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Influence of 2,4-Diamino-6-Phenyl-1-3-5-triazine on bio synthesized TiO₂ dye-sensitized solar cell fabricated using poly (ethylene glycol) polymer electrolyte

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Abstract

An ecofriendly TiO₂ from a plant extract of Averrhoa bilimbi with cost effective and non-toxic with cis dithiocynato-N, N-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid)ruthenium(II) (N3 dye) in dye-sensitized solar cells (DSSC) reports better efficiency of 5.2%. The green synthesized TiO₂ nanoparticles along with 2,4-Diamino-6-Phenyl-1-3-5-Triazine (DPT) doped Poly(ethylene glycol) (PEG)/KI/I₂/Pt shows better efficiency in dye-sensitized solar cells. The green TiO₂ was characterized with XRD, UV, FTIR, SEM, TEM and EDX techniques confirm the band gap of 3.2 eV and 15 nm size for TiO₂. The mechanical and electrical properties of DPT doped PEG/KI/I₂ polymer electrolyte were characterized with XRD, FTIR, EIS, DSC and TGA and it was confirmed that the DPT well miscible with PEG polymer electrolyte and improves the electrical conductivity and enhances the efficiency of DSSC.

1. Introduction

Dye sensitized solar cells (DSSCs) is a device that utilizes renewable energy sources for power generation. Michael Gratzel and Brian O’ Regan developed the next generation of Dye sensitized solar cells in 1991. The parts of DSSCs are Photo anode (TiO₂ coated FTO Plate), Photosensitizer (Ruthenium complex based dyes), electrolyte (I₂/KI in organic solvents) and counter electrode (Platinum coated FTO Plate). The dye molecules adsorbed at the surface of the TiO₂ nanoparticles ready to gain sunlight and generate the electrons via oxidation of dye. Redox couple (I⁻ /I₂) the electrolyte is placed in between photo anode and counter electrode and serves for the mobility of electron and regeneration of the dye. Platinum is used as the counter electrode to collect electron from the external circuit and catalyze the redox couple regeneration reaction [1–5]. The nanocrystalline TiO₂ is used in many applications such as photocatalytic, photovoltaic, pigments, paints and antimicrobial activities [6–10]. Different types of physical and chemical methods such as chemical vapor deposition [11], hydrothermal [12], solvothermal [13], sol-gel [14], Sonochemical method [15], microwave method [16], and Electrophoretic deposition [17] were used to prepare TiO₂ nanoparticles. All these methods are very expensive, it takes high pressure, requires high energy or causes environmental pollution while the green synthetic method is found to be advantageous over other methods reported. Green synthesis method provides the nanocrystalline TiO₂ coating FTO glass with the plant extracts. The plant extract plays a role in reducing and capping agents on the TiO₂ nanoparticle with the help of TiO₂ nanoparticles. TiO₂ with the green synthesized method was introduced in 2011 using Nyctanthes arbor-tristis [20, 21]. TiO₂ plays a vital role in dye sensitized solar cell, because of its small particle size, highly active anatase phase, high surface area, high band gap energy, low density and high electron mobility [22–24]. TiO₂ is an n-type semiconductor with an energy band gap of 3.2 eV. Averrhoa bilimbi is one of the medicinal plants which are used for the treatment of diabetes, hypertension and act as an anticancer and antimicrobial agent [25]. From phytochemical studies, it is found to contain phenol, flavonoids and tannins. So, the plant extract can act as a good capping and stabilizing agent [26, 27]. In recent studies, the polymer
component-based electrolyte like poly(ethylene oxide) (PEO), poly-urethane (PU), poly(vinylidene fluoride) (PVDF), poly acrylonitrile (PAN), poly(vinyl chloride) (PVC), etc, were used for DSSC application to improves the stability and increases the efficiency [28–30].

In this study, a green synthesized TiO₂ nanoparticle from Averrhoa bilimbi extract with Poly(ethylene glycol)/KI/I₂/2, 4-Diamino-6-Phenyl-1-3-5-Triazine (DPT) improves the ionic conductivity, long term stability of the polymer electrolyte and enhances the solar to electric energy conversion efficiency. The organic compound DPT doped Polymer electrolytes (PEG/KI/I₂) with nanocrystalline TiO₂ tends to shift the negative band of TiO₂ and enhance the V<sub>oc</sub>.

2. Experimental

2.1. Materials

Averrhoa bilimbi fruit were collected from the Kanyakumari district. TiO(SO₄) and 2,4-Diamino-6-Phenyl-1-3-5-Triazine PEG, KI, I₂ and DMF solvent purchased from sigma Aldrich. All the above chemicals were used without further purification.

2.1.1. Preparation of TiO₂ nanoparticles

Averrhoa bilimbi fruits were washed thoroughly 2–3 times using DI water and cut into small pieces. To 50 g of the fruit is added in 100 ml of DI water followed by heated for at 1 h. The above reaction mixture filtrated by using 125 mm Whatman filter paper. Finally, fruit extract is collected. Then, 10 ml of extract (Averrhoa bilimbi) is taken along with 8 ml of TiO(SO₄) dissolved in 100 ml of DI water and stirred well using a magnetic stirrer with high rpm. After 4 h, a white precipitate of nanoparticles slowly formed. The precipitates were centrifuged 3–4 times. The colloidal nanoparticles were dried at 100 °C overnight and calcinated at 400 °C and the nanoparticles were collected.

2.1.2. Preparation of DPT polymer electrolyte

Poly(ethylene glycol) (300 mg), Potassium iodide (30 mg), Iodine (10 mg) and 2, 4-Diamino-6-Phenyl-1–3–5-Triazine (10 mg) were dissolved in DMF solvent. The electrolyte solution was constantly stirred at 60 °C for 3 h and it is used in DSSC.

2.1.3. DSSCs cell fabrication

The nanocrystalline TiO₂ working electrode (synthesized TiO₂ and commercial TiO₂) was prepared by the doctor blade method as reported [P.M. Srrimanne, T. Shirata, T.J. Soga, J. Solid State Chem. 166 (2002) 142]. The prepared TiO₂ electrodes on Fluorinated tin oxide (FTO) were immersed in a 5 × 10<sup>−4</sup> M solution of the dye cis-diithiocynato-N,N-bis(2,2-bipyridyl)-4,4-dicarboxylic acid)ruthenium(II) (N3 dye) in ethanol for 24 h. The dye coated working electrode was dried and used for the measurement of conversion of solar energy to electrical energy. They are two types of electrolytes were used in the current study which are liquid electrolyte (300 mg of KI, 30 mg of I₂, and 30 mg of 4-tert-butylpyridine (4-TBP) additives in 15 ml DMF solvent) and DPT polymer electrolyte (300 mg of PEG, 30 g of KI, 10 mg of Iodine and 10 mg of 2,4-Diamino-6-Phenyl-1-3-5-Triazine). A sandwich type of photo electrochemical cell consisting of the N₃ dye coated TiO₂ (working electrode) and Platinum on FTO (counter electrode) was used. The prepared redox electrolyte (I<sup>−</sup>/I<sup>3−</sup>) solutions were placed in between N₃ dye coated TiO₂ and Pt electrodes. The fabricated DSSCs are used in current-voltage (I–V) measurements for under sunlight.

2.2. Characterization

Synthesized TiO₂ nanoparticles analyses the crystal size and phase form using XRD (Malvern Panalytical). The optical properties of synthesized TiO₂ nanoparticles were recorded by UV-Visible spectrometer (Agilent Cary 5000). The functional group present in the synthesized TiO₂ particles were characterized by FTIR using BRUKER-E-ATR, Lab India Instruments Pvt. Ltd), absorbed in the range 400–1000 cm<sup>−1</sup>. Nanoparticles surface morphological and element compositions were determined by SEM with EDX (Quanta 200, FEI). Synthesized nanoparticles size analyzed using TEM (JEOL, TEM-2100 plus electron microscopy, made in Japan). Conductivity was recorded by Biologic SP-300. The photo electrochemical properties were studied under the illumination of 100 mW cm<sup>−2</sup> at AM 1.5. The current-voltage (I–V) curve was obtained using a BAS 100A electrochemical analyzer. The active cell area was 1 cm<sup>2</sup> (1 cm × 1 cm).
3. Results and discussions

3.1. Characterization for green synthesized TiO$_2$ nanoparticles

3.1.1. XRD studies

The synthesized TiO$_2$ nanoparticles using Averrhoa bilimbi fruits extract were analyzed by x-ray diffraction spectroscopy. In this figure 1, showed the XRD analysis of synthesized TiO$_2$ diffraction peaks at 25.3$^\circ$, 37.8$^\circ$, 47.9$^\circ$, 53.9$^\circ$, 55.1$^\circ$, 62.5$^\circ$, 68.9$^\circ$, 74.0$^\circ$ which corresponds to planes 101, 004, 200, 105, 211, 204, 116 and 107 respectively of the tetragonal structure. Crystallographic plane 101 is of an anatase phase structure of TiO$_2$ matched in ref No.01-084-1285. Scherrer’s formula was used to calculate the average crystalline size of nanoparticles \[ D = K \lambda / \beta \cos \theta \] 

The average crystalline size of green synthesized TiO$_2$ nanoparticles was found to be 23.8 nm.

3.1.2. UV–visible spectroscopy

The optical properties of nanoparticles were studied using UV–Visible spectroscopy. The energy band gap is one of the important studies of semiconductor nanomaterials. The green synthesized TiO$_2$ nanoparticles showed the absorbance peak at 320 nm. The band gap energy was calculated by using the Tauc equation \[ \alpha h \nu = \alpha_0 (h \nu - E_g)^{1/m} \]

Figure 2(b) band gap energy of green synthesized TiO$_2$ Nanoparticles.

3.1.3. SEM and TEM analysis

The surface morphology and particle size of green synthesized TiO$_2$ were analyzed using SEM and TEM. The SEM micrographs were observed at 5 $\mu$m (figure 3(a)) and it shows the bio synthesized TiO$_2$ nanoparticles appeared aggregated and irregular shape. TEM (figure 3(b)) confirms the average particle size of 15 nm. The anatase phase of TiO$_2$ tetragonal lattice planes of (101) is similar to the lattice spacing of 0.35 nm derived using the XRD analysis [33].

3.1.4. FTIR spectroscopy

FTIR spectrum of green synthesized TiO$_2$ transmittance pattern observed the range of 4000 cm$^{-1}$ to 500 cm$^{-1}$. FTIR spectroscopy was analyses the Averrhoa bilimbi fruits extract possible organic functional group act as a play of reducing and capping agents of synthesized TiO$_2$ nanoparticles. The peaks (figure 4) showed at the frequencies 3441 cm$^{-1}$, 2924 cm$^{-1}$, 1631 cm$^{-1}$, 1384 cm$^{-1}$, 1103 cm$^{-1}$, 598 cm$^{-1}$, 503 cm$^{-1}$ were corresponds to OH group, C–H stretching, and bending, C=O stretching, C–O vibration, C–N stretching group respectively [34]. The absorption peak between 500–600 cm$^{-1}$ corresponds to the Ti–O stretching modes [35].
3.1.5. EDX analysis

The EDX analysis is shown (figure 5) reveals the purity of the synthesized TiO$_2$ nanoparticles and the presence of Ti and O with the atomic percentage 45.71 and 54.29 respectively. No other peak determined the EDX spectrum, so this spectrum clearly showed the purity of the synthesized TiO$_2$ nanoparticles.

3.2. Characterization of DPT polymer electrolyte

3.2.1. XRD studies

The XRD study of the PEG revealed major peaks at $2\theta = 23.3^\circ$ and $19.8^\circ$ with (figure 6) high intensity for PEG/KI/I$_2$ and reveals that more crystalline phase. In the case of PEG/KI/I$_2$/DPT polymer electrolyte shows less intense diffraction peaks at $2\theta = 23.3^\circ$ and $19.8^\circ$ and with more broadening, which suggests a relatively low crystallinity of polymer [36]. This observation illustrates that the potassium iodide salt is completely miscible in the polymer matrix and decreases the crystallinity of polymer electrolyte. The more broadening and fewer intensities are observed when the polymer electrolyte (PEG/KI/I$_2$/DPT) is doped with the organic compound DPT, as shown in figure 6. This observation indicates that PEG crystallization was influenced by the incorporation of the synthesized organic compound DPT.

3.2.2. FTIR spectroscopy

PEG polymer electrolyte FTIR spectrum observed the range of 4000–500 cm$^{-1}$. Figure 7 shows the broad absorption peak at 3300–3500 cm$^{-1}$ presents the O–H and N–H group in the polymer electrolyte. The high intensity peaks were observed at 2882 cm$^{-1}$–1342 cm$^{-1}$ explains about the C–H stretching and bending. Shortened and sharpened peak observed at 1280 cm$^{-1}$ and 1094 cm$^{-1}$ that implies O–H and C–O–H stretching respectively [37]. The FTIR studies reveals that the miscibility DPT with PEG/KI/I$_2$.
3.2.3 DSC and TGA studies

The polymer electrolyte thermal stability was characterized by using the DSC analysis measured range was fixed between 40 °C–300 °C. Figure 8 shows the DSC curves of the PEG polymer electrolyte from 40 °C–300 °C at a nitrogen atmosphere. The interesting fact was observed from the DSC curves in figure 8 is the presence of melting temperature for prepared polymer electrolyte (PEG/KI/I₂) electrolytes confirms not only the miscibility of PEG polymers with KI and I₂ but also their smooth reaction with the potassium iodide and the organic compound DPT. The sharp melting temperature at 58 °C was observed for PEG/KI/I₂ with a less broadening peak. However, the melting temperature at 85 °C was observed more broadening and less intensity with the addition of DPT shows the well miscibility of DPT with PEG/KI/I₂ and it confirms the decreases of

![Image](image_url)
crystallinity of the polymer. Thermo gravimetric analysis (TGA) was elucidating about the weight loss of the PEG polymer electrolyte. Figure 9 shows the PEG polymer electrolyte weight loss at 420 °C the scan range fixed between the 50 °C–500 °C [38]. The TGA graph indicates that the DPT well interact with PEG and maintains the thermal stability and confirms that the synthesized organic compound doped polymer electrolyte decomposed above 420 °C.

3.2.4. Electrochemical impedance spectroscopy

EIS (Electrochemical Impedance Spectroscopy) was characterized by TiO2/PEG/KI/I2/DPT interfaces during the electrochemical process. The single sign mode of set Ewe to E of synthesized TiO2 as 0.800V scan range was observed in 400 kHz to 300 MHz. The conductivity was calculated using the following equation.

\[ \sigma = \frac{t}{R_b A} \]

Here, t - thickness of the electrode, A - Area of the sample surface, \( R_b \) - bulk resistance of the nanomaterial [39]. The impedance spectrum was shown in figure 10. The electrical conductivity of synthesized TiO2/PEG/KI/I2 was calculated at 2.9788 \( \times \) 10\(^{-4}\) Scm\(^{-1}\) under room temperature. The TiO2/PEG/KI/I2/DPT (figure 10) polymer electrolyte interfaces show electrical conductivity as 5.7836 \( \times \) 10\(^{-4}\) Scm\(^{-1}\). In general, the conductivity is increased by the addition of KI and I2 to the polymer electrolyte, in this case, the conductivity is increased by

Figure 5. EDX pattern of Green synthesized TiO2 nanoparticles.

Figure 6. XRD pattern for the prepared DPT polymer electrolyte and PEG/KI/I2.
the incorporation of organic compounds. It is well known that the decrease in crystallinity leads to improvement in the randomness of the polymer matrix that finally concludes free space towards better ion mobility. The high conductivity of PEG doped with DPT has recognized the increased interaction of nitrogen in DPT with the iodine in the redox couple. The conductivity results satisfy the concept that incorporation of polymer matrix with organic compound and I/I₃ redox pair for enhancing the conductivity of the PEG based polymer electrolyte to enhance efficiency of DSSCs with better stability.

### 3.2.5. I-V characteristic of DSSC

Photo electrochemical properties of Standard TiO₂ and green synthesized TiO₂ with DPT polymer electrolyte under the illumination of 100 mWcm⁻² at A.M. 1.5. The photo electrochemical properties showed in figure 11 and the short-circuit current (Isc), the open-circuit voltage (Voc), the fill factor (ff), and the energy conversion efficiency (η) are summarized in table 1. The solar energy to electrical energy conversion efficiency was observed for four days and it remains the same.
The calculation of Fill factor (ff) was performed using the below formula

$$ ff = \frac{I_{\text{max}} \times V_{\text{max}}}{I_c \times V_c} $$

The $I_{\text{max}}$ and $V_{\text{max}}$ represent the maximum current density and voltage values identified from the corresponding I-V curve. The solar cell conversion efficiency ($\eta$) is calculated using the formula

$$ \eta = \frac{I_c \times V_c \times ff}{P} $$

Where P is the intensity of incident light.

The N3 dye coated bio synthesized TiO$_2$ along with PEG/KI/I$_2$/DPT polymer electrolyte reports better efficiency in the dye-sensitized solar cell field. The present study thus confirms that the feasibility to develop DPT doped PEG polymer electrolyte with novel lab-synthesized green TiO$_2$ reports better efficiency in the photovoltaic properties of DSSCs. The bio synthesized TiO$_2$ obtained by ecofriendly method shows good efficiency.
4. Conclusion

TiO₂ nanoparticles were successfully synthesized using Averrhoa bilimbi by green synthesis eco-friendly method. The surface morphology of synthesized TiO₂ was analyzed using XRD, UV and SEM confirmed the green TiO₂ more crystallite, band gap of 3.2eV and particle size is found to be 15 nm. FTIR confirmed that the functional group acts as a capping agent in the nanoparticles. PEG/KI/I₂ polymer electrolyte with dopant DPT improves the ionic mobility, stability and conductivity of the polymer and enhances the energy conversion efficiency in DSSC owing to the presence of more electron donating species in dopant DPT. Bio Synthesized TiO₂ was used as the photo anode with PEG polymer electrolyte based DSSC shows an efficiency of 5.2%. It opens a way of utilizing natural TiO₂ in DSSC applications with eco-friendly, reduced cost, and reduces chemicals requirement and also usage of PEG polymer with dopant DPT for stability improvements in DSSCs.

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Conflicts of interest

There are no conflicts of interest to declare.

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