

Fabrication and Characterization of Natural Dye Sensitized Solar Cell based on CdSe nanorods

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Abstract: The research study represents fabrication and characterizations of CdSe nanorod based dye-sensitized solar cells (DSSCs). In this work natural dyes are used as a photosensitizer to enhance the efficiency of the as prepared solar cells. It was extracted from *Clitoria ternatea*, *Hibiscus rosa-sinensis* and *Ixora chinensis* petals in a cost effective way. A comparative study is made to find the effect of optical absorption properties of different natural dyes on the CdSe nanorod-based DSSCs. The fill factor (FF), efficiency (η), short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}) of the DSSCs are determined from current-voltage measurements and power –voltage characteristics. The incident photon-to-current efficiencies (IPCE) of the DSSCs are also reported.

Keywords: Cadmium Selenide. Nanorods. Natural dye-sensitizer. solar cell. Conversion efficiency.

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I. Introduction

One of the most promising way to convert solar energy to electrical energy is the use of dye-sensitized solar cells which were first developed by Grätzel *et al.* in 1991[1-7]. As the research progresses, the DSSCs are becoming an efficient device for converting the photon energy into electrical energy [7-8]. The synthetic and natural dyes were developed for sensitization. It was reported that synthetic dyes like N3 and N719 can reach the conversion efficiency up to 12% [5-6]. The main interest to fabricate a natural dye sensitized solar cell is to avoid the use of synthetic dye which leaves a toxic effect to the environment [9-10]. The methods to fabricate the DSSCs are not involved with a complex technology, which in effect reduce the production cost [11]. The natural dyes may be extracted easily from various flowers, fruits and leaves [12]. Natural dyes pigments like anthocyanin, betacyanin, tannin, β -carotene, flavonoid, chlorophyll are used as a sensitizer of DSSCs [13]. Chang *et al.* used chlorophyll dye from wormwood and anthocyanin dye from red cabbage as a sensitizer in the DSSCs to get energy conversion efficiency of 0.9% and 1.47% respectively [14]. In the year 2015, Shalini *et al.* extracted the dyes from seeds, fruits, vegetables, tree barks, and successfully used these natural pigments as a sensitizer [15-16]. Among the different pigments, anthocyanins are generally stable. However the stability of anthocyanin is affected by several factors like pH, storage temperature, solvent used for extracting anthocyanins and sunlight exposure [17]. The optical absorption of the natural dyes plays a vital role on the surface of semiconductor nanoparticles to excite the valance electron and hence the energy conversion efficiency and quantum efficiency of the DSSCs [18-19]. Fluorine doped tin oxide (FTO) or Indium tin oxide (ITO) is generally used as a transparent conducting oxide on the glass substrate. Semiconductor layers from different nanostructured materials are used as photo anode and Platinum, Carbon and/or Graphite is used as a counter electrode in the fabrication of DSSCs. Dye molecules act as a photosensitizer and electrolyte is used for electron transfer media [20]. In the present work CdSe nanorod based dye sensitized solar cell is fabricated in a cost effective way and photo-voltaic characterizations are made.

II. Experimental

2.1 Sample Preparation and characterization

At first stoichiometric amount of anhydrous cadmium chloride ($CdCl_2$), selenium powder and sodium borohydride are taken and as a capping agent Ethylenediamine is used. The stirring is continued for 6 hours at a particular speed. The grown samples are filtered and centrifuged. Transmission electron micrograph and diffraction pattern (TEM and TED) of the samples are taken using JEOL-JEM-200 transmission electron microscope operating at 200 kV. Optical absorption measurements of the dispersed samples are studied in the range of 500 nm – 800 nm using Shimadzu Pharmaspec 1700 UV-VIS spectrometer.

2.2 Dye Extraction

Clitoria ternatea, *Hibiscus rosa-sinensis* and *Ixora chinensis* petals are collected and washed with distilled water and cut into small pieces. The petals are finely blended and mixed with ethanol to get dye solutions. The solutions are filtered to remove solid residues. The optical absorption measurements of the as prepared dyes are studied in the range of 500 nm to 800 nm using Shimadzu Pharmaspec 1700 UV-VIS spectrometer.

2.3 Device fabrication

3 ml concentrated acetic acid is added to 0.5 g of CdSe powder and the mixture is ultrasonicated for ten minutes then vigorously stirred with a pestle and a mortar till a very fine reddish black paste is obtained. The conductive face of ITO glass slides are fixed rigidly with face-up on a flat surface using a clear tape such in a way that it should cover a 3-4 mm area from the edge of the slide to establish an ohmic contact. The as-prepared CdSe paste is then applied on ITO slides and a spin coater is used to spread the paste over the ITO slide uniformly. The glass slides are annealed for one hour at a moderate temperature. Slides are then allowed to cool down to room temperature and placed their face down in a petridish containing the natural dye extracts. The glass slides are kept for one hour for proper and adequate adsorption. After adsorption, the glass substrates are cleaned with distilled water and dried. To prepare the cathode slide graphite paint is used at the sensitive part of the ITO with similar resistance and an identical border is created as that of the anode side. The two conductive sides are coupled together using a binder clips and finally added a few drops of I^- / I_3^- solution to ensure the connectivity and the schematic diagram is shown in Figure 1.

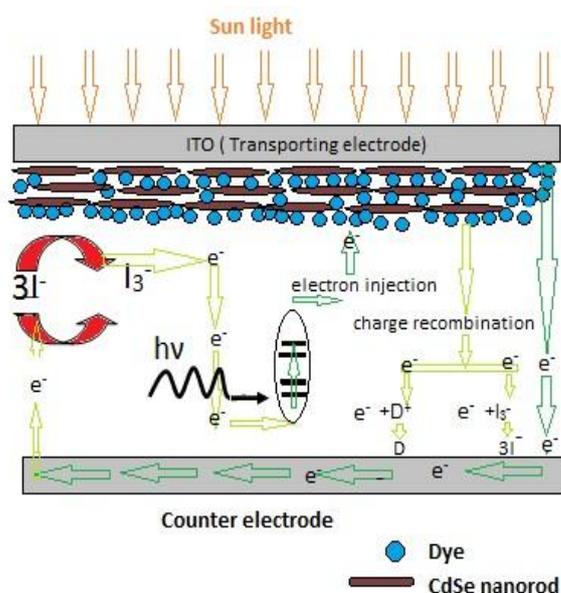


Fig. 1 The schematic diagram of fabricated DSSC.

The DSSCs are characterized by current density (J) vs. voltage (V) and incident photon-to-current efficiency (IPCE) both measurements using 100 mW/cm^2 radiation from a solar simulator.

III. Result and Discussion

3.1 Structural Characterization of the CdSe nanorod

Nanorods are formed at lower growth temperature. CdSe nanorods and the selected area electron diffraction pattern (SAED) are shown in Figure 2. TEM image clearly shows formation of nanorods. The size of the nanorods is determined from TEM to be approximately 350-375 nm in length 20-25 nm in diameter.

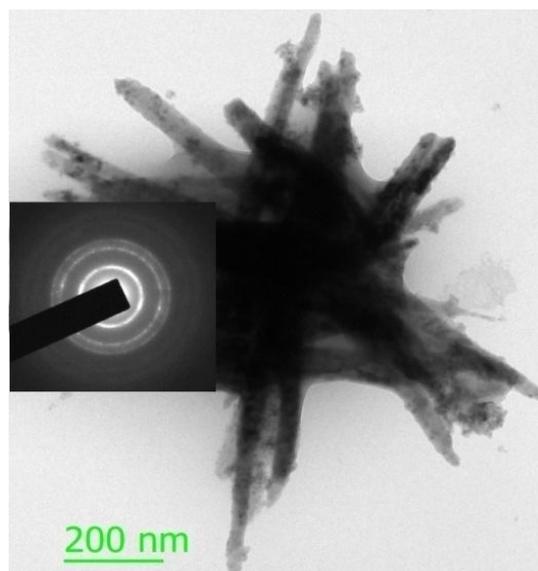


Fig. 2 TEM and SAED image of CdSe nanorod.

3.2 Optical Characterization of the sample and the dye

Figure 3 shows the variation of optical absorbance with wavelength of prepared nanorods. Optical absorption coefficient has been calculated in the wavelength region of 500 – 800 nm. The band gap of the nanorod is determined and is found to be 2.49 eV which is shown in the inset of Figure 3.

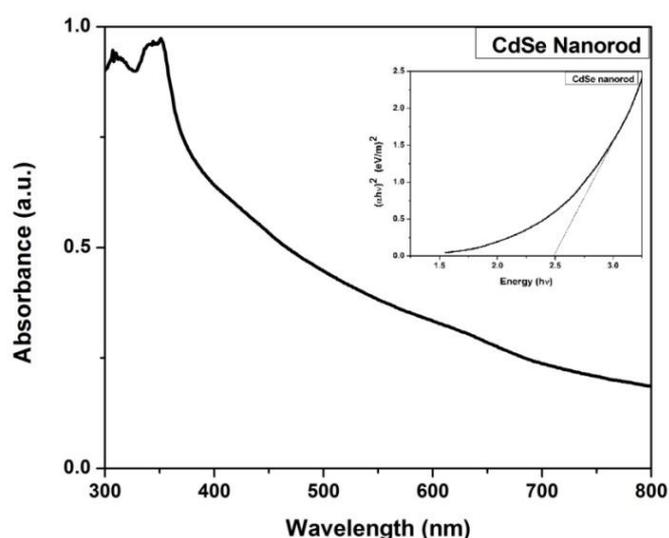


Fig. 3 Optical absorption spectra (band gap determination at the inset) of the CdSe nanorods.

The optical absorption spectra of different anthocyanin dye extracts are depicted in Figure 4. The optical absorptions of anthocyanin dye of *Clitoria ternatea*, *Hibiscus rosa-sinensis* and *Ixora chinensis* are lying in the range of 410-650nm, 450-650 nm and 500-650 nm respectively. This result confirms that the solution of different dyes can be used as a photosensitizer because their absorption peaks are lying in the visible region. It can be seen that there is an absorption peak at about 528 nm for the extract of *Clitoria ternatea*. The absorption ascribes to the component namely, anthocyanin, a group of natural phenolic compounds [21-23]. Anthocyanin is the core component of natural dyes and is often found in the fruits, flowers and leaves of the plant. Because anthocyanin shows colours in the range of visible light from red to blue, it is predicted to become highly efficient sensitizer for wide range of semiconductors.

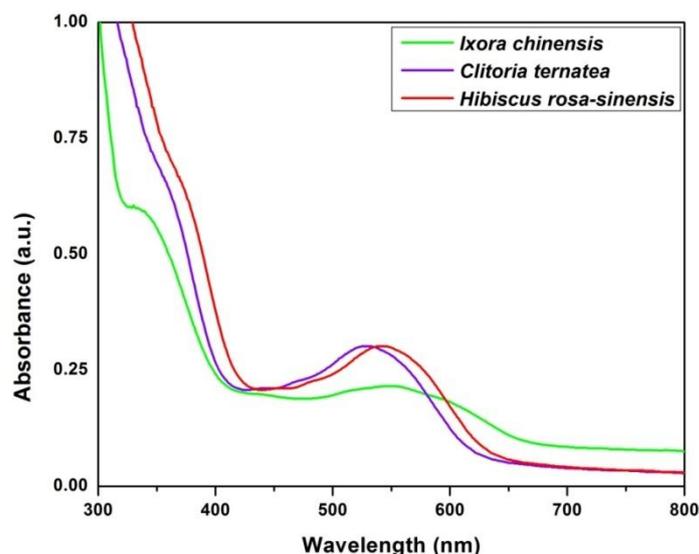


Fig. 4 The optical absorption spectra of different natural dyes.

From the table 1 it is noted that the total anthocyanin content (TAC) is maximum for *Clitoria ternatea* compared to that in other two dyes. As a result the optical absorption is maximum for such a dye. It is also noted in Figure 4 that a blue shift of the absorption peak occurs with the increase of TAC

3.3 Electrical Characterization of the device

The J-V characteristics of fabricated DSSCs using three different natural sensitizers are shown in Figure 5a.

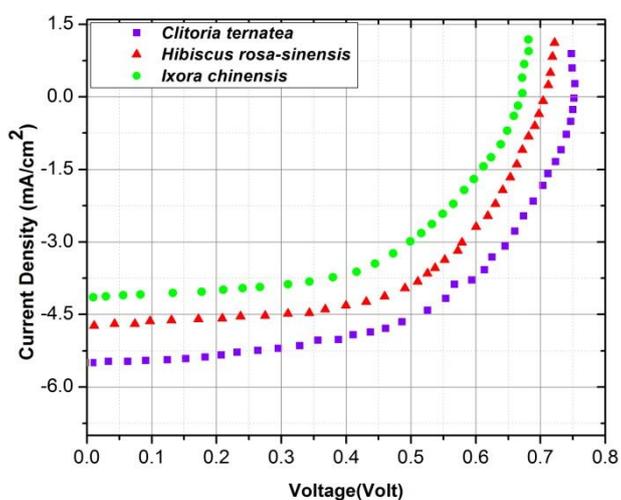


Fig. 5a. Current density (J) - Voltage (V) characteristics of DSSCs.

From the curve open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and the maximum power of the devices are determined. Fill Factor (FF) and efficiency (η) are calculated using the well known relations.

$$FF = \frac{V_{max} J_{max}}{V_{oc} J_{sc}} \quad \text{and} \quad \eta = \frac{V_{oc} J_{sc} FF}{P_{in}}$$

where V_{max} is maximum voltage, J_{max} is maximum current density, V_{oc} is open circuit voltage, J_{sc} is sort circuit current, FF is Fill Factor and P_{in} is the power of the incident light . It is observed that efficiency of *Clitoria ternatea* dye sensitized solar cell is 2.3 % whereas that for *Hibiscus rosa-sinensis* and *Ixora chinensis* are 1.9 % and 1.52 % respectively.

Table 1. TAC and photovoltaic parameters of different natural dye sensitized solar cell.

Natural Dye	TAC (mg/kg)	V _{max} (V)	J _{max} (mA/cm ²)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	η (%)
<i>Clitoria ternatea</i>	227.42	0.525	4.4	0.751	5.5	55.9	2.3
<i>Hibiscus rosa-sinensis</i>	52.94	0.510	3.825	0.706	4.731	58.4	1.9
<i>Ixora chinensis</i> petals	50.84	0.472	3.239	0.671	4.145	54.96	1.52

Figure 5b shows the variation of power density with the voltage for the DSSCs prepared with different dyes.

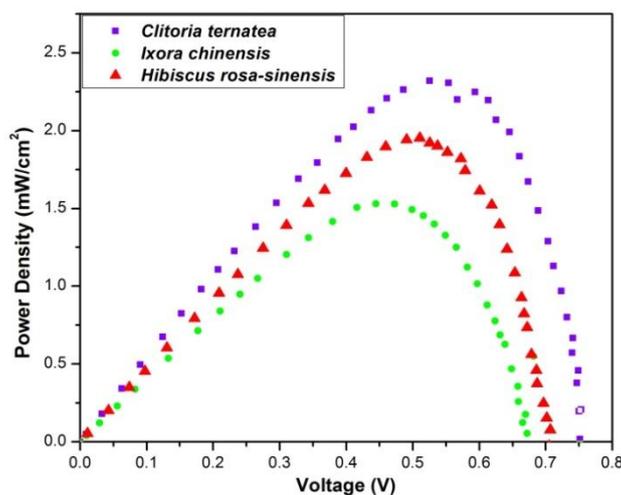


Fig. 5b. Variations of Power density (P) with Voltage (V) for DSSCs.

From the Figure it is noted that *Clitoria ternatea* dye sensitized solar cell produces a maximum power probably due to the presence of high content of anthocyanin therein. The efficiencies of DSSCs not only depend on the molecular structure of the pigments, but also depend strongly on properties viz. morphology, self-assembly, aggregation of the dye molecules and the total amount of the anthocyanin present in the dyes [24-26]. Because of a modified surface morphology in CdSe nanorod based DSSCs a strong bonding between the hydroxyl and carboxyl groups present in anthocyanin with the nanorods resulting in a better performance. The IPCE is calculated using equation [24].

$$IPCE(\%) = \frac{1240 J_{sc}}{\lambda P_{in}}$$

where λ is the wavelength of the incident light and P_{in} is the power of the incident light. The variations of IPCE with λ are shown in Figure 6. The light absorbed by the photo-anodes ranged from 400-800 nm is in accordance with the absorption range of the CdSe nanorod. It is observed from the IPCE characteristics that the photon-to-

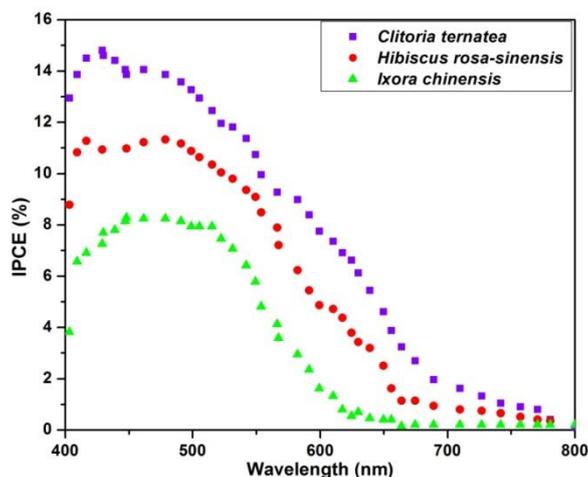


Fig. 6 The variations of IPCE with wavelength for DSSCs.

current conversion efficiency is maximum for *Clitoria ternatea*, which supports the J-V characteristics. The nanorod structure of the CdSe and a large content of anthocyanin in the *Clitoria ternatea* extracted natural dye produce the maximum light harvesting efficiency of the DSSCs.

IV. Conclusions

CdSe nanorods are grown chemically at low temperature in a cost effective way. Optical absorption study shows the increase in bandgap due to quantum confinement. Three different dyes are selected on the basis of their absorptions in the range 450–650 nm range. Extracted dyes are used as a sensitizer with CdSe nanorods to fabricate dye sensitized solar cells. The efficiency is found to be maximum for DSSC based on *Clitoria ternatea* dye. This is possibly due to the large anthocyanin content compared to that in other two dyes.

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