectra were recorded by a Shimadzu UV-1700 spectrophotometer. The Fourier transform infrared (FTIR) spectra were recorded using a Varian 3100 FT-IR spectrometer.

#### Methods

## Dye Extraction for Use as Sensitizer

Fresh flowers of *Cassia surattensis*, *Cassia tora*, *Cassia alata* and *Cassia occidentalis* were taken and washed with de-ionized water and then vacuum-dried at 60°C. The dried flowers were crushed into fine powder using a mortar and pestle and 1 g of each powder was separately dispersed in 50 mL of pure ethanol and kept for 24 h. The solid residue was filtered out and the resulting solution was used as dye sensitizer without any further purification (Fig. 1). The extracts were properly stored and protected from direct sunlight exposure.

#### *Dye* /*TiO*<sub>2</sub> *Photoanode, Platinum Counter Electrode and DSSC Device Fabrication*

TiO<sub>2</sub> thin film electrodes were prepared by spreading TiO<sub>2</sub> paste (HT) on clean conductive glass plates by the doctor's blade technique. The films were dried at room temperature, annealed at 450°C for 30 min in a muffle furnace and then allowed to cool down at room temperature in the furnace itself. The film thickness obtained was ~6  $\mu$ m. The dye was coated onto the TiO<sub>2</sub> surface by immersing the TiO<sub>2</sub> electrodes in dye solution for 24 h at room temperature. The non-adsorbed dye was washed off with anhydrous ethanol. The counter electrode was prepared by coating the fluorine-doped tin oxide (FTO) glass with Pt catalyst (T/SP paste, Solaronix SA) and annealed at 400°C for 30 min in air.

The photovoltaic performances of the dyes were assessed using sandwich type DSSC in which the platinum catalyst-coated counter electrode was placed in such a way that the conductive side of this electrode faced the dye-coated  $\text{TiO}_2$  film. The cell was then sealed from all sides except one (for adding electrolyte) using a hot melt sealant film that also acted as a spacer. The electrolyte solution was added from the open side into the space between the electrodes using capillary flow. The copper lids were attached on the electrodes using silver paste and then covered with Araldite for making intact external connections.<sup>27</sup>

#### **RESULTS AND DISCUSSIONS**

#### **UV-Vis Absorption Spectra**

The absorption spectra of the dyes obtained from the flowers of *C. tora*, *C. surattensis*, *C. alata* and *C. occidentalis* in solution (ethanolic extract) and in adsorbed state onto  $\text{TiO}_2$  film is shown in Figs. 2 and 3, respectively. The absorption spectra of dye-coated  $\text{TiO}_2$  films were recorded using  $\text{TiO}_2$  film (without dye) as a reference. These natural dye extracts have shown absorption in the range of 400–500 nm with the absorption maxima at around 445 nm which was evidence of the presence of anthocyanin pigment in the natural dyes. Anthocyanins, being water-soluble



Fig. 1. Images of (a) C. tora, (b) C. surattensis, (c) C. alata and (d) C. occidentalis flowers and their extracts in ethanol.



Fig. 2. UV–Vis absorption spectra of natural dye solutions extracted from (a) *C. tora*, (b) *C. surattensis*, (c) *C. alata* and (d) *C. occidentalis*.

flavonoids, are responsible for the red to blue colour of many flowers, fruits and leaves. These also act as photo-protective agents, osmotic regulators and antioxidants.

The absorption spectra of the adsorbed dye on  $TiO_2$  electrodes was found to be significantly modified compared with that of dye in solution, as shown in Fig. 3. It was broadened from 350 nm to 500 nm after adsorption of dyes on the  $TiO_2$  photoanode for



Fig. 3. UV–Vis absorption spectra of natural dyes adsorbed on  $TiO_2$  (a) *C. tora*, (b) *C. surattensis*, (c) *C. alata* and (d) *C. occidentalis*.

C. tora, C. alata and C. occidentalis, whereas in the case of C. surattensis, the broadening was from 350 nm to 550 nm. The absorption maxima for dye extract of C. surattensis adsorbed on  $TiO_2$  thin film has shown a red shift of ~50 nm (curve 'b'), while C. tora, C. alata and C. occidentalis revealed blue shifts of around 50 nm toward the UV region and insufficient absorption in the visible region (curves 'a', 'c' & 'd' respectively). The intensity of absorption was also reduced in these cases.

Spectral changes induced by adsorption of dye molecules over  $\text{TiO}_2$  have been attributed to a variety of reasons; however, it is mainly due to the interaction between dye and  $\text{TiO}_2$  surface. The direction of shift depends on the strength of interaction and aggregation; if strong, it's a red shift, otherwise a blue shift.<sup>28</sup> Moreover, aggregations of dye were reported as early as in 1936 and from then, it has been accepted that the dyes have a strong tendency to aggregate at the solid/liquid interface due to strong attractive forces between molecules. Usually, dye aggregates have three forms: blue-shifted H-aggregates (tilted orientation), red-shifted J-aggregates (tilted orientation) and both red- and blue-shifted herring-bone aggregates.

In the present case, though dyes are otherwise chemically identical, having similar chromophore, it has been confirmed that their functionality strongly depended on different anchors present. This suggested that none of the associated anchors of *C. tora*, C. alata or C. occidentalis are sufficiently strong enough to affect the intermolecular interactions of the dye on the  $TiO_2$  surface. Additionally, aggregation, in which anthocyanin molecules align in faceto-face mode on the surface of TiO<sub>2</sub> film, may also cause a blue shift. Besides, the anthocyanin molecules adsorbed on the surface of  $TiO_2$  can be considered as an electron-attracting group, which can also convey the blue shift of absorption wavelength.<sup>31,32</sup> The change in environmental conditions such as solvent polarity, which causes solvatochromism, may not be completely ruled out for such shifts. However, the absorption spectrum of dye-coated  $TiO_2$  as shown in curve 'b' is quite extended and more intense, revealing strong interaction between dye/TiO<sub>2</sub>. This may be due to the presence of strong binding groups such as carboxylic/hydroxyl in C. surattensis, though we have not isolated the dye constituents. The increment in absorption testifies the strong chelation of anthocyanin and  $TiO_2$ . It also affects the energy levels of the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular level orbital (LUMO) of the dye, which, in turn, may cause a shift in the peak of the absorption spectra.

Therefore, it became evident that though all the four natural dyes extracts have shown almost similar absorption in solution, indicating the presence of the same pigment in the flowers, their adsorptions, however, on  $\text{TiO}_2$ , which is decided by the anchoring species, were quite different. Thus, we expected different photovoltaic conversion output with the use of these natural dyes as sensitizers for an oxide nanostructure.

#### **Fourier Transform Infrared Analysis**

The constituents present in plants and their functional groups were qualitatively found out using FTIR spectroscopy. The FTIR spectra of the four natural dye extracts of flowers C. surattensis, C. tora, C. alata and C. occidentalis as shown in Fig. 4a and b exhibited similar spectral characteristics and demonstrated the presence of anthocyanin.<sup>18</sup> In the spectrum, a broad absorption in the range of  $3000-3700 \text{ cm}^{-1}$  indicated the -OH stretching and the wide variety of hydrogen bonding.<sup>33</sup> The two peaks observed at 2926 cm<sup>-1</sup> and the other as a small shoulder at around 2853 cm<sup>-1</sup> are assigned to the symmetric and antisymmetric –CH stretching modes of vibrations of methyl and methylene groups, respectively.<sup>34</sup> In the spectra, the peak observed at 1745 cm<sup>-1</sup> was assigned to the vibrations of carbonyl groups.<sup>17</sup> The spectral range from 1550 cm<sup>-1</sup> to 1700 cm<sup>-1</sup> adduces the infrared absorption of C=C. Therefore, the double bond (=) stretching vibration at 1630 cm<sup>-1</sup> corresponds to the aromatic C=C stretching in anthocyanin. The peak observed at  $1446 \text{ cm}^{-1}$  corresponds to the phenolic –OH group,<sup>34</sup> and the strong peak around 1030–1060 cm<sup>-1</sup> represents ester acetate's C–O–C stretching vibration. The carbonyl (C=O) group and



Fig. 4. FTIR spectra of the dyes' extracts (a) C. tora and C. alata, (b) C. occidentalis and C. surattensis.



Fig. 5. J-V characteristics of the DSSC based on TiO<sub>2</sub> anchored with natural sensitizer dyes (a) *C. tora*, (b) *C. surattensis*, (c) *C. alata* and (d) *C. occidentalis* under irradiation of 100 mW/cm<sup>2</sup>. The curve for bare TiO<sub>2</sub> is shown separately in the figure.

hydroxyl group (O-H) of the anthocyanin molecule are reported to form bonds with the oxygen atom of the TiO<sub>2</sub> layer.<sup>35</sup> The bonding can be either monodentate or bidentate bridging. When illuminated, anthocyanin absorbs light; the electron present in the HOMO gets excited to the LUMO state and further injection of the electron takes place through the functional C=O and O-H groups into the conduction band of TiO<sub>2</sub>.

#### **Device Performance**

#### Current–Potential (J–V) Characteristics

The cells (dye-capped TiO<sub>2</sub> photoanode/electrolyte/Pt counter) were characterized for photovoltaic performance under illumination of 100 mW/ cm<sup>2</sup> and resultant curves are shown in Fig. 5. The current–voltage (*J*–*V*) curve provides information regarding the operational parameters of the cell such as short-circuit current density ( $J_{\rm SC}$ ), opencircuit voltage ( $V_{\rm OC}$ ), fill factor (FF), overall conversion efficiency ( $\eta$ ). The FF and solar cell efficiency were obtained using Eqs. 1 and 2, respectively.

$$FF = \frac{J_{\max} \times V_{\max}}{J_{SC} \times V_{OC}}$$
(1)

$$\eta(\%) = \frac{J_{\rm SC} \times V_{\rm OC} \times \rm FF}{I_{\rm inc}} \times 100 \tag{2}$$

where  $V_{\rm max}$  = maximum voltage (V);  $J_{\rm max}$  = maximum current density (mA/cm<sup>2</sup>);  $J_{\rm SC}$  = short-circuit current density (mA/cm<sup>2</sup>);  $V_{\rm OC}$  = open-circuit voltage (V) and  $I_{\rm inc}$  = light intensity (W/cm<sup>2</sup>). The maximum power output, which is the ratio of output energy to the incident energy, was evaluated as follows

$$P_{\max} = J_{\max} imes V_{\max}$$

which is obtained by taking a point on the experimentally obtained (J-V) curve corresponding to the maximum value of the product of current and potential and shown in Fig. 6. These output



Fig. 6. Power curves for cells (a) *C. tora*, (b) *C. surattensis*, (c) *C. alata* and (d) *C. occidentalis*.

parameters for the cell based on C. surattensis-, C. tora-, C. alata- and C. occidentalis-sensitized  $TiO_2$  are summarized in Table I.

The conversion efficiencies of DSSC sensitized by natural dyes are much lower compared to Ru dyes. This is because the molecular structure of natural dyes which mostly have OH and C=O functional groups and lack COOH, as possessed by ruthenium dyes which combines with the hydroxyl of the  $TiO_2$  particles producing ester that boost the coupling effect of electrons on the  $TiO_2$  conduction band and leads to very facile electron transport.<sup>14</sup>

Despite low output, the undertaken natural dyes demonstrated the applicability of these plant extracts for photovoltaic energy conversion. The reason of low light-to-electrical conversion efficiency may also be an inadequate overlapping of the excited states of natural dyes and the conduction band of TiO<sub>2</sub> or due to feeble interaction and weak adsorption of dyes on the TiO<sub>2</sub> film.<sup>31</sup>

#### Transient Photocurrent-Time Profile

The transient current-time profiles were recorded to know whether the photocurrent observed initially on illumination of the semiconductor electrode is sustained or it goes down with time. The shortcircuit photocurrent at a constant bias potential (0.0 V versus Ag/Ag<sup>+</sup> in ACN) was monitored as a function of time and shown in Fig. 7. Initially, the dark current was monitored for a few seconds, then the semiconductor electrode was illuminated with light and the photocurrent was recorded until it became stable, and finally in the dark again. In each case, the current attained initially was sustained with no significant loss or decay after 20 s. This shows that the dye regeneration process is fast enough to cope with the rate of electron injection from the excited dye molecules to the conduction band of the  $TiO_2$  and recombination of charge carriers is almost trivial. The nature of transients is governed to a great extent on the structure of the interface. However, the exact structure of the interface comprising TiO<sub>2</sub>, adsorbed dye & a diffuse layer of electrolyte is quite complex, and to

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Table I. Photovoltaic parameters of DSSC making use of natural dyes extracted from flowers as sensitizers					
Dye-sensitizer	$J_{\rm sc}~({\rm mA/cm}^2)$	$V_{\rm oc}~({ m mV})$	FF	η (%)	<b>IPCE</b> (%)
C. tora	0.06	292	0.72	0.013	13
C. surattensis	0.13	475	0.74	0.046	16
C. alata	0.16	800	0.95	0.122	17
C. occidentalis	0.20	833	0.90	0.150	20



Fig. 7. Transient current–time ( $J_{photo}$ –t) profiles obtained under 100-mW/cm<sup>2</sup> light illumination for the DSSC employing (a) *C. tora*, (b) *C. surattensis*, (c) *C. alata* and (d) *C. occidentalis*.

rationalize their explicit effect on the dynamics of the process is really difficult, and the net effect of all these factors are revealed from the current transients.

# Incident Photon-to-Current Conversion Efficiency (IPCE)

The short-circuit photocurrent  $(J_{\rm photo})$  spectra of dye adsorbed on TiO<sub>2</sub> electrodes were obtained for ascertaining the sensitization of photocurrent by the dyes under investigation. The incident photonto-current conversion efficiency (IPCE) was calculated at each excitation wavelength ( $\lambda$ ) using the values of  $J_{\rm photo}$  and the intensity of the employed monochromatic light ( $I_{\rm inc}$ ) with the help of following equation

$$IPCE(\%) = \frac{1240 J_{photo} (A/cm^2)}{\lambda(nm) \times I_{inc}(W/cm^2)} \times 100$$
 (3)

In Fig. 8, the IPCE versus wavelength ( $\lambda$ ) curves for different dyes are shown. From this figure, it can be observed that the nature of the IPCE curve and absorption spectrum of respective dyes are similar, providing proof of the sensitization of the photocurrent by the dye. The IPCE values ranged from 13% to 20% and varied as *C. occidentalis* > *C. ala*ta > *C. surattensis* > *C. tora*. The change in IPCE values for different natural dyes could be due to several facts such as the amount of dye loaded onto the TiO<sub>2</sub> thin film being different, the extent of charge carrier's recombination not being the same,



Fig. 8. Photo-action spectra of DSSC making use of (a) *C. tora*, (b) *C. surattensis*, (c) *C. alata* and (d) *C. occidentalis* natural sensitizer dye.

the excited dye molecule's energy levels being different and the probability that the excited state quenching can't be ignored.<sup>36</sup>

# CONCLUSIONS

DSSC were fabricated using natural dyes extracted from four different flowers, C. surattensis, C. tora, C. alata and C. occidentalis. The dye extracts have shown absorption in the visible range of 400–500 nm, and after adsorption onto a  $TiO_2$ photoanode, it was extended in the range of 350-550 nm. The maximum current density was observed for C. occidentalis (0.20 mA/cm<sup>2</sup>), whereas the minimum was shown by C. tora  $(0.06 \text{ mA/cm}^2)$ . DSSC employing a C. occidentalis-coated TiO<sub>2</sub> photoanode has shown the higher conversion efficiency of 0.15%, with C. alata & C. surattensis showing 0.122% and 0.046% respectively, while a quite low conversion of 0.013% was observed for C. tora. Though the solar-to-electrical conversion efficiencies obtained for these natural dyes are quite modest as compared to the commercial photosensitizers, they still offer the advantages of natural abundance, low cost and environmental friendliness.<sup>37</sup> Even for the system under investigation, improvements can possibly be made by adopting more effective extraction procedures for quantification of anthocyanin pigment present in the extracted dye, varying the thickness of the TiO<sub>2</sub> layer, etc., and efforts in these directions are underway.

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