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A Preliminary Study On the Development of Cost Effective Dye Sensitized Organic Solar Cell Using TiO_2

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Abstract: The dye-sensitized solar cell (DSSC) is thelatest concept of solar cell which converts the visible light into electricity by using the photo electrochemical system. It offers reliable alternative thought for inorganic solid-state photovoltaic cells. The preparation of Low Cost Dye sensitized Organic Solar Cell has been developed by using TiO_2 based thin film that has been fabricated using natural dye extracted from pomegranate, Malabar spinach seeds and red spinach. In this study, five TiO_2 based thin films have been prepared using different compositions and investigated by several techniques like X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). It has been found that the paste of Titanium dioxide (TiO_2), Polyethelene glycol (PEG), Titan X-100, Titanium tetrachloride ($TiCl_4$) and Iso-propanol composite (S-3) which has been used as an electrode in a DSSC with Malabar spinach seeds dye shows efficient photovoltaic properties when exposed to solar-like light. The voltage and current of composite (S-3) electrode with Malabar spinach seeds dye have been measured with an electric multimeter and found 0.75 mV and corresponding 0.15mA. The electrical properties of the electrode have been measured by Inductance Analyzer, scanning electric morphology and X-ray diffraction morphology which revealed composite (S-3) electrode of TiO_2 is more efficient for producing solar energy. This paper show up and discusses the improvement of natural dye photosensitizers and the efficiency of the DSSC which is useful for the preparation of environmentally friendly, low-cost, renewable and clean sources of energy.

Key words: Organic dye · Dye-sensitized solar cell · Titanium tetrachloride · Nanocrystalline titanium dioxide · Sensitizer · Semiconductor · Solar cell efficiency

INTRODUCTION

Dye sensitized solar cells (DSSC, DSC or DYSC) have become a focus of significant study in the last twenty years because of their basic and scientific significance in the area of renewable energy. The use of artificial dyes as sensitizer in DSSC gives better efficiency and high stability, but there are some limitations for example cost, tendency to go through degradation and involvement of toxic materials. Due to these limitations analternate sensitizers have developed that are bio friendly natural sensitizers. Natural sensitizers have plant dyes such as anthocyanin, carotenoid, flavonoid and chlorophyll which are liable for chemical reactions like as absorption of light in addition toinsertion of charges to the conduction band of TiO_2 by the sensitizer. Therefore, dyes having these pigments can simply be extracted from natural products like fruits, flowers, seeds, barks, leavesetc and can be utilized as sensitizer for DSSC.

A DSSC [1] is aeconomical solar cell belonging to the set of thin film solar cells. DSSCs are considered the third generation of photovoltaic devices for the conversion of visible light into electrical energy [2]. This cell is based on a semiconductor that formed sandwiched between a photo sensitized an electrolyte and anode, a *photo electrochemical* method. This cell is also called Grätzelcell

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and was originated by Michael Grätzel and Brian O'Regan at the École Polytechnique Fédérale de Lausanne in [3]. DSSCs are based on a porous thin film that is modified by dye molecules of a wide-band gap semiconductor oxide. The assembling charge of DSSCs are approximately 1/3 to 1/5 times lower than that of silicon solar cells [1]. This film increases the light absorption owing to its spongelike behaviors and amplified surface area. The nano-crystalline substancetakes part in an vital role in electron insertion and carrying, identifying the activeness of the DSSCs [4]. The overall conversion efficiency of DSSCs was reported to be proportional to the injection of electrons in wide-band gap nano-structured semiconductors. Still now, the efficiency of DSSCs are around 11.1% for a tiny cell and for large-scale this is not yet declared [5]. Hence, DSSCs have several advantages in comparison with silicon solar cells.

The purpose of this research is to manufacture dye sensitized solar cells by means of a simple pressing method and to inspect whether this technique is probable to sensitize them with plant extract-based dyes rather than the ruthenium-based dyes are commonly used in DSSCs which are expensive and highly toxic [6]. The plant-extract dyes in this study are cheap, available, non-toxic and simple to manufacture and less harmful to the environment than ruthenium. We chose to concentrate on dyes obtainable from plants such as Malabar spinach seeds, red spinach and pomegranate burgs dyes. The plants were chosen for their color and their convenient accessibility. The open sandwich configuration of the solar cells built for this study is designed for short-time use, since it is not sealed (so the electrolyte is allowed to evaporate). Therefore, issues of long-time use have not been considered in this study.

MATERIAL AND METHODS

Materials: The materials used in this experiment wereTitanium dioxide(TiO_2)P25 Degussa (USA), Nitric acid (HNO_3), Polyethelene glycol (PEG), Titan X-100 (Merck, Germany), Ethanol(Germany), Titanium tetrachloride ($TiCl_4$), Iso-propanol (Merck, Germany).

Dye Extraction: Three types of organic dye are extracted from pomegranate, Malabar spinach seeds and red spinach. Pomegranate skin grinds down by mortar then 20 grams of them sock in 200ml water and stirred 2 hours by electrical stirrer. Then filter the dye. Malabar spinach dye was achieved by blending the sample with a commercial blender to obtain a slurry mixture. This mixture was then filtered carefully. Red spinach dye extracted by heated the sample with water and then filtered.

The dye extraction process includes the subtraction of water from the desired sample. The obtained juice extract was sublimed utilizing the dehydration process of Lyophilizationwith the aim of preserve the intentioned anthocyanins. The process of freeze-drying aresplit into three stages like freezing, primary drying and secondary drying.

Preparation of TiO_2 Paste: TiO_2 sol-gel paste is produced in the laboratory using nanocrystalline grade TiO_2 powder. Following types of sample paste produce and then coated on TCO glass where side of conductive layer [7].

Sample 1: 2gramms TiO_2 +15ml EtOH → Ultra-sonicate about 40 mins + 0.5ml solution of $TiCl_4$ and 2-propanol (1:4) mixture → sonicate 10 mins.

Sample 2: 2gramms TiO_2 +2ml 0.4M HNO_3 + 1.4ml polyethelene glycol(PEG) + 0.5 ml Titan X-100 + 0.5ml solution of $TiCl_4$ and 2-propanol (1:4) mixture → Ultra-sonicate about 40 mins.

Sample 3: 2gramms TiO_2 + 3ml solution of $TiCl_4$ and 2-propanol (1:4) mixture + 1.4ml polyetheleneglycol(PEG) + 0.5 ml Titan X-100 → Ultra-sonicate about 40mins.

Sample 4: 2gramms TiO_2 +2ml 0.4M HNO_3 + 1.4ml polyetheleneglycol(PEG) + 0.5 ml Titan X-100 → Ultra-sonicate about 40 mins.

Sample 5: 2gramms TiO_2 +2ml 0.16 M HNO_3 + 1.4ml polyetheleneglycol(PEG) + 0.5 ml Titan X-100 → Ultra-sonicate about 40 mins.

Preparation of TiO_2 Electrode: The conducting side of a tin oxide-coated piece of glass is identified by using a multimeterfor themeasurement of resistance. The resistance of conducting side was around 20-30 ohms. The TiO_2 electrode was prepared by placing the conducting side up, tape the glass on three sides with one thickness of Scotch brand Magic™ tape. By using wet tissue with ethanol fingerprints or oils were wipe off. The titanium dioxide paste was added and spreadlike a thin film with the help of a glass rod. The tape serves as a 40-50 micrometer spacer to control the thickness of the paste layer.

The tape was removed carefully without scratching the TiO_2 coating. Put this electrode on top of a hot plate and heat it at approximately 350°C for 3 hours. Then sock this electrode into the dye solution for overnight. The TiO_2dye electrode was took out from the dye solution and rinsed it with HPLC grade ethanol after that the electrode was dried in room temperature [8].

Preparation of Counter Electrode Spacer: A plastic film (like as Parafilm or Scotch tape) of dimensions of 1.5 cm by 2 cm was cut and a hole(s) was made on the film. The electrode spacer was produced by placing the film on a conducting side of Hg coated counter electrode.

Electrolyte and Counter Electrode Preparation: The solution was prepared by using 10ml ethylene glycol with the mixture of 0.83g of 0.5M potassium iodide and 0.127g of 0.05M iodine. The solution was stored in a black bottle to avoid photosynthesis. This solution was used as electrolyte. The counter electrode was made of by revealing the conductive side of an ITO coated glass to candle light for 2-3 minutes which left a dark shade of carbon on the glass.

Preparation of Electrolyte: The electrolyte consists of iodine (I^-) and tri-iodide (I_3^-) as a redox couple in a solvent with possibly other substances was included to enhance the properties of the electrolyte [9] and the performance of the operating DSSC.

DSSC Assembling: The mercury coated slide was placed face down on top of the dry organic dye soaked TiO_2 coated side of the second slide. The slides were placed a little off set to permitadequatespace on the end to place an alligator clip. Two binder clips was used to hold the two slides together. One to two drops of liquid iodide/iodine electrolyte solution was added with the help of an eyedropper to the crease between the two slides [10]. The solution was drawn into the cell by capillary action and was stain the entire inside of the slides. The alligator clips were attached to the two overhanging edges of the slides and a multi-meter was attachedwith the negative terminal to the TiO_2 coated slide and positive terminal to the mercury coated slide. The currents and corresponding voltages were measured of the cell in direct sunlight and indoors.

RESULTS

Solar cells as well as photovoltaic cells converts the solar energy directly into electricity [11]. By using multi-meter the voltage, resistance and electricity were measured for various samples with electrolyte.

Fig.1 shows the variation of conductivity of five different DSSCs electrode with respect to frequency from 1 KHz to 500 KHz. It was observed from the conductivity measurement that Sample 3 DSSC electrode showed the highest conductivity value of 102.4 nF using Malabar Spinach Seeds dye at lower frequency.

The dielectric properties greatly influenced by the frequencies. Fig. 2 shows the variation of dielectric constant with frequency from 1 KHz to 500 KHz at room temperature. From Fig. 2 it can be seen that, the dielectric constant is increased with decreasing frequency for different DSSCs electrodes. It can also be seen from Fig. 2 that, dielectric constant is found to reduce continuously with rising frequency for all specimens revealing a normal dielectric characteristics of materials, which is due to the interfacial polarization as predicted by Maxwell and Wagner. The dielectric constant varies with frequency and achieves a constant value at 2 MHz because of the fact that beyond a certain frequency of external AC field.

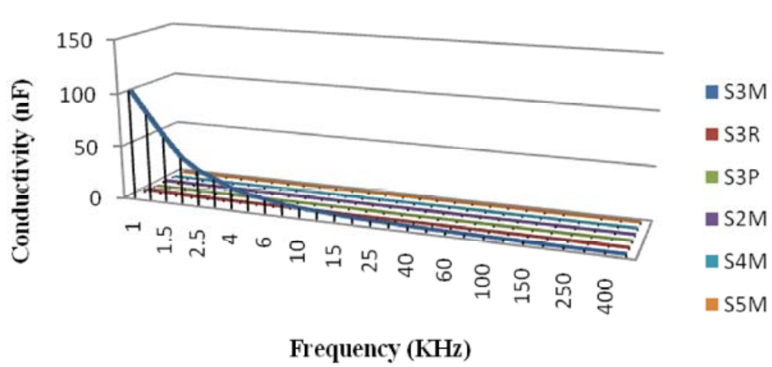


Fig. 1: Conductivity of different DSSCs electrode as a function of frequency

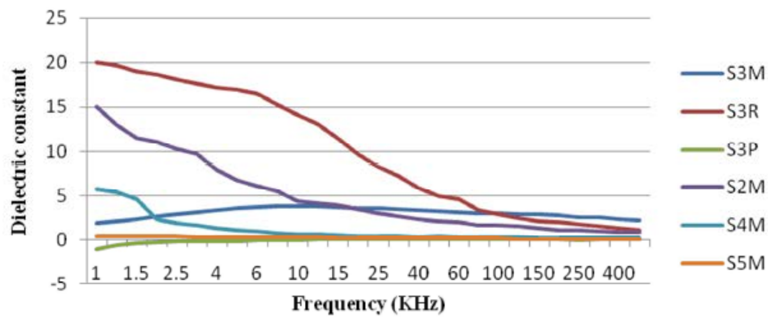


Fig. 2: Dielectric constant of different DSSCs electrode as a function of frequency

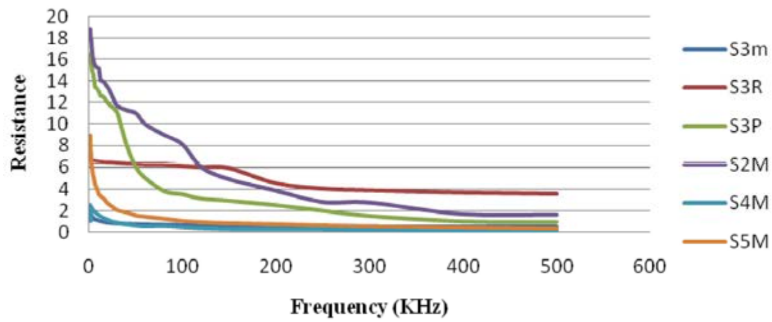


Fig. 3: Resistance of different DSSCs electrode as a function of frequency

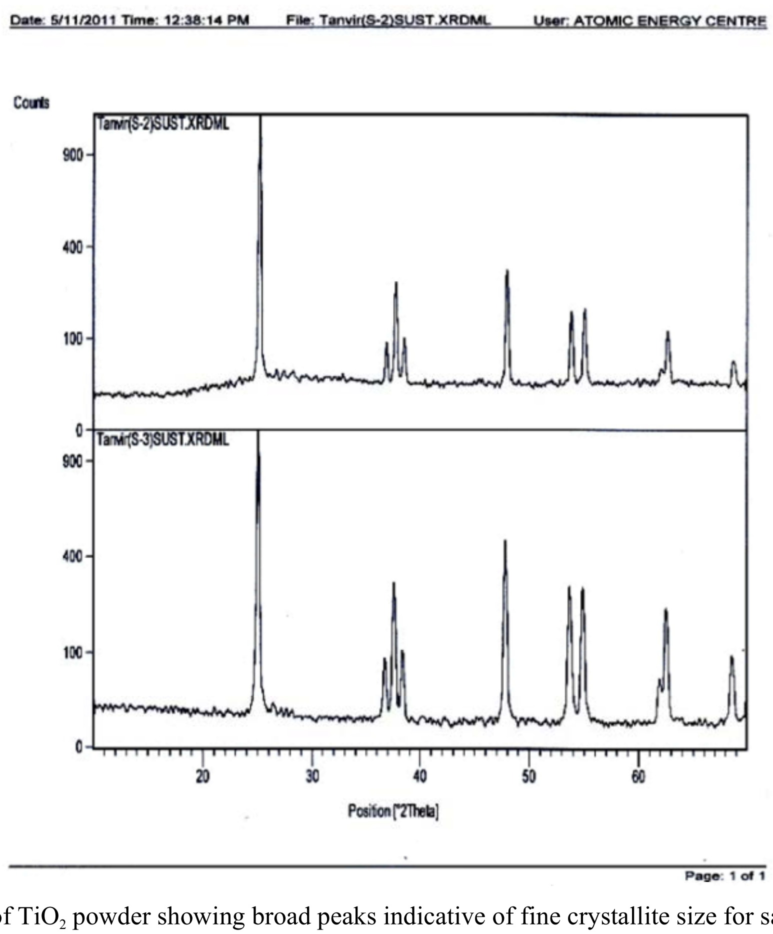


Fig. 4: XRD pattern of TiO_2 powder showing broad peaks indicative of fine crystallite size for sample 2 & 3.

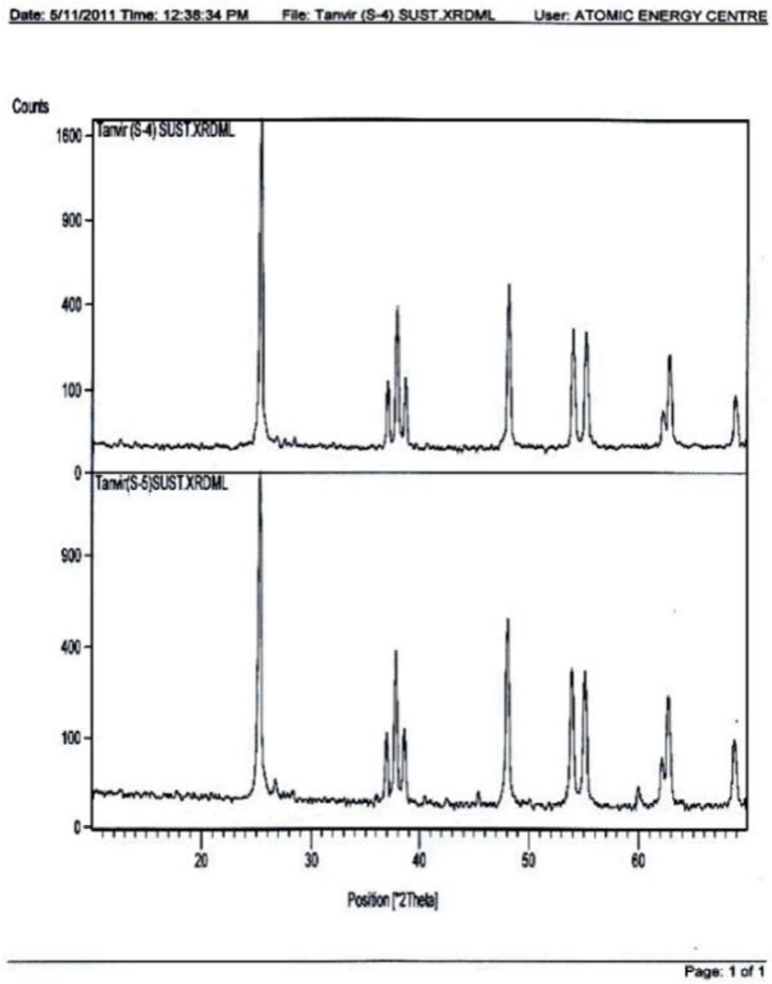


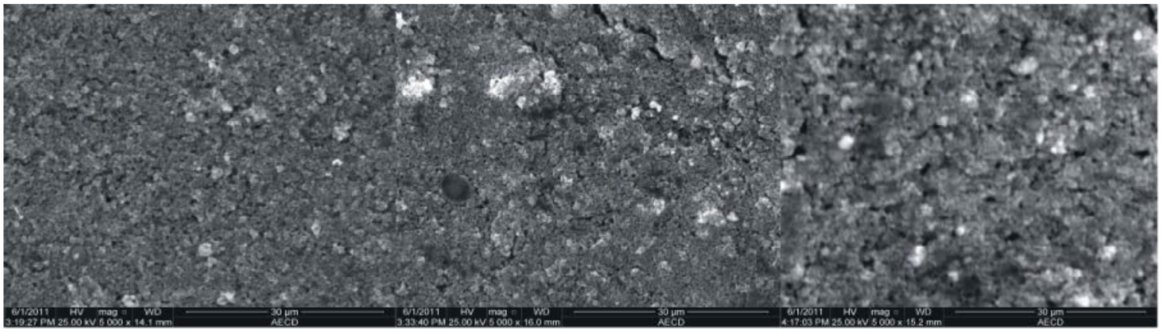
Fig. 5: XRD pattern of TiO_2 powder showing broad peaks indicative of fine crystallite size for sample 4 & 5

At high frequencies the current isno longer flows in the film, but effectively flows on the surface of the film, within a thickness of a few skin depths. Increase the resistance of DSSCs electrode film decrease the current. The Fig. 3 showed that sample 3 electrode has lower resistance with lower frequency.

XRD Spectral Analysis: The crystalline phase of synthesized nano-TiO_2 films was analyzed by XRD and their XRD patterns are shown in Figure 4 & 5. The polycrystalline anatase phase was confirmed by (101), (004), (200), (211) and (204) diffraction peaks. TiO_2 layers formed from the commercial Ti-Nanoxide paste appeared transparent but absorbed light below about 370 nm, which is consistent with the anatase band gap of 3.2eV (about 385 nm). An XRD study of the layer detected only a crystalline phase of anatase.

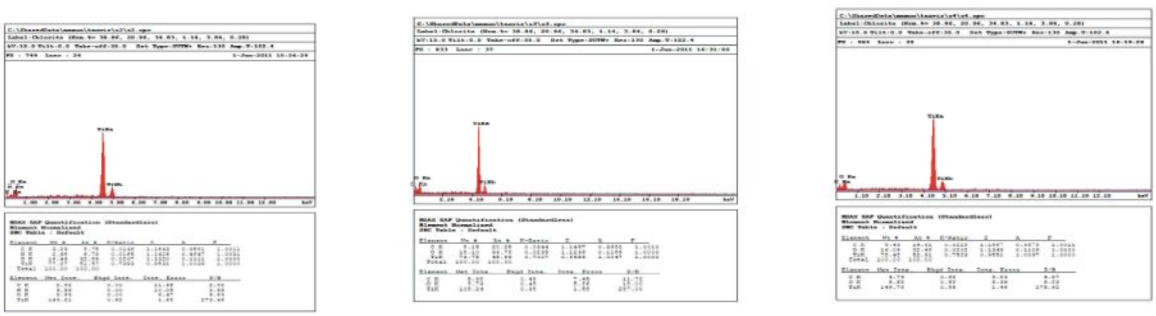
SEM Analysis of TiO_2 Paste: The SEM images of nano- TiO_2 film calcined at 500°C are shown in Figure 6. In this figure the particle morphology is found spherical. The crystallite sizes of TiO_2 are in between 10 nm and 100 nm which are bigger than those of estimation from XRD data. Many small crystals of TiO_2 are present in the spheres due to agglomeration. Porous structure of the film was observed by the SEM image. The pore diametervaries from 20 nm to 100 nm.

Energy-dispersive X-ray Spectroscopy (EDS or EDX): Energy Dispersive X-ray analysis is a technique that is used for identifying the elemental composition of desired specimen. The energy spectrum of different samples are shown in Fig. 7. From the energy spectrum of sample S-2, S-3 and S-4, it is found that the presence of Tiis around 78% and Ois around 16%. As we described the process of



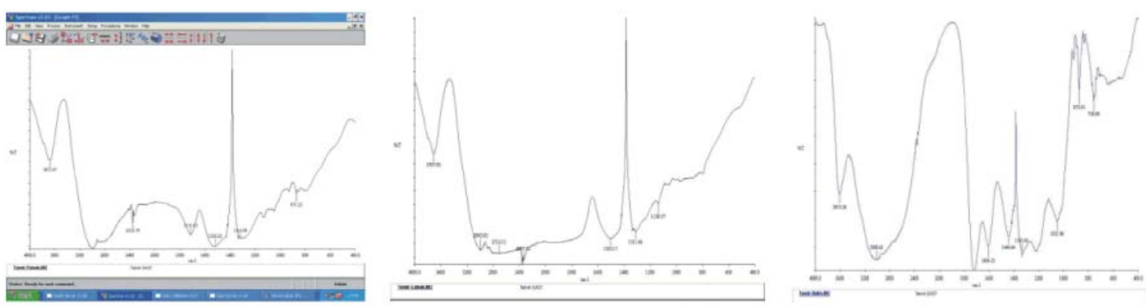
Sample-2 Sample-3 Sample-4

Fig. 6: Scanning electron micrographs of the TiO_2 films of sample-2, sample-3 and sample-4 electrode. Scales and magnifications are indicated on the photographs.



Sample-2 Sample-3 Sample-4

Fig. 7: Energy-dispersive X-ray spectroscopy for three DSSCs TiO_2 electrodes.



Malabar spinach Red spinach Pomegranate burgs

Fig. 8: FTIR spectroscopic data for Malabar spinach seeds, Red spinach and Pomegranate burgs dyes.

preparing TiO_2 paste and the result is matched with the spectrum obtained by the Energy Dispersive X-ray analysis.

FTIR Spectroscopic Analysis: The spectra analysis of three organic natural dyes (Malabar spinach seeds, Red spinach and Pomegranate burgs) are showed that they have contained -OH stretch, =C-H, C=C, C=C, C=O, C=N functional groups. All functional groups have more free electrons that's photo chemically exited in DSSCs.

DISCUSSION

The performance of dye sensitized solar cells are mainly based on the dye as a sensitizer. The efficiency of aDSSCis depend upon the dye used for coated TiO_2 film [12]. Natural dyes have become a feasible alternative because of its cost effectiveness, easy reasonability, available supply of raw materials and absent of environment pollution risk, since those dyes are obtained from natural sources.The homogeneity of the natural dye extraction greatly affected the cell efficiency. In order to obtain even cheaper dyes for DSSC, metal-free organic photosensitizes are strongly desired. Hence natural dyes extracted from Malabar spinach seed, Red spinach and pomegranate burgs are the suitable alternative for possible application as sensitizers to inorganic dyes in DSSC. In this research, we conducted a few experiments in order to find the best power production for this research. We divide the whole experiments into four parts. The first one is the particle size assessment of titanium then the outcome of molecular binder PEG to TiO_2 paste after that the effect of dye and finally the thickness of TiO_2 layer. Three types of organic dye are extracted from pomegranate, Malabar spinach seeds and red spinach. We used all three types of dye as sensitizer in each five paste (Sample 1-Sample5), among them we found that,Sample 3 electrode with Malabar spinach seeds dye has higher conversion rate compared to others sample. It was also observed from the conductivity measurement that, Sample 3 DSSC electrode showed the highest conductivity value of 102.4 nF using Malabar Spinach Seeds dye at lower frequency and has lower resistance with lower frequency which is suitable for DSSC. The crystallite sizes of TiO_2 obtained from SEM image are between 10 nm and 100 nm. The SEM image also reveals a porous structure of the film. The pore size ranges from 20 nm to 100 nm in diameter. The porosity may occur when aqueous polyethylene glycol which is used as a binder leaves the surface of the substrate at high calcination temperature. The spectra analysis of three organic natural dyes are showed that they have contained -OH stretch, =C-H, C=C, C=C, C=O, C=N functional groups. All functional groups have more free electrons that's photo chemically exited in DSSCs.

CONCLUSION

In this paper, DSSCs were prepared using dyes those were extracted from the Malabar spinach seed, Red spinach and pomegranate burgs. Solution casting method was followed to prepare titanium dioxide nanocomposite paste of five different compositions and light sensitize electrode produce on ITO coated glass. The electrical, crystalline and morphological properties of the electrode were improved. By using electric multimeter,it was found that S-3 electrode with Malabar spinach seeds dye gives 0.75 mV and 0.15mA current. Also electrical property by Inductance Analyzer, scanning electric morphology, X-ray diffraction morphology showed that S-3 electrode of TiO_2 is more efficient for solar energy. Although the efficiencies obtained from the natural dyes that are below the requirements for large scale production, the results are hopeful and can added studies oriented to the search of new natural sensitizers and to the optimization of solar cell components compatible with such dyes. Hence there is still remains scope for further development for this technology.

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