

Chapter

Green Synthesis of TiO₂ Nanoparticles Using Averrhoa Bilimbi Fruits Extract and DPT-PEG Polymer Electrolyte for Enhance Dye-Sensitized Solar Cell Application

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Abstract

Green synthesis of nanoparticles has grown substantial interest as a developing technology to reduce the toxicity of metal oxide commonly associated with conventional physical and chemical synthesis methods. Among these, green synthesis of nanoparticles from plants parts to be a very active method in developing nontoxic, eco-friendly and clean technology. We prepared green synthesized TiO₂ using a fruits extract of *Averrhoa bilimbi* with a cost effective and non-toxic method and reports better PCE of DSSCs application. The green synthesized TiO₂ nanoparticles (working electrode) with DPT dopant PEG polymer electrolyte shows better power conversion efficiency in dye-sensitized solar cells. The green TiO₂ was characterized with XRD, UV, FTIR, SEM, TEM and EDX techniques analysis the band gap, crystallite size and shape for green synthesized TiO₂ nanoparticles. The electrical and mechanical properties of DPT organic doped PEG/KI/I₂ polymer electrolyte were characterized with XRD, FTIR, EIS, DSC and TGA and it was analysis that the DPT well miscible with PEG polymer electrolyte and improves the electrical conductivity and enhances the efficiency of DSSC.

Keywords: *Averrhoa bilimbi*, green synthesis, titanium dioxide, DPT organic compound, DSSCs

1. Introduction

Dye-Sensitized Solar Cells (DSSCs) have attracted researchers owing to their unexpected potential of lightweight, inexpensive cost materials, flexible structure, and easy fabrication. Substantial researches have been conducted for the progress of Dye

sensitized solar cells but the development of DSSCs is still not feasible. Although the PCE of the DSSCs are lower while comparing the first and second-generation PV (photovoltaic) cells and there still the development of a high potential for significant efficiency [1, 2]. Vogel et al. in 1870 proposed a first DSSCs by using silver halide, but the device could not show any output. In 1887 James Moser, developed initial voltage was around 0.04 V in DSSCs. Hishiki and Gerischer (1965–1968) introducing ZnO and sensitizer (Rose Bengal and Cyanine). In 1977, ZnO was replaced with TiO₂ by Spitler & Calvin group and they were clarified two factors, which are the dye molecules absorbed on the TiO₂ surface and pH solution used for the dye absorption process. After many years, these cells were developed in 1991 by Michael Gratzel and Brian O' Regan, they achieved a PCE of 7.1%. The use of TiO₂, Zinc porphyrin dye and Co^{2+/3+} tris (bipyridine) based electrolyte reached a PCE of 12.3%. Recently, DSSCs achieved a PCE 14.3% efficiency by using two metal-free organic dyes. TiO₂ coated on conductive substrate (photo anode), sensitizer (dye), electrolyte (redox couple) and counter electrode (platinum) [3, 4]. The photo-anode has a wide bandgap of metal oxides such as ZnO, ZrO₂, CuO and SnO₂ etc. commonly used to deposit on the surface of the TCO glass substrate and is used in FTO glass. The dye molecules (sensitizer) are usually absorbed on the surface of the metal oxides. The main components of the dye are part of the DSSCs, which creates light harvesting and produce photoexcited electrons. Electrolyte in DSSCs is used to transfer electrons between both electrodes and regenerate of oxidized dye [5]. The counter electrode is an important component and promotes high catalytic activity owing to the redox pair reaction by electron recombination process, requires high electron transport to improve the conductivity and high reflectance cell assembly to divert the unabsorbed light energy and improve sunlight capture [6].

1.1 Nanocrystalline TiO₂

The nanocrystalline TiO₂ (Titanium Dioxide) is used in several applications such as pigments, photocatalytic, paints, photovoltaic and antimicrobial activities [7–11]. TiO₂ plays an important role in dye sensitized solar cells, because of its small particle size, high surface area, highly active anatase phase, low density, high electron mobility and high band gap energy [12–15]. TiO₂ is an n-type semiconductor material with a 3.2 eV band gap energy. It has three natural mineral forms in the earth that are rutile, anatase and brookite. The most stable form among them is rutile, which is in the equilibrium phase at any temperature. When used in dye-sensitized solar cells, anatase is perceived to be more chemically active than rutile form. Anatase is a metastable, and when heated, it tends to convert to rutile. As a result, the synthesis has a significant impact on the phase constituents. At approximately 25 nm, the commercial product DeGussa P25 contains 80% anatase and 20% rutile. The simulated AM 1.5 solar illumination was used to test dye-sensitized solar cells (DSSCs) made with rutile and anatase films of the same thickness. The results showed that the open-circuit voltage (V_{oc}) is essentially the same, but the short-circuit photocurrent (I_{sc}) of the anatase-based cell is 30% higher than that of the rutile-based cell. The variance in short circuit current is attributed to the rutile film's lower dye absorption due to a smaller specific surface area [14, 16].

Generally, TiO₂ nanoparticles were prepared using a different type of physical and chemical methods, including microwave method, chemical vapor deposition, solvothermal, hydrothermal, sonochemical method, sol-gel, and electrophoretic deposition [17–23]. All of these methods are very expensive, require a lot of pressure, a lot of energy, and pollute the environment, whereas the green synthetic method has

been found to be more advantageous than the other methods reported. Plant extracts and plant parts such as leaves, fruits, flowers, seeds, yeast, fungi, bacteria and algae were used in the green synthesis method to produce nanoparticles in the nano range (10–100 nm) [24, 25]. The plant extract supports in the reduction and capping of agents on the surface of nanoparticles. In 2011, *Nyctanthes arbor-tristis* was used to synthesize TiO₂ using a green synthetic method [13, 26]. *A. bilimbi* is a medicinal plant that is used to treat diabetes, hypertension, and acts as an anticancer and antimicrobial agent [27]. The plant extract contains flavonoids, phenol and tannins found out by phytochemical studies. This functional compound can play as a good stabilizing and capping agent for the formation of nanoparticles [28–30].

1.2 Organic compound dopant electrolytes

The polymer-based electrolytes like poly-urethane (PU), poly (ethylene oxide) (PEO), poly (vinylidene difluoride) (PVDF), poly (vinyl chloride) (PVC), poly acrylonitrile (PAN), etc., were used for DSSCs applications to improve the efficiency and stability [31–36]. Additionally, researchers improve the electrolyte stability using organic dopant as an additive molecule such as alkylaminopyridine, pyridine, alkylpyridine, pyrrole, benzimidazole, triphenylamine, quinoline, etc. The addition of small number of organic molecules changed the the redox potential, surface of the semiconductor, TiO₂ conduction band edge shift and change the recombination kinetics [37]. Boschloo et al. found the additives affect the TiO₂ semiconductor. These effects, increase of V_{oc} is due to a combination of TiO₂ conduction band edge change toward negative potentials and improve the electron lifetime [38]. As a polymer gel electrolyte content, phenanthroline-based cobalt redox couple and thiourea derivatives were used as additives with hydroxyl propyl cellulose polymer host, resulting in a 9.1% performance. The most stable thioureas have more electron donation groups and have high adsorption energy toward TiO₂. The Fermi level of TiO₂ (101) anatase was shifted by these additives. Furthermore, the performance of the Cobalt redox pair was increased due to its predominating properties [39]. Omid et al., introduced new inexpensive propyl isonicotinate and isopropyl isonicotinate by pyridine derivative as an additive in bromide/tribromide electrolytes revealed PCE 2.81–3.76% [40]. Ganesan et al., investigated the PVdF-PEO/KI/I₂ polymer mixture electrolyte system with DPA (Diphenyl amine) and PT (Phenothiazine) obtained an PCE 8.5% [32].

2. Experimental

2.1 Materials

A. bilimbi fruits were collected from Kanyakumari district, Tamilnadu, India. TiO (SO₄), 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

First the fruits were cleaned thoroughly 2–3 times using distilled water and cut into small pieces. Then, 50 g of the fruits was added in DI water (100 ml) followed by heated for at 1 h. The above mixture filtrated by using Whatman filter paper (125 mm). Filtered fruits extract was collected and stored in refrigeration for using further usages.

Furthermore, 10 ml of fruits extract was taken along with $\text{TiO}(\text{SO}_4)$ (8 ml) dissolved in DI water (100 ml) and stirred well using a magnetic stirrer with high rpm. After 4 h, the white precipitate gradually formed. Finally, the precipitates were centrifuged for 3–4 times using distilled water. The colloidal mixture was dried at 100°C and calcinated at 400°C and the nanoparticles were collected.

2.1.2 Preparation of DPT polymer electrolyte

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

2.1.3 DSSCs cell fabrication

The prepared TiO_2 (working electrode) was coated by the doctor blade method as previous literature [41]. The TiO_2 coated on FTO (Fluorinated tin oxide) were immersed in a N_3 dye (5×10^{-4} M dye) solution in ethanol for 24 hrs. Then, dye coated TiO_2 plate was dried and used for the measurement of conversion of solar energy to electrical energy. Preparation of electrolyte, PEG (300 mg), KI (30 g), Iodine (10 mg) and 2,4-Diamino-6-Phenyl-1-3-5-Triazine (10 mg) dissolved in DMF solvent. A sandwich type of DSSC cell consisting of N_3 dye-coated TiO_2 and Platinum coated on FTO was used. Then, prepared iodine electrolyte (I^-/I_3^-) solutions were placed in between the N_3 dye coated TiO_2 and Pt electrodes. Finally, the fabricated DSSC are measured in current–voltage (I–V) under sunlight.

2.2 Characterization

Prepared TiO_2 nanoparticles characterize the phase form and crystal size using XRD (Malvern Panalytical). Optical properties of prepared TiO_2 nanoparticles were analyzed by UV–Visible spectroscopy (Agilent Cary 5000). The functional groups present in the prepared TiO_2 nanoparticles were recorded by FTIR using BRUKER α -E (ATR, Lab India Instruments Pvt. Ltd), and the absorbed range of $400\text{--}1000\text{ cm}^{-1}$. Surface morphological and element compositions were observed by SEM and EDX (Quanta 200, FEI). Size of the TiO_2 nanoparticles were measured using TEM (JEOL, TEM-2100 plus electron microscopy, made in Japan). Conductivity study was recorded by Biologic SP-300. Photo electrochemical (IV) properties were studied under the sun illumination of 100 mWcm^{-2} at AM 1.5. The I–V curve was measured using a BAS 100A electrochemical analyzer. The DSSC active cell area was 1 cm^2 ($1\text{ cm} \times 1\text{ cm}$).

3. Results and discussions

3.1 Characterization for green synthesized TiO_2 nanoparticles

UV–Visible absorption spectroscopy was used to examine the optical properties of the GS- TiO_2 nanoparticles. The light absorption characteristics of GS- TiO_2 nanoparticles are shown in **Figure 1a**. GS- TiO_2 nanoparticles showed a strong absorption peak at 320 nm in the UV–Visible spectrum. This value matches well with the

Com-TiO₂ (Commercial TiO₂) reported in the literature [11]. The optical band-gap of the nanoparticles was calculated using the following equation,

$$(\alpha h\nu)^{\frac{1}{2}} = \beta (h\nu - E_g) \quad (1)$$

Where, β -constant, α -absorption coefficient (cm⁻¹), E_g -band gap of material, ν -photon frequency, h -Planck's constant.

The optical band gap energy (**Figure 1b**) derived from Tauc's plot corresponds to 3.2 eV (Indirect band gap) good agreement with the anatase phase of Com-TiO₂, which is found to be GS-TiO₂ nanoparticles has good band gap energy of semiconductor materials for photoanode in DSSCs application.

X-ray diffraction spectroscopy was identified crystallite structure and phase formation of GS-TiO₂ nanoparticle by using *Averrhoa bilimbi* fruits extract. **Figure 2 (a)** showed the XRD pattern of GS-TiO₂ nanoparticles. From the XRD pattern, displayed diffraction peaks at 25.3° (101), 37.8° (004), 47.9° (200), 53.9° (105), 55.1° (211), 62.5° (204), 68.9° (116), 74.0° (107) which corresponds to tetragonal structure. The crystallographic plane 101 indicated the anatase phase structure

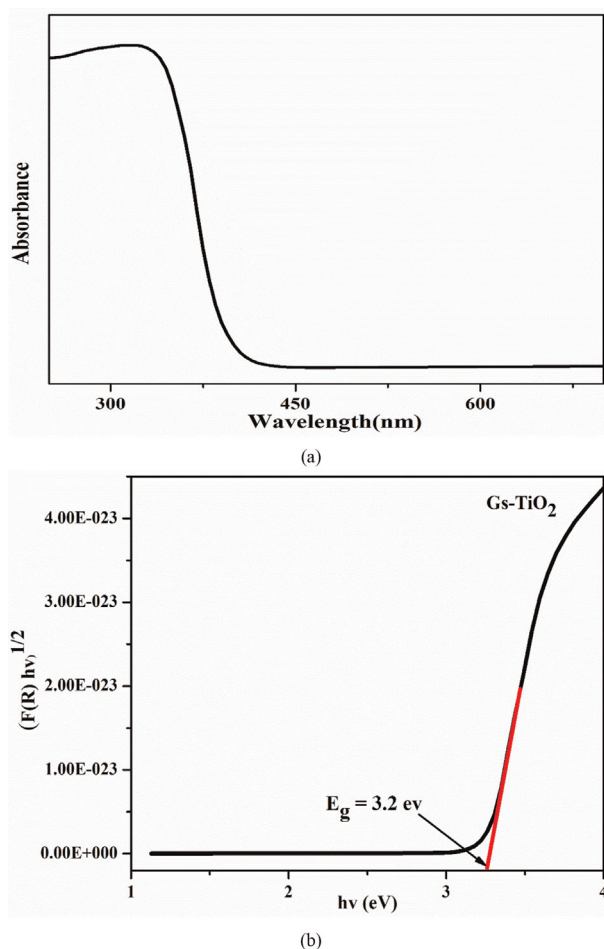


Figure 1.
(a) UV-visible spectrum of GS-TiO₂ nanoparticles. (b) Band gap of GS-TiO₂ nanoparticles.

formation of GS-TiO₂ was matched with ref. No. 01-084-1285 and that the GS-TiO₂ nanoparticles showed highly crystalline and pure phase formation. Com-TiO₂ XRD pattern showed in **Figure 2(b)**. The average crystalline size of GS-TiO₂ nanoparticles was calculated using Scherrer's formula [42]. The estimated average crystallite size was measured by using the first 3 major peaks of GS-TiO₂ nanoparticles was found to be 23.8 nm based on FWHM (full width at half-maximum) from the XRD pattern.

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

Where, D—average crystallite size, λ —wavelength, k—Debye Scherrer constant, θ —Bragg's diffraction angle, β —full width half-maximum (FWHM).

The FTIR spectrum of GS-TiO₂ and *Averrhoa bilimbi* fruits extract were show in **Figure 3(a)** and **(b)** respectively. The transmittance was observed in the 4000–500 cm^{−1} range. The *A. bilimbi* fruits extract was analyzed using FTIR spectroscopy to see if any organic functional groups could act as a capping agent on the GS-TiO₂ nanoparticles. The peaks (**Figure 3(a)**) at the frequencies 3440, 2926, 1635,

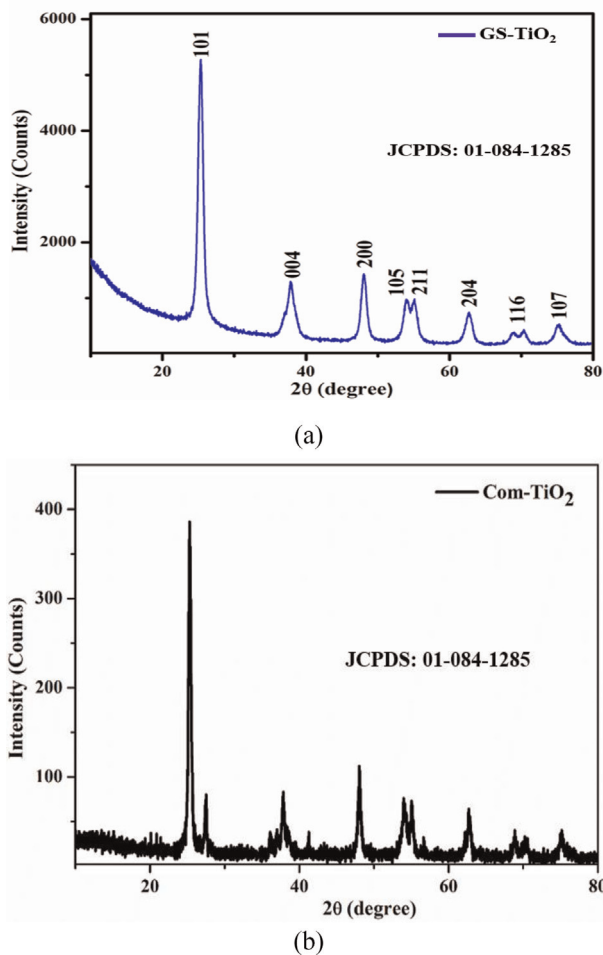


Figure 2.

(a) XRD pattern of GS-TiO₂ nanoparticles. (b) XRD pattern of Com-TiO₂ nanoparticles.

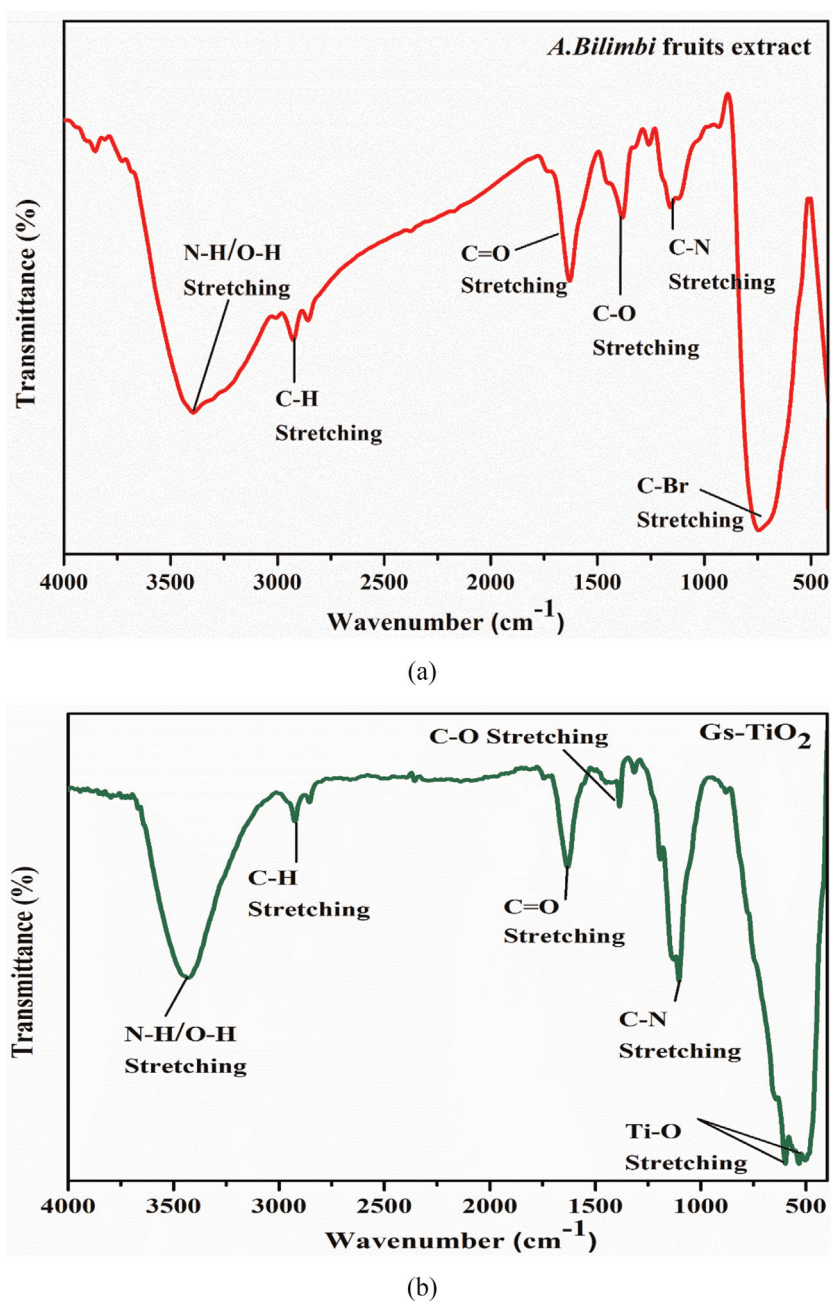


Figure 3.
(a) FTIR spectrum of *Averrhoa bilimbi* fruits extract. (b) FTIR spectrum of GS-TiO_2 nanoparticles.

1382, 1104, 750 cm^{-1} corresponded to the NH and OH group, C—H stretching and bending, C=O stretching, C—O stretching, C—N stretching and C-Br stretching frequency respectively [43]. In **Figure 3(b)**, Ti-O stretching modes are represented by the absorption peak between 500 and 600 cm^{-1} [44]. From the **Figure 3(a)** and **(b)** showed the FTIR spectroscopy of GS-TiO_2 and *A. bilimbi* fruits extract similar vibration frequency. The stretching frequency of alkyl halide peak was shifted from

750 to 600 cm^{-1} . This demonstrated that *A. bilimbi* fruits extract acts as a capping layer on the GS-TiO₂ nanoparticles.

Morphology and particle size of the GS-TiO₂ nanoparticles were characterized by SEM and TEM analyses. **Figure 4** showed the GS-TiO₂ nanoparticles was agglomerated and uneven spherical shape. TEM images (**Figure 5**) revealed that similar morphology structure with uneven particle size and highly crystallized with average particle size was found to be 15 nm of GS-TiO₂ nanoparticles, respectively. The anatase phase form of GS-TiO₂ nanoparticles tetragonal lattice planes (101) was matched to the lattice spacing of 0.35 nm, which were obtained from XRD pattern [45].

Overall, the SEM and TEM analyses demonstrated that the green synthesis method was very useful for the preparation of nano sized, pure anatase phase and mesoporous structural properties of GS-TiO₂ nanoparticles. Because of the developed GS-TiO₂ has the greatest potential for charge transfer process and dye adsorption on the pure anatase surface of TiO₂, it could be used to develop an efficient DSSCs device.

The EDX analysis (**Figure 6**) showed the purity of the GS-TiO₂ nanoparticles as well as the presence of Ti and O at atomic percentages of 45.71 and 54.29, respectively. Because no other peaks determined in the EDX spectrum, the purity of the GS-TiO₂ nanoparticles was clearly shown.

3.1.1 Characterization of DPT doped polymer electrolyte

DSC analysis was used to study about the thermal stability of the polymer electrolytes. The DSC curves of the polymer electrolyte measurement range was set between 40°C and 300°C in nitrogen atmosphere. As shown in **Figure 7**, the melting temperature of prepared polymer electrolyte (PEG/KI/I₂) observed a sharp endothermic peak at 58°C and after DPT doped in electrolyte exhibited more broadening endothermic peak at 86°C, respectively. This broadening endothermic peak confirms the DPT organic compound well interacted with the PEG/KI/I₂ electrolyte and improved the conductivity in PEG polymer.

The weight loss of the PEG polymer electrolyte was determined using thermogravimetric analysis. **Figure 8** depicts the PEG polymer electrolyte weight loss at 420°C with the scan range set between 50 and 500°C [46]. All the electrolyte showed the first stage of weight loss from 100 to 180°C, due to the decomposition of PEG polymer matrix. The

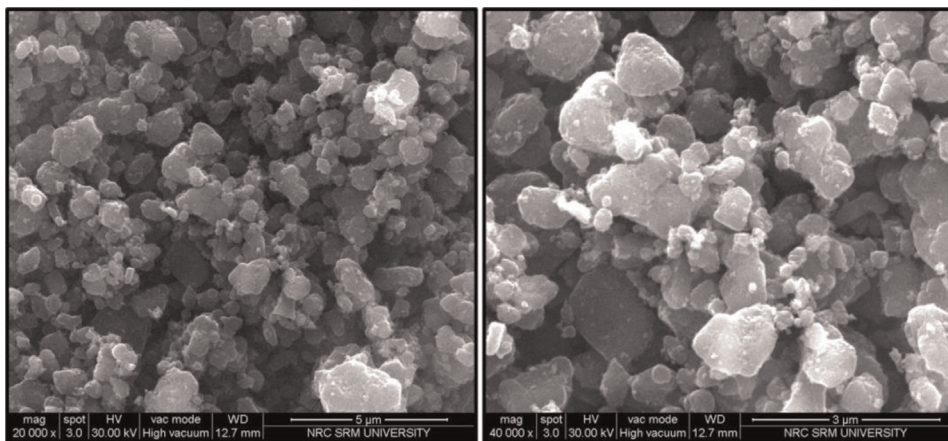


Figure 4.
SEM images of GS-TiO₂ nanoparticles.

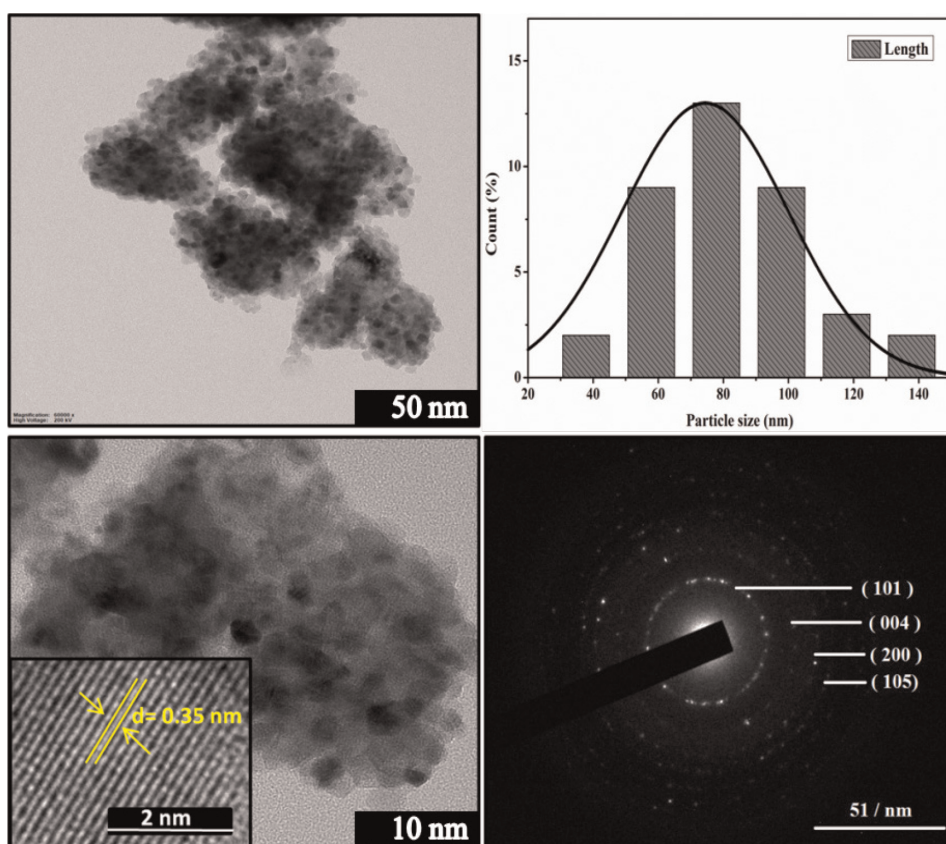


Figure 5.
 TEM images of GS- TiO_2 nanoparticles.

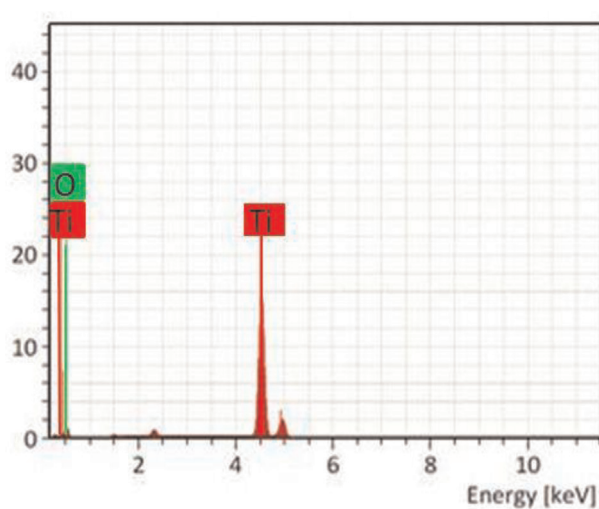


Figure 6.
 EDX spectrum of GS- TiO_2 nanoparticles.

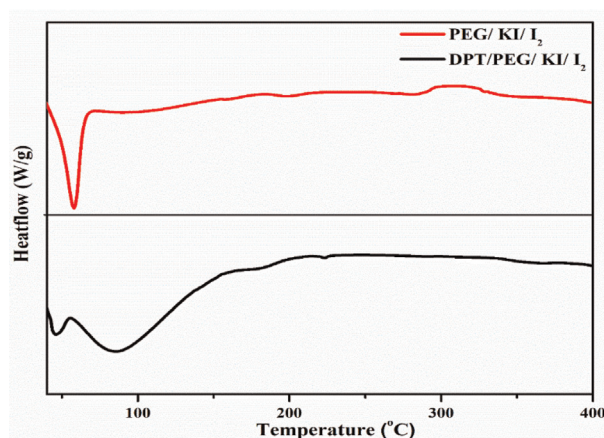


Figure 7.
DSC analysis of polymer electrolytes.

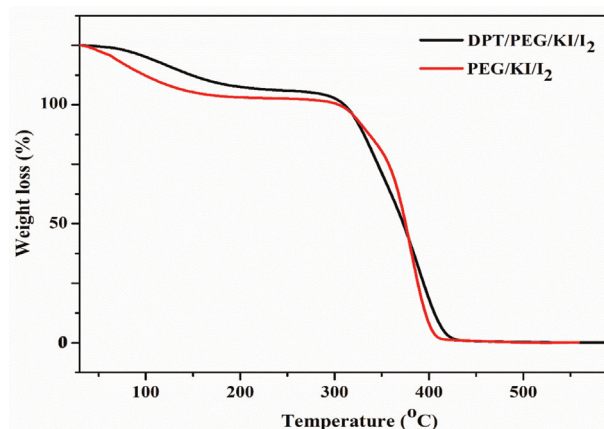


Figure 8.
TGA analysis of polymer electrolyte.

TGA graph showed that the DPT interacts well with PEG and maintains thermal stability, confirming that the synthesized organic compound doped polymer electrolyte decomposed above 420°C. Altogether, both thermal stability changes in the melting temperature and weight loss range can be observed, after the addition of DPT doped PEG polymer electrolyte. Thermal stability study, clearly explained about the thermal behavior in DPT doped electrolyte which is a good stability electrolyte in DSSCs performances.

The PEG polymer XRD (**Figure 9**) revealed that major peaks with high intensity observed at $2\theta = 19.8^\circ$ (120), 23.2° (032), 27.0° (024), 27.4° (024), 31.0° (220), 36.4° (111) and 43.3° (200) for PEG/KI/I₂ and reveals that more crystalline phase. This intensity peak was matched with PEG polymer [47]. In the case of PEG/KI/I₂/DPT polymer electrolyte, showed the similar diffraction and low intensity peaks were observed, indicating that the polymer has a low crystallinity. This finding showed that the potassium iodide salt is completely miscible in the polymer matrix and reduces the crystallinity of the polymer electrolyte. When the polymer electrolyte (PEG/KI/I₂/DPT) is doped with the organic compound DPT, more broadening and fewer intensities are observed, as shown in **Figure 9**. These finding suggests that the incorporation

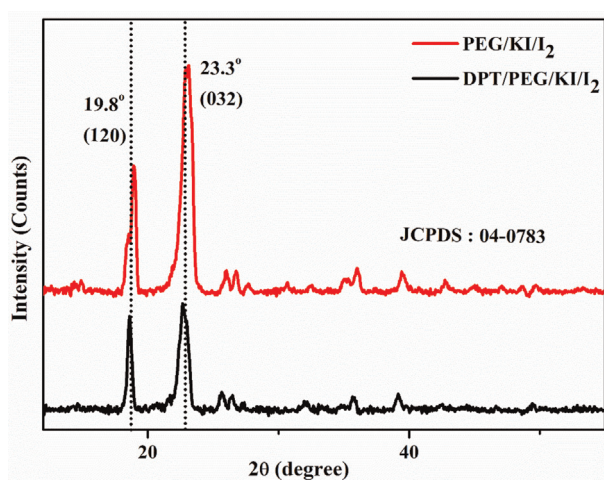


Figure 9.
XRD pattern of polymer electrolytes.

of the DPT organic compound influenced PEG crystallization and good amorphous electrolyte for DSSCs applications.

Functional groups of PEG polymer electrolyte were characterized by FTIR, ranges from 4000 to 500 cm^{-1} . **Figure 10** showed a wide absorption peak displayed at $3300\text{--}3500\text{ cm}^{-1}$ contributed to the O—H and N—H functional groups present in the polymer electrolyte. The C—H bending and stretching was observed at $2882\text{--}1342\text{ cm}^{-1}$, O—H frequency at 1280 cm^{-1} , C—O—H stretching frequency observed at 1094 cm^{-1} , respectively. All the PEG polymer functional groups exactly matched with the prepared electrolyte [48]. From the FTIR spectrum the vibration frequency intensity was changed in the DPT doped polymer electrolyte and the peak was shifted from 1450 to 1533 cm^{-1} . This statement the miscibility of the DPT organic compound doped in PEG polymer electrolyte revealed by FTIR.

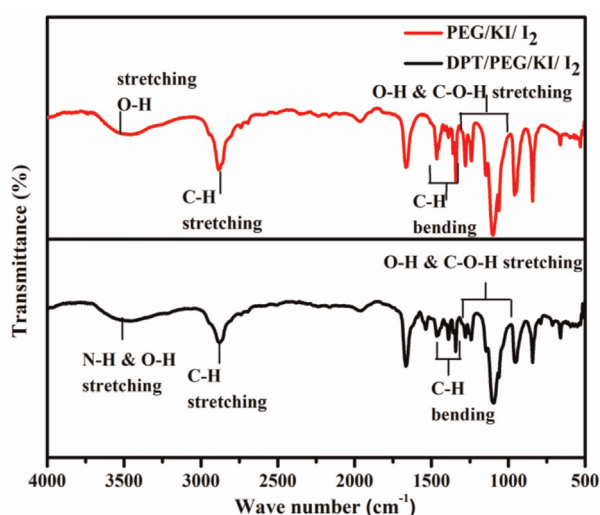


Figure 10.
FTIR spectrum of polymer electrolytes.

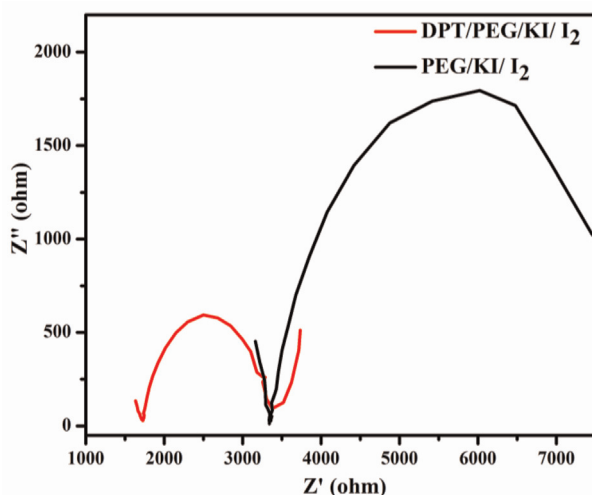


Figure 11.
Nyquist plot of polymer electrolytes.

The interfaces of GS-TiO₂/PEG/KI/I₂/DPT and GS-TiO₂/PEG/KI/I₂ were measured under dark condition during the electrochemical process. The scan range was measured at 400 kHz–300 MHz using a single sign mode of set Ewe to E of 0.800 V. In specific, the potential values were taken from the Nyquist plot which is given in **Figure 11**. Thickness of the electrolyte measured by vernier caliper. The conductivity of the electrolyte was derived from the Eq. (3).

$$\sigma = \frac{t}{R_b} A \quad (3)$$

Where, t —thickness of electrolyte, R_b —Bulk resistance, A —surface area [39].

The ionic conductivity values calculated for the GS-TiO₂/PEG/KI/I₂ and GS-TiO₂/PEG/KI/I₂/DPT electrolyte. The GS-TiO₂/PEG/KI/I₂ and GS-TiO₂/PEG/KI/I₂/DPT electrolyte attained conductivity at 2.9788×10^{-4} and $5.7836 \times 10^{-4} \text{ Scm}^{-1}$ respectively. The conductivity of DPT doped electrolyte was found to be increased. In general, the addition of KI and I₂ to the polymer electrolyte, increases conductivity. Therefore, the conductivity is accelerated by the incorporation of organic compounds. It is well known that decrease in crystallinity improves the randomness of the polymer chain, resulting in free space and improved ion mobility. The increased interaction of nitrogen present in DPT compound with iodine in the redox mediator has been recognized by the high conductivity of DPT doped in the PEG polymer electrolyte. The conductivity results supported the concept of incorporating a polymer matrix with an DPT organic compound and an I[−]/I₃[−] redox pair to improve the conductivity of a PEG polymer electrolyte in order to improve the efficiency and stability of DSSCs device.

3.2 I-V studies

Comparison of Com.TiO₂ and GS-TiO₂ photoelectrochemical behavior with DPT doped polymer electrolyte measured under 100mWcm^{−2} sun illumination at A.M. 1.5. **Table 1** summarizes the photo electrochemical properties and showed in **Figure 12**. In

System	J_{oc} (mA/cm ²)	V_{oc} (V)	FF	Efficiency (η) %
TiO ₂ (p-25)/N3dye/KI/I ₂ /PEG/DPT/Pt	14.7	0.86	0.53	6.7
Green TiO ₂ /N3dye/KI/I ₂ /PEG/DPT/Pt	11.6	0.84	0.53	5.2

Table 1.
Photo electrochemical properties of GS-TiO₂ and Com-TiO₂ with DPT doped polymer electrolyte.

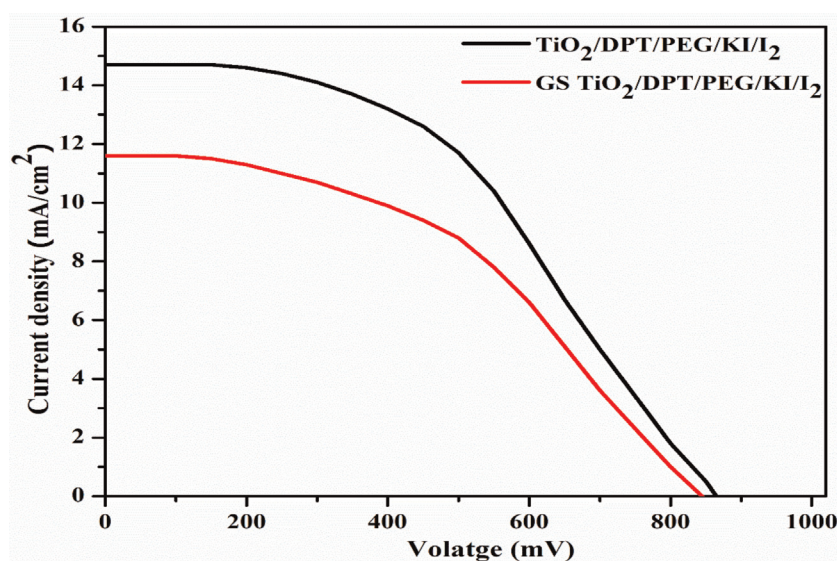


Figure 12.
I–V curves of GS-TiO₂ and Com-TiO₂ with DPT doped polymer electrolyte.

the dye-sensitized solar cell field, N3 dye coated GS-TiO₂ with PEG/KI/I₂/DPT polymer electrolyte reported a higher efficiency of 5.2%. At the same time Com.TiO₂ with PEG/KI/I₂/DPT polymer electrolyte showed the efficiency of 6.7%. The current study thus confirms the feasibility of developing DPT doped PEG polymer electrolyte with novel lab-prepared GS-TiO₂ to improve the photovoltaic properties of DSSCs. The GS-TiO₂ obtained through an environmentally friendly method has a high efficiency.

3.3 Conclusion

TiO₂ nanoparticles were effectively prepared using *A. bilimbi* fruits by green synthesis method. The GS-TiO₂ surface morphology was analyzed using SEM, UV and XRD confirmed the GS-TiO₂ is a more crystallite structure, good band gap (3.2 eV) and small particle size (15 nm). FTIR spectrum confirmed that the present of plant functional group acts as a capping agent on the GS-TiO₂ nanoparticles. The PEG/KI/I₂ electrolyte with DPT dopant improve the conductivity, stability and ionic mobility of the PEG polymer and improves the power conversion efficiency in DSSC device owing to the presence of more electron donating group in dopant DPT. The GS-TiO₂ and PEG polymer electrolyte based DSSC cell attained energy conversion efficiency of 5.2%. This way of utilizing natural TiO₂ in DSSC applications with reduced cost and chemicals requirements, eco-friendly and also the usage of PEG polymer with DPT dopant-based electrolyte for stability improvements in the DSSCs performances.

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References

- [1] Vipinraj S, Elsa J, Sudhakar K. Recent improvements in dye sensitized solar cells: A review. *Renewable and Sustainable Energy Reviews*. 2015;**52**:54-64
- [2] Kumar B. Natural pigments and dye-sensitized solar cells (DSSC): A correlation. In: *Engineering Practices for Agricultural Production and Water Conservation*. 1st ed. Apple Academic Press; 2017. pp. 26. ISBN: 9781315365954
- [3] O'Regan B, Gratzel M. High-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature*. 1991;**353**:737-740
- [4] Geetam R, Anil K, Perapong T, Bhupendra G. Natural dyes for dye sensitized solar cell: A review. *Renewable and Sustainable Energy Reviews*. 2017;**69**:705-718
- [5] Mian EY, Kah YC. Recent advances in photo-anode for dye-sensitized solar cells: A review. *International Journal of Energy Research*. 2017;**41**(15):2446-2467
- [6] Islam A, Chowdhury TH, Qin C, Han L, Lee J-J, Bedja IM, et al. Panchromatic absorption of dye sensitized solar cells by co-sensitization of triple organic dyes. *Sustainable Energy and Fuels*. 2018;**2**(1):209-214
- [7] Muniandy SS, Kaus NHM, Jiang ZT, Altarawneh M, Lee HL. Green synthesis of mesoporous anatase TiO₂ nanoparticles and their photocatalytic activities. *RSC Advances*. 2017;**7**(76): 48083-48094
- [8] Son YJ, Kang JS, Yoon J, Kim J, Jeong J, Kang J, et al. Influence of TiO₂ particle size on dye-sensitized solar cells employing an organic sensitizer and a cobalt (III/II) redox electrolyte. *The Journal of Physical Chemistry C*. 2018; **122**(13):7051-7060
- [9] Grzmil B, Glen M, Kic B, Lubkowski K. Preparation and characterization of single-modified TiO₂ for pigmentary applications. *Industrial and Engineering Chemistry Research*. 2011;**50**(11):6535-6542
- [10] Wang Y, Li J, Wang L, Xue T, Qi T. Preparation of rutile titanium dioxide white pigment via doping and calcination of metatitanic acid obtained by the NaOH molten salt method. *Industrial and Engineering Chemistry Research*. 2010;**49**(16):7693-7696
- [11] Maurya IC, Singh S, Senapati S, Srivastava P, Bahadur L. Green synthesis of TiO₂ nanoparticles using Bixa orellana seed extract and its application for solar cells. *Solar Energy*. 2019;**194**:952-958
- [12] Park NG, Van de Lagemaat J, Frank AA. Comparison of dye-sensitized rutile-and anatase-based TiO₂ solar cells. *The Journal of Physical Chemistry B*. 2000;**104**(38):8989-8994
- [13] Frank AJ, Kopidakis N, Van De Lagemaat J. Electrons in nanostructured TiO₂ solar cells: Transport, recombination and photovoltaic properties. *Coordination Chemistry Reviews*. 2004;**248**(13-14):1165-1179
- [14] Carp O, Huisman CL, Reller A. Photoinduced reactivity of titanium dioxide. *Progress in Solid State Chemistry*. 2004;**32**(1-2):33-177
- [15] Gong J, Liang J, Sumathy K. Review on dye-sensitized solar cells (DSSCs): Fundamental concepts and novel materials. *Renewable and Sustainable Energy Reviews*. 2012;**16**(8):5848-5860

- [16] Shinde PS, Bhosale CH. Properties of chemical vapour deposited nanocrystalline TiO₂ thin films and their use in dye-sensitized solar cells. *Journal of Analytical and Applied Pyrolysis*. 2008;**82**(1):83-88
- [17] Nagaraju P, Khunphonoi R, Puttaiah SH, Suwannaruang T, Kaewbuddee C, Wantala K. Photocatalytic paraquat degradation over TiO₂ modified by hydrothermal technique in alkaline solution. *Journal of Advanced Oxidation Technologies*. 2017;**20**(2):1-12
- [18] Wahi RK, Liu Y, Falkner JC, Colvin VL. Solvothermal synthesis and characterization of anatase TiO₂ nanocrystals with ultrahigh surface area. *Journal of Colloid and Interface Science*. 2006;**302**(2):530-536
- [19] Bhogaita M, Yadav S, Bhanushali AU, Parsola AA, Nalini RP. Synthesis and characterization of TiO₂ thin films for DSSC prototype. *Materials Today: Proceedings*. 2016;**3**(6): 2052-2061
- [20] Arami H, Mazloumi M, Khalifehzadeh R, Sadrnezhaad SK. Sonochemical preparation of TiO₂ nanoparticles. *Materials Letters*. 2007;**61** (23–24):4559-4561
- [21] Falk GS, Borlaf M, López-Muñoz MJ, Fariñas JC, Neto JR, Moreno R. Microwave-assisted synthesis of TiO₂ nanoparticles: Photocatalytic activity of powders and thin films. *Journal of Nanoparticle Research*. 2018;**20**(2): 1-10
- [22] Bandy J, Zhang Q, Cao G. Electrophoretic deposition of titanium oxide nanoparticle films for dye-sensitized solar cell applications. *Materials Sciences and Applications*. 2011;**2**(10):1427-1431
- [23] Subhapriya S, Gomathipriya P. Green synthesis of titanium dioxide (TiO₂) nanoparticles by *Trigonella foenum-graecum* extract and its antimicrobial properties. *Microbial Pathogenesis*. 2018;**116**:215-220
- [24] Rajakumar G, Rahuman AA, Priyamvada B, Khanna VG, Kumar DK, Sujin PJ. *Eclipta prostrata* leaf aqueous extract mediated synthesis of titanium dioxide nanoparticles. *Materials Letters*. 2012;**68**:115-117
- [25] Nabi G, Khalid NR, Tahir MB, Rafique M, Rizwan M, Hussain S, et al. A review on novel eco-friendly green approach to synthesis TiO₂ nanoparticles using different extracts. *Journal of Inorganic and Organometallic Polymers and Materials*. 2018;**28**(4):1552-1564
- [26] Manikandan V, Velmurugan P, Jayanthi P, Park JH, Chang WS, Park YJ, et al. Biogenic synthesis from *Prunus × yedoensis* leaf extract, characterization, and photocatalytic and antibacterial activity of TiO₂ nanoparticles. *Research on Chemical Intermediates*. 2018;**44**(4):2489-2502
- [27] Alhassan AM, Ahmed QU. *Averrhoa bilimbi* Linn.: A review of its ethnomedicinal uses, phytochemistry, and pharmacology. *Journal of Pharmacy & Bioallied Sciences*. 2016;**8**(4):265-271
- [28] Hasanuzzaman M, Ali MR, Hossain M, Kuri S, Islam MS. Evaluation of total phenolic content, free radical scavenging activity and phytochemical screening of different extracts of *Averrhoa bilimbi* (fruits). *International Current Pharmaceutical Journal*. 2013; **2**(4):92-96
- [29] Hussain I, Singh NB, Singh A, Singh H, Singh SC. Green synthesis of nanoparticles and its potential

application. *Biotechnology Letters*. 2016;
38(4):545-560

[30] Singh S, Maurya IC, Tiwari A, Srivastava P, Bahadur L. Green synthesis of TiO₂ nanoparticles using Citrus Limon juice extract as a bio-capping agent for enhanced performance of dye-sensitized solar cells. *Surfaces and Interfaces*. 2022; **28**:101652

[31] Wu J, Li P, Hao S, Yang H, Lan Z. A polyblend electrolyte (PVP/PEG + KI + I₂) for dye-sensitized nanocrystalline TiO₂ solar cells. *Electrochimica Acta*. 2007;**52**(17): 5334-5338

[32] Ganesan S, Mathew V, Paul BJ, Maruthamuthu P, Suthanthiraraj SA. Influence of organic nitrogenous compounds phenothiazine and diphenyl amine in poly(vinylidene fluoride) blended with poly (ethylene oxide) polymer electrolyte in dye-sensitized solar cells. *Electrochimica Acta*. 2013; **102**:219-224

[33] Chalkias DA, Giannopoulos DI, Kollia E, Petala A, Kostopoulos V, Papanicolaou GC. Preparation of polyvinylpyrrolidone-based polymer electrolytes and their application by in-situ gelation in dye-sensitized solar cells. *Electrochimica Acta*. 2018;**271**:632-640

[34] Yang Y, Zhang J, Zhou C, Wu S, Xu S, Liu W, et al. Effect of lithium iodide addition on poly (ethylene oxide) —poly(vinylidene fluoride) polymer-blend electrolyte for dye-sensitized nanocrystalline solar cell. *The Journal of Physical Chemistry B*. 2008;**112**(21): 6594-6602

[35] Li C, Xin C, Xu L, Zhong Y, Wu W. Components control for high-voltage quasi-solid state dye-sensitized solar cells based on two-phase polymer gel

electrolyte. *Solar Energy*. 2019;**181**: 130-136

[36] Abisharani JM, Dineshkumar R, Devikala S, Arthanareeswari M, Ganesan S. 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. *Materials Research Express*. 2020;**7**(2):025507

[37] Wu J, Lan Z, Lin J, Huang M, Huang Y, Fan L, et al. Electrolytes in dye-sensitized solar cells. *Chemical Reviews*. 2015;**115**(5):2136-2173

[38] Boschloo G, Häggman L, Hagfeldt A. Quantification of the effect of 4-tert-Butylpyridine addition to I⁻/I₃⁻ redox electrolytes in dye-sensitized nanostructured TiO₂ solar cells. *The Journal of Physical Chemistry B*. 2006; **110**(26):13144-13150

[39] Karthika P, Ganesan S, Thomas A, Sheebarani TM, Prakash M. Influence of synthesized thiourea derivatives as a prolific additive with tris(1,10-phenanthroline) cobalt (II/III) bis/tris (hexafluorophosphate)/hydroxypropyl cellulose gel polymer electrolytes on dye-sensitized solar cells. *Electrochimica Acta*. 2019;**298**:237-247

[40] Bagheri O, Dehghani H, Afrooz M. Pyridine derivatives; new efficient additives in bromide/tribromide electrolyte for dye sensitized solar cells. *RSC Advance*. 2015;**5**(105):86191-86198

[41] Sirimanne PM, Shirata T, Soga T, Jimbo T. Charge generation in a dye-sensitized solid-state cell under different modes of illumination. *Journal of Solid State Chemistry*. 2002;**166**:142-147

[42] Yang L, Qin X, Jiang X, Gong M, Yin D, Zhang Y, et al. SERS investigation of ciprofloxacin drug molecules on TiO₂

nanoparticles. Physical Chemistry
Chemical Physics. 2015;**17**(27):
17809-17815

[43] Isaac RS, Sakthivel G, Murthy CH.
Green synthesis of gold and silver
nanoparticles using *Averrhoa bilimbi*
fruit extract. Journal of Nanotechnology.
2013;1-6

[44] Goutam SP, Saxena G, Singh V,
Yadav AK, Bharagava RN, Thapa KB.
Green synthesis of TiO₂ nanoparticles
using leaf extract of *Jatropha curcas* L. for
photocatalytic degradation of tannery
wastewater. Chemical Engineering
Journal. 2018;**336**:386-396

[45] Ong WL, Lim YF, Ong JLT, Ho GW.
Room temperature sequential ionic
deposition (SID) of Ag₂S nanoparticles
on TiO₂ hierarchical spheres for
enhanced catalytic efficiency. Journal of
Materials Chemistry A. 2015;**3**(12):
6509-6516

[46] Jayaramudu T, Raghavendra GM,
Varaprasad K, Reddy GVS, Reddy AB,
Sudhakar K, et al. Preparation and
characterization of poly(ethylene glycol)
stabilized nano silver particles by a
mechanochemical assisted ball mill
process. Journal of Applied Polymer
Science. 2016;**133**(7):1-8

[47] Bhattacharyya R, Ray SK. Removal
of Congo red and methyl violet from
water using nano clay filled composite
hydrogels of poly acrylic acid and
polyethylene glycol. Chemical
Engineering Journal. 2015;**260**:269-283

[48] Shameli K, Bin Ahmad M,
Jazayeri SD, Sedaghat S, Shabanzadeh P,
Jahangirian H, et al. Synthesis and
characterization of polyethylene glycol
mediated silver nanoparticles by the
green method. International Journal of
Molecular Sciences. 2012;**13**(6):
6639-6650