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Fabrication, Optimization and Characterization of TiO_2Photoanode Utilizing Natural Photosensitizerfor Dye Sensitized Solar Cell Application

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ABSTRACT

In this study, the dye sensitized solar cells (DSSC) were assembled by using natural dyes extracted from pomegranate juice as sensitizer graphite coated FTO plate used a counter electrode for nanocrystalline TiO_2. The photo electrode prepared using doctor –blade technique using commercial titanium dioxide nanopowder. The aim of this work is to develop photoelectrodes using natrual dye and low cost graphite counter electrode to increase the efficiency of this type of solar cells. Dyes obtained from fresh sources of pomegranate were used in ethanol. The functional groups analysed using FTIR spectrum for Natural dye. The structural, morphological and optical studies were analyzed using X-ray diffractometer (XRD), Scanning electron microscope (SEM) and UV-Vis spectroscopy. Their photovoltaic properties such as efficiency, fill factor, open circuit voltage and short circuit current were studied using a solar simulator.

Keywords: TiO_2 photoanode, Structural, Optical, Natrual dye, DSSc.

I. INTRODUCTION

Dye-sensitized solar cells (DSSCs) are third generation solar cells industrial by O'Regan and Gratzell in 1991 [1]. In recent years, a spurt of activities could be seen on the synthesis of metal oxide semiconducting (MOS) nanomaterials like TiO_2, SnO_2, ZnO, ZrO_2, and Al_2O_3 in both industrial and academic side due to their extensive applications in electronic, photovoltaic devices, pigments, and photocatalysis [2]. Dye sensitized solar cell (DSSC), one of the most broad and hopeful photovoltaic technologies for the clean, production of renewable and affordable energy with easy fabrication method is being given a huge thrust with these materials. TiO_2 is the most broadly studied DSSC photoanode material where a highest solar conversion efficiency of 11.2% [3] is reported. Anatase phase of TiO_2, among three phases of TiO_2 is considered as an active DSSC material because of its higher band gap (3.2 eV), superior surface chemistry, andappreciable electron diffusion [4]. In DSSC, the charge separation procedure and optical absorption can be well achieved with the involvement of sensitizer as light-absorbing material in broad band gap semiconductors [5, 6]. The presentation of DSSC depends equally on the type of the sensitizer and the nature of broad band gap semiconducting materials. Several studies have addressed that the effective dye absorption on the surface of broad band gap semiconductor nanomaterials is one of the solution parameter in determining the DSSC efficiency. One of the main efficient sensitizer, ruthenium polypyridyl complex is widely used for the reasons (i) strong charge transfer absorption in visible region, (ii) long excited lifetime, and (iii) extremely efficient metal to ligand charge transfer [7]. It involves very difficult preparation process and hence as well expensive for large scale productions and applications. Still no new sensitizers are available to break or exceed the presentation of ruthenium based DSSC. But, some of the notable difficulties stimulated the researchers and industrialists to develop alternate sensitizers, particularly organic dyes. Next to ruthenium complex, organic dyes based DSSC offers maximum efficiency of up to 9% and it shows highest absorption coefficient [8]. Most of the literature supports that the organic dyes employed in DSSC can as well be replaced with the dyes extracted from natural products like flowers, fruits, vegetables, leaves etc. It is highly desirable to explore this type of non toxic natural dye with good optical properties to the research. Easy availability, eco friendly, easy fabrication, low extraction temperature and cost of purification are the important advantages of the natural dyes over other type of sensitizers. Most of the natural products show various colors and this may be attributed to the various pigments such as anthocyanins, carotenoids, and chlorophyll present in it. Generally, the increase in the ratio between the rate of forward (charge injection) and reverse (recombination) reaction process is the key tool to optimize the sensitizer [9]. Enough energy levels for efficient electron transport and more anchoring groups to bind semiconductors are the two important features that sensitizer should meet [10]. Orttiz*et al.* [11] achieved the efficiency of 0.19% for annatto dye sensitized ZnOnanoparticles and 0.01% for bixin sensitized ZnO cells. Wongcharee*et al.* [12] fabricatedsolar cells using natural dyes extracted from rosella, blue pea and a mixture of the extracts and has reported the efficiency to lie in the range of 0.57–0.33%. Thambidurai*etal* [13] observed the solar cell efficiency as 0.33%, 0.41% and 0.28% for ixoracoccinea, mulberry and beetroot dye based ZnO solar cells.

All these studies use eco-friendly and low-cost natural dyes, but they still use an expensive metal such as platinum (Pt) as a counter electrode due to its high catalytic activity. However, some reports have claimed that platinum gets corroded with triiodide containing electrolytes and forms platinum iodides such as PtI4 [14, 15]. Huge-scale solar energy alteration systems need in abundance obtainable low-cost materials in the long run and, hence, there is a need to investigate a counter electrode that is less expensive and noncorrosive in electrolyte [16, 17]. In this study, we have used graphite as a counter electrode in order to achieve this goal.

From the above discussions, it is understood that the use of non toxic natural dye solutions as sensitizer and graphite coated FTO as a counter electrode are expected to offer good alternative to the expensive dyes along with improvement in environmental and commercial benefits. Here, in this manscript, an attempt is made to extract of dye solution from Pomegrante natural products by simple process and graphite coated counter electrode were tested the DSSC performance based on this dye solution for the solar cells studied earlier.

II. MATERIALS AND METHODS

2.1. Preparation of TiO_2Photoanode

All chemicals and reagents used in this work were of analytical grade. Doctor blade technique was used to prepare TiO_2 film. TiO_2 nano powder (particle size <25 nm) was dispersed in acetic acid by grinding it in a mortar. Little drops of Triton X-100 (surfactant) be extra to lower the surface tension of the colloid in order to assist the dispersal onto the conducting glass plate [18]. After drying, it was annealed at 450 °C for an hour in muffle furnace [19]. Natural dyes were adsorbed onto this TiO_2 surface by immersing TiO_2 coated fluorine doped tin oxide (FTO) electrodes in dye solution for 24 h at room temperature. Surplus dye was washed off by dipping it in ethanol. This dye/TiO_2/FTO/glass structure forms the photo anode for DSSC. Graphite coated glass with resistance in the order of few ohms was used as the counter electrode for DSSC; 0.5 M potassium iodide (KI) and 0.05 M iodine added to acetonitrile were used as the redox electrolyte.

2.6 Graphite Coated Counter Electrode

Figure1 shows the graphite coated counter electrode. To prepare the counter (positive) electrodesusinggraphite (soft pencil) to apply a light carbon film to the entire conductive side of the FTO plate.

Figure 1. Graphite coated counter electrode

2.2. Preparation of Natural Sensitizer

To obtain the Anthocyanin Pigment from Pomegranate, we bought fresh pomegranate fruit, grabbing the seeds and after removing any white pith from the seeds, we put it in clean mortar to grinding the seeds, we finally got the pomegranate juice and putting it in a clean dish.

2.3. Characterizations

Crystallinity and the phase purity of the synthesized materials were determined by X-ray diffraction (XRD) recorded at room temperature using PAN alyticalX'Pert X-ray diffractometer with Cu-Kαradiation (wavelength: 1.54056 Å). The morphology, size distribution, and the elemental compositions of nanostructures were determined by scanning electron microscope (SEM, JEOL JSM-6390) along with energy dispersive X-ray spectroscopy (EDS, Oxford Instruments, Model No: 7582). UV-Vis absorption measurements were carried out at room temperature by using UV-Vis absorption spectrometer (Shimadzu-2450). The room temperature photoluminescence (PL) spectra were recorded by using spectroflurophotometer (Shimadzu RF-5000) with the excitation wavelength of 280 nm. The performance of the DSSC was evaluated from manually recorded photocurrent-photovoltage curves by using the simple electronic circuit discussed in figure 2.

III. RESULTS AND DISCUSSION

3.1. Structural analysis

Figure. 2 shown in XRD patterns of nano-TiO_2anatase phases. All peaks can be indexed to the anatase phase (JCPDS No. 89-4921). Using Scherrer equation [1] calculate the crystallite size From the XRD pattern, the crystallite size were calculated for the highest anatase diffraction (110) plane .

$$\mathbf{D} = \frac{\mathbf{K\lambda}}{\mathbf{ß\cos\theta}} \quad (1)$$

Where D is the mean size of crystallites (nm), K is crystallite shape factor a good approximation is 0.9, **λ** is X-ray wave-length, ß is full width at half the maximum (FWHM) in radi-ans of the X-ray diffraction peak and θ is the Bragg angle [20].

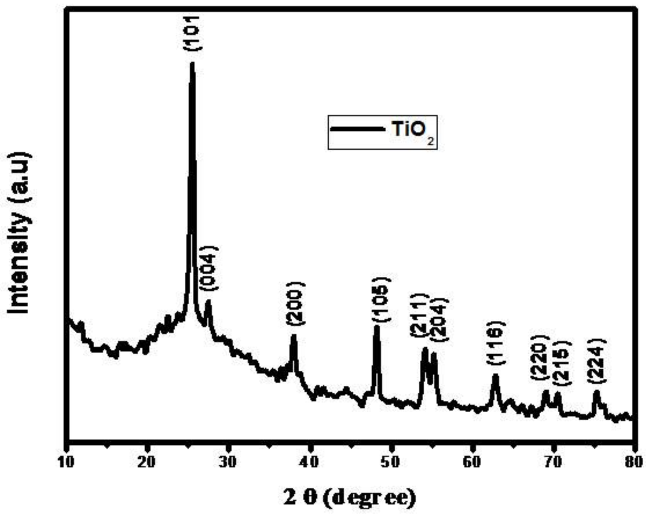

Figure 2. XRD patterns of the TiO_2 nanoparticles

3.2. Morphologicla analysis

Figure 3 shows the SEM image of TiO_2 nanoparticles. From SEM we obtain the spherical shape nanoparticles. It shows no gaps and no fracture on the surface. The nanoparticles areequaly agglomerated between them, indicating excellent inter-particle connectivity and inter-layer attachment. Figure.4 shows the particle size distribution TiO_2 nanoparticles.

Using Image J software to calculate the average particles size of the TiO_2 nanoparticles.

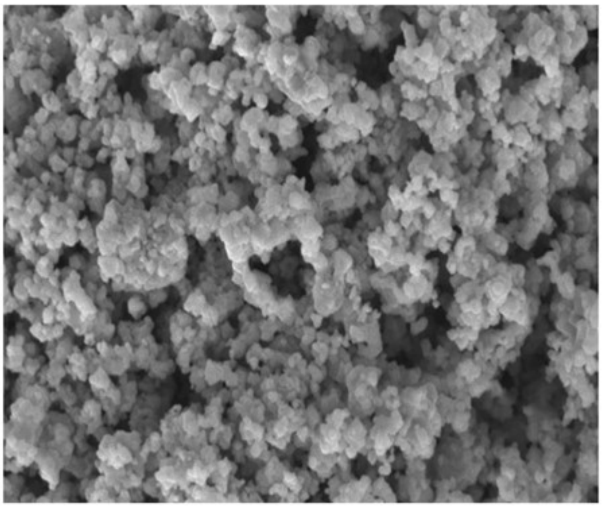

Figure. 3 SEM micrograph of TiO_2 nanoparticles

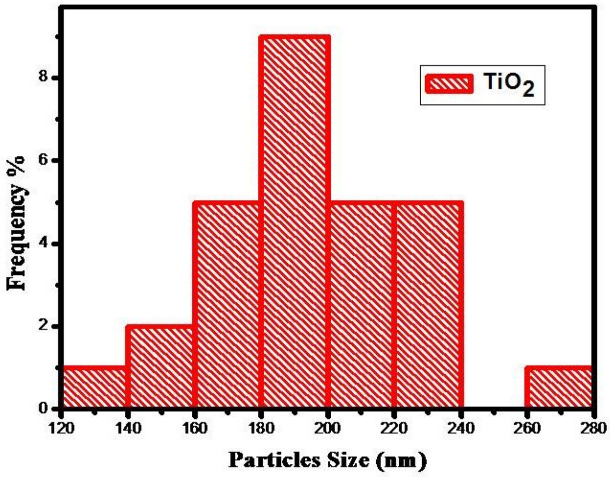

Figure 4.shows the particle size distribution of TiO_2nanoparticles

3.4. UV-Visible absorption analysis of TiO_2

Figure 5 shows the UV-Vis absorption spectra of TiO_2 NPs which show strong absorption in the UV region and in the visible region high transparency. The absorption peaks occurred at 383 for TiO_2 NPs respectively can be assigned to intrinsic band-band transitions (2p orbitals of anions to 3d orbitals of cations (Ti^{4+})),due to the weak quantum confinement effect, which are slightly blue shifted from bulk anatase (388 nm). The theory of optical absorption provides the reliance of the absorption coefficient (α) on the photon energy (hv) to find out the band gap and type of the transition. From the theory, the direct allowed transition can be expressed as [18],

$(\alpha h\vartheta)^2 = A(hv - E_g\ )$ ------------ (2)

The $(\alpha hv)^2$ is plotted against (hv) using the data obtained from optical absorption spectra and then extrapolated to α = 0 to get the optical band gap, termed as Tauc's plot. From the inset figure, band gap of TiO_2NPs are calculated as 3.25 eV respectively, in accord with the results of Xu*et al.* [22].

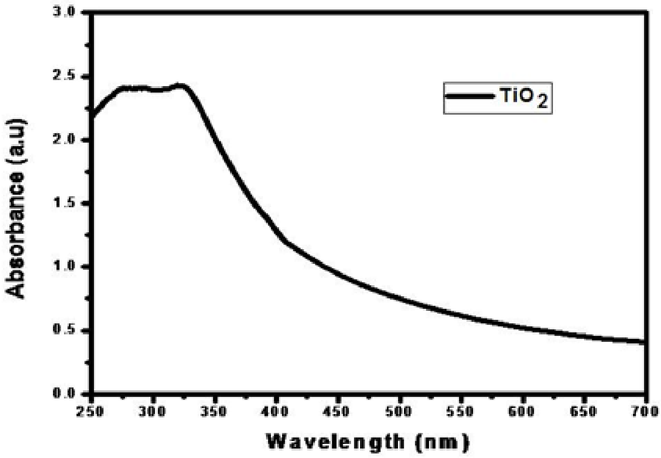

Figure 5. shows the optical absorbance spectra of TiO_2 nanoparticles

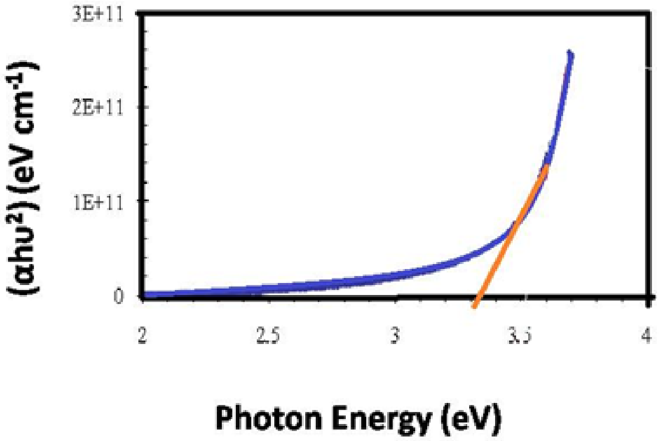

Figure 6.shows the Plot of $(\alpha h\upsilon)^2$ vs. ($h\upsilon$) for TiO_2 samples:

3.5. UV-Visible Spectroscopy for the Dye

The absorption spectra of anthocyanin pigment are shown in figure (7).The absorption spectra showed also the presence of peak at (503-510 nm) for anthocyanin pigment dye [20]. Results show that the absorption intensity of anthocyanin dye is highest that than other natural dye it can be seen the absorption of two dyes in the visible region (approximately 400 - 620 nm). This proves the possibility used as sensitizers to fabricate dye-sensitized solar cells (DSSCs) as mentioned by Chang et al. [23].

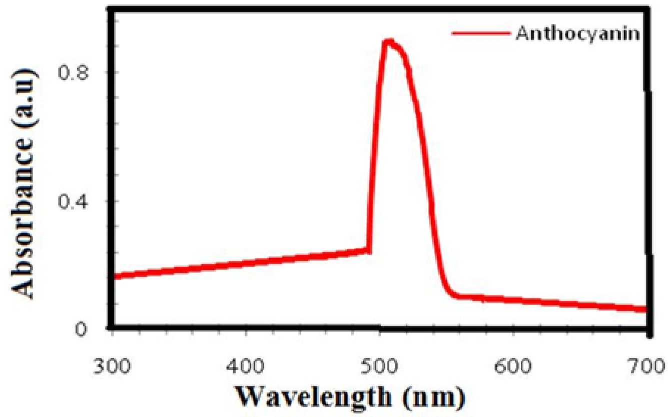

Figure. 7 Shows the absorption spectra of anthocyanin pigment .

3.6. FTIR analysis

FTIR spectrum is recorded in the region 4000–400 cm^{-1}. Fig.8 shows the FTIR spectra of TiO_2 samples From IR spectrum, a broad peak appearing at 3,100–3,600 cm^{-1} (precisely at 3,432 cm^{-1}) is assigned to fundamental stretching vibration of O–H hydroxyl groups (free or bonded) [24]. The band at 2,920 cm-1 is assigned to C–H vibrations. The C–H can be attributed to the organic residues, which remain in TiO_2 even after calcination [25]. Also, the sharp peaks centred on 1,621, 1,451, and 1,080 cm^{-1} can be attributed to C = C (in unsaturated hydrocarbon dehydrated, such as butene, propene from precursors) stretching, –C–H (methyl or methylene) bending and –C–O stretching, respectively [26]. The shoulder observed at 690 cm-1 may have been due to the vibration of the Ti–O–O bond [22]. The peak between 800 and 450 cm-1 is assigned to theTi–O stretching bands [27]

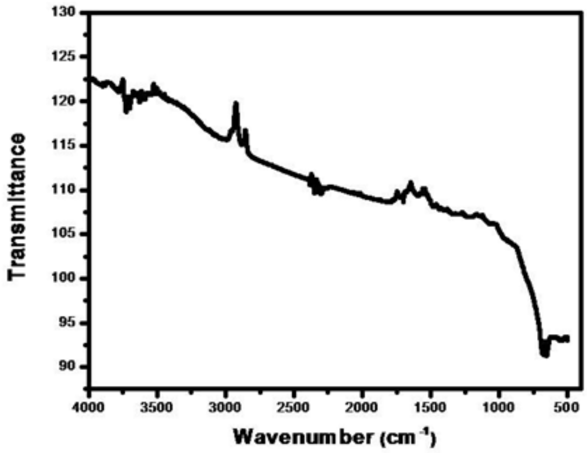

Figure. 8 FTIR pattern of TiO_2 nanoparticles

Performance of fabricated cell

Photovoltaic tests of the fabricated DSSCs using these natural dyes as sensitizers were performed by measuring the I–V curve of each cell under irradiation with white light (100 mW/cm^2) from xenon arc lamp and at room temperature (22.3° C with cell area 0.25cm^2.The values of fill factor (FF) was calculated by applying the following generalized equation

$$FF = \frac{P_{max}}{I_{SC}.V_{OC}} \qquad (4)$$

Where V_{OC} and I_{SC} respectively the open circuit voltage and short circuit current. P_{max} is the maximum power delivering point. The I-V characteristics of the prepared DSSCs taking pomegranate juice, as the natural dye by using Doctor-blade with TiO_2 nanoparticles is shown in figure (8). The photoelectric conversion efficiency (η) of DSSC is given as

$$\eta = \frac{I_{SC}.V_{OC}}{P_{in}}.FF \qquad (5)$$

TiO_2Photoanode	J_{sc} (Acm^{-2})	V_{oc} (V)	J_{max}(Acm^{-2})	V_{max} (V)	FF	η % x10^{-2}
using Pomegrante extract (anthocyanin)	2.55 x 10^{-4}	0.85	1.58x10^{-4}	0.505	0.455	0.89

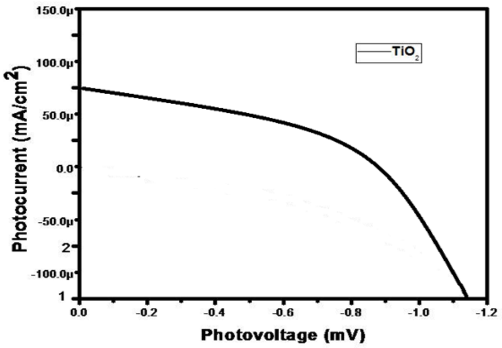

Figure 8. shows the I-V measurement of TiO_2 nanoparticles using pomegranate dye

Where is the incident light power. Table (2) shows the data acquired from measuring thePhotoelectric conversion efficiency of the DSSCs. The DSSC output power was calculated using the I-V data. Figure (8) shows the power as a function of V for the DSSC sensitized by pomegranate juice. Compare than other natural dye anthocyanin- platinum counter electrode were give good efficiency [26]

Some research workers have found that the energy conversion efficiency was 0.0277%. With anthocyanin dye Extracted from strawberry [20]. However, our results made an attempt using natural dye using a photosensitizer and graphite coated FTO plate used an counter electrode for TiO_2 based Solar cell application we got, the efficiency 0.89×10^{-2}%.

IV. CONCLUSIONS

In summary, the TiO_2 NPs based photoanode films are prepared by doctor blade technique using the commercial nanopowders. Fabrication of TiO_2 dye-sensitized using natural dye (pomegranate) and graphite coated counter electrode by using liquid electrolyte with KI_3 redox couple. Natural dyes as another sensitizers for DSSCs are predictable to be hopeful because of several reasons such as the easy preparation technique and little cost. The Preparation and characterization of TiO_2 nanoparticles using XRD, SEM, UV and FTIR are presented in this work. While the efficiency of the using natural dye and graphite coated counter electrode on TiO_2NPs based liquid-state DSSCs is low, we trust that the performance of these cells can be better further with employing an efficient dye-sensitizer.

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