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PERFORMANCE OF DYE-SENSITIZED SOLAR CELL BASED ON POLYANILINE COMPOSITES

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Abstract

Two series of polyaniline (PANI) are prepared by using HCL (PANI-1) or oxalic acids (PANI-2) as dopants. Polymer composites of PANI-1 are synthesized by using polyethylene oxide 300 (PEO300-PANI-1), polyethylene oxide 2000 (PEO2000-PANI-1), TiO_2 in different ratios, and ZnO nanoparticles. The hybrid of water soluble PANI-2 with polyethylene oxide 2000 (PEO2000-PANI-2) was also prepared. Polymer samples and composites are characterized by using FTIR, UV and their morphology was examined by TEM. Electrical conductivity measurements for polymer composites showed that addition of 0.1% TiO_2 to PANI increases its electrical conductivity value from 1.15×10^{-4} to $3.35\ \text{S.cm}^{-1}$, while the water soluble PANI (PANI-2) has moderate electrical conductivity value of $(0.56 \times 10^{-2}\ \text{S.cm}^{-1})$. Dye-sensitized solar cells (DSSCs) (1cm^2) are assembled using polymer electrolytes based on polyaniline (PANI) and its nanocomposites as gel electrolytes and a synthetic dye (N3) as a sensitizer. The DSSC showed short-circuit current (I*sc*) of $90.32\ \text{A/m}^2$ and open-circuit voltage (V*oc*) 0.50V with cell efficiency 2.63% on using PANI-2.

1. Introduction

Dye-sensitized solar cells (DSSCs) based on the mechanism of a fast regenerative photo-electrochemical process represent the recent development of photovoltaic cells. Conventional DSSCs consist of a self-assembled monolayer of molecular dye at the interface between a mesoporous wide-band gap semiconductor oxide and a liquid electrolyte [1]. The redox couple commonly used is iodide/tri-iodide (I^-/I^{3-}) in an organic liquid electrolyte. However, this combination suffers from many disadvantages, such as leakage of the liquid electrolyte and volatility of the redox couple beside it is highly corrosive. Consequently, these drawbacks affect DSSC performance and durability. Employing of polymer electrolytes in DSSC have been receiving great interest to overcome all the problems of liquid electrolyte and complex chemistry. Koh et al. [2] used one-pot reaction between the amines of methyl isocytosine (MIC) and the epoxy groups of poly(ethylene glycol diglycidyl

ether) (PEGDGE) to produce quadruple hydrogen bonding units. He investigated the hydrogen bonding interactions and dissolution behaviour of salt in supramolecular electrolytes, then used this supramolecular electrolyte in DSSC, which gave efficiency of 2.5% at 100mW/cm^2. Trials for increasing cell efficiency have been performed through using of plasticized polymer electrolytes [3] or by utilization of size-controlled TiO_2 nanotubes during DSSC fabrication [4].

Conductive polymers (CP)-semiconductor hybrids can play a role in photovoltaic cells as hole-acceptors. The electron transfer from CP to the semiconductor layer can be detected by measuring the quenching of photoluminescence from conducting polymer after addition of semiconductor nanocrystals [5-7] or by photoinduced absorption experiments [8]. Polyaniline (PANI) is widely used in DSSC as both a sensitizer and a polymer electrolyte with an efficiency of 0.1-0.8%. Sergawie et al. [9] fabricated a photoelectrochemical cells using the emeraldine base form of polyaniline (EB) as a photoactive material and Eu^{2+}/Eu^{3+} redox couple. The cell produced an open-circuit voltage (V*oc*) of – 0.132V and a short-circuit current (I*sc*) of $0.64\mu\text{A.cm}^{-2}$ under 50mW.cm^{-2} white light illumination from Xe lamp.

The influence of polyanilines with the intermediate conductivity value (3.5S/cm) as hole conductors on the photovoltaic behaviours of dye-sensitized solar cells is studied by Tan et al. [10]. At the conductivity of 3.5S/cm, the largest values of I*sc* is (0.77mA/cm^2) and η (0.10%). Tan et al. reported that when the conductivity is lower, the I*sc* obviously decreases because lower conductivity leads to slower charge transport and higher series resistance of the device. Moreover, using of PANI as counter electrode in DSSC is also reported by Li et al. used microporous polyaniline (PANI) as a substitute for platinum to construct the counter electrode in (DSSCs). The PANI counter electrode with microporosity and a size diameter of about 100nm possesses lower charge-transfer

resistance and higher electrocatalytic activity for the I-3/I- redox reaction than Pt electrode does. The overall energy conversion efficiency of the DSSC with PANI counter electrode reaches 7.15%, which is higher than that of the DSSC with Pt counter electrode [11]. Chen et al. developed a flexible counter electrode by electrochemical deposition of polyaniline nanofibers on graphitized polyimide carbon films for use in a tri-iodide reduction. In combination with a dye-sensitized TiO_2 photoelectrode and electrolyte, the photovoltaic device with the polyaniline counter electrode shows an energy conversion efficiency of 6.85% under 1 sun illumination [12]. Two kinds of TiO_2/sulphonated polyaniline (SPAn) nanocomposite ultrathin films were fabricated by Zhang et al. [13] using layer-by-layer (LBL) self-assembly technique on various solid surfaces. One was fabricated with self-doped sulphonated polyaniline (SD-SPAn) and TiO_2 sol, and the other was prepared with externally (HCl)-doped sulphonated polyaniline (ED-SPAn) and $TiCl_4$. The morphology of ED-SPAn/TiO_2 LBL films is evener and smoother than that of SD-SPAn/TiO_2 LBL films. By optimizing the preparation conditions and film parameters, the two kinds of nanocomposites could be used in photoelectrochemical applications. A dye-sensitized solar cell was constructed by Kim et al. [14] by using a porphyrin photosensitizer and, in place of the usual iodide redox system, a solution in aniline solvent containing lithium perchlorate electrolyte, camphorsulphonic acid, and poly(ethylene oxide) copolymer. Irradiation generated polyaniline within the cell, initially following a proposed photoelectro-polymerization mechanism, and eventually operating as a solar cell with polyaniline as a hole-transport medium. Overall energy conversion efficiency was 0.8% at moderate light intensities ($14.6 mW.cm^{-2}$), but lower at higher light intensities due to conductivity limitations. Recently, the quasi-solid-state gel electrolyte based on PANI has attracted attention due to high conductivity, long term stability, and high ionic conductivity compared with liquid electrolytes. Tang et al. prepared microporous hybrid polymer of poly

(acrylic acid)-g-cetyltrimethylammonium bromide/polyaniline (PAA-g-CTAB/PANI). The quasi-solid-state dye-sensitized solar cells (QS-DSSCs) based on the hybrid gel-electrolyte reach a light-to-current efficiency of 6.68% [15].

In this study, it is aimed to manufacture a stable and non-expensive dye-sensitized solar cells through improving the electrolyte applied by introducing polymer electrolyte based on conductive polymer hybrids, instead of volatile, highly oxidized, and corrosive liquid one.

2. Experimental Procedures

2.1. Materials

Aniline (ANI), polyethylene oxide 2000 (PEO2000), polyethylene oxide 300 (PEO300), and acetylacetone 99.3% were purchased from Fluka. Oxalic acid purified LR, dichloroethane (DCE) and potassium per sulphate (PPS) laboratory chemical, potassium iodide extra pure are products of S.d. Fine-Chem Ltd., Mumbai. Potassium permanganate ($KMnO_4$) purified LR is obtained from S.d. Fine-Chem Ltd., Boisar. Zinc acetate 2-hydrate $Zn(CH_3COO)_2 \cdot 2H_2O$, AR grade, Arablab. Sodium hydroxide (NaOH) pellets 99% is obtained from Modern Lab. Acetone, hydrochloric acid 30-34% pure reagent for analysis and ethyl alcohol are products of Adwic. N3 or Ru 535, TCO glass, and platisol solution (transparent platinum catalyst paint), were purchased from Solaronix, Switzerland. Propylene carbonate (PC), ethylene carbonate (EC) anhydrous 99% are purchased from Sigma-Aldrich. Triton® X-100 for gas chromatography and titanium tetrachloride (IV) $TiCl_4$ are obtained from Merck. Isopropanol Extra Pure AR., from Sisco Research Laboratories PUT. LTD., Mumbai. Titanium (IV) oxide TiO_2, powder 99.8%, anatase and TiO_2 anatase < 25nm particle size are Sigma Aldrich products. Polycarbonate sheet is obtained from General Electric, USA.

2.2. Characterization

Functional groups of the prepared polymeric samples and composites were studied by using Fourier transform infrared (FTIR), which were collected from KBr disks using Nicolet, Nexus 821 spectrophotometer, electronic spectra were detected by using T80+UV/VIS Spectrometer, PG instruments Ltd.. For powders, the sample was dissolved in DMSO. The morphology of the samples was studied by using SEM, JXA-840A Electron probe micro analyzer. The microstructure of the samples was examined for very dilute suspensions of the corresponding polymer samples in toluene by using JEOL JEM-1230 TEM with acceleration voltage of 80kV. The microscopy probes of the nano composites were prepared by adding a small drop of the toluene dispersions onto a Lacey carbon film-coated copper grid and allowed to dry initially in air then by applying high vacuum. Electric conductivity measurements were carried out by using HIOKI Z-HITESTER 3522-50 LCR Bridge and HIOKI 9261 TEST FIXTURE in frequencies ranging from 100Hz up to 100kHz. The powder samples were pressed between two parallel brass plates in a special measuring cell for powders. The simulator system is connected manually to be the sun light is the light source that its radiation intensity was measured by a thermopile pyranometer of type Kipp & Zonen (model CM5-774035). The measuring system consists of four components.

The fabricated DSSC, two digital multimeters, one was connected in series to the DSSC to measure output current, while the other is connected parallel to DSSC to measure the voltage and a variable resistance from $0.1\text{-}10^{10}\Omega$.

2.2.1. Synthesis of polyaniline and its composites

I. Synthesis of polyaniline (PANI-1)

A mixture of 1ml Ani and 90ml 1M HCl was set in a reaction vessel. The mixture was stirred with a magnetic stirrer in ice water bath for 1h until a clear solution is formed. To this mixture, 100ml pre-cooled 1M HCl solution containing 2.5g PPS was added drop wise. The resulting

mixture was allowed to react in ice bath for 4hrs. The product was washed with distilled water then with methanol to remove low molecular weight oligomers along with other impurities. Then the sample was dried in an oven at 80°C.

II. Preparation of ZnO nanoparticles

ZnO nanoparticles were prepared hydrothermally from $Zn(CH_3COO)_2 \cdot 2H_2O$ according to [16] as follows: 0.5g $Zn(CH_3COO)_2 \cdot 2H_2O$ was dissolved in 110ml water under stirring. After 10 min, 0.5g citric acid (CA) was added into the above solution. After the dissolution of CA, 10ml (2M) NaOH solution was to the previous mixture resulting in a white aqueous solution (PH value was equal to 12). The solution was introduced into a Teflon lined stainless steel autoclaves, which was sealed and maintained at 120°C for 20hrs. After the reaction completed, the resulted white solid product was separated by centrifugation, washed with distilled water and ethanol to remove ions possibly remaining in the final product, and finally dried at 60°C in air.

III. Synthesis of ZnO-PANI-1 nanocomposite

0.1g of ZnO nanoparticles was added to the initial mixture of 1ml aniline and 90ml 1M HCl and stirred for 1h in ice bath to get uniform suspension of ZnO. To this mixture, 100ml pre-cooled 1M HCl solution containing 2.5g PPS was added drop wise, the reaction was left to proceed in ice bath for 4hrs. The polymer composite was washed with distilled water and methanol and dried in an oven for 12hrs.

IV. Synthesis of 0.1 TiO_2-PANI-1 and 0.5 TiO_2-PANI-1 nanocomposites

PANI-TiO_2 nanocomposites were prepared by oxidative polymerization according to [17] as follows: 0.1g (or 0.5g) TiO_2 (anatase, average particle size = 100nm) was added to the initial mixture of 1ml aniline and

90ml 1M HCl and stirred for 1h in ice bath to get uniform suspensions of TiO_2. To these mixtures, 100ml pre-cooled 1M HCl solutions containing 2.5g PPS were added drop wise. The resulting mixtures were allowed to react in ice bath for 4hrs. From these reactions, $0.1\,TiO_2$-PANI-1 and $0.5\,TiO_2$-PANI-1 were obtained, respectively. The products were washed with distilled water for several times and dried in an oven for 12hrs.

V. Synthesis of PANI and 1% molar ratio PEO hybrids (PEO300-PANI-1) and (PEO2000-PANI-1)

0.03ml PEO-300 or 0.22g PEO-2000 were added to the initial mixture of 1ml aniline and 90ml 1M HCl and stirred for 1h in ice bath to get uniform clear solutions. To these solutions, 100ml pre-cooled 1M HCl solutions containing 2.5g PPS were added drop wise. The resulting mixtures were allowed to react in ice bath for 4hrs. From these reactions, PEO300-PANI-1 and PEO2000-PANI-1 were formed, respectively. The products were washed with distilled water and methanol and dried in an oven for 12hrs.

VI. Synthesis of oxalic acid doped PANI (PANI-2)

In order to prepare water soluble polyaniline, oxalic acid is used as dopant and the method is as follows: 1M oxalic acid (6.30g) was added to 50ml, 0.22M Ani-HCl and stirred for 1h in ice bath. 50ml of 0.2M $KMnO_4$ was added drop wise and stirred for 2hrs in ice bath, then for 24hrs at room temperature. The polymerization reaction proceeded for 4 days; the polymer is filtered and finally washed with 0.2M HCl and acetone. The obtained polymer PANI-2 was dried at 60°C under vacuum.

VII. Synthesis of PANI and PEO hybrid (PEO2000-PANI-2)

2.12g of PEO2000, 10% molar ratio to monomer, was added to 50ml, 0.22M Ani-HCl and stirred for 1h in ice bath. 50ml of $0.2M\,KMnO_4$ was added drop wise and stirred for 2hrs in ice bath, then for 24hrs at room temperature. After reaction completion, the product is filtered, washed with 0.2M HCl and acetone and finally dried at 60°C under vacuum.

The polymer and its hybrid are fully characterized and discussed in article [18] by Abdel Rehim et al..

2.3. Fabrication of DSSC

The conductive TCO glass was firstly washed carefully by immersing in isopropanol solution for 48hrs to remove any impurities, then triton X-100 aqueous solution, finally washed with absolute ethanol and treated with $0.2\text{M}\ TiCl_4$ aqueous solution at 70ºC for 30 min. The washed glass is masked on its four sides by a scotch tape of thickness $35\mu m$ to unify the layer thickness in all samples to give active area of $0.5 \times 0.5 cm^2$.

I. Preparation and sensitization of the titanium dioxide layer

The TiO_2 paste was prepared by grinding 6g of TiO_2 (particle size < 25nm) and 33% by weight PEG 20,000 in a mortar with 14ml of deionized water and 0.2ml of acetyl acetone for 30 min, then adding 2 drops of triton X-100 and grinding for another 15 min. The deposition of the TiO_2-layer was done by doctor blade technique. The prepared paste was spread on the $TiCl_4$ pretreated conductive glass, sintered for 30 min at 450ºC in air, then left to cool down. A further treatment with $0.2\text{M}\ TiCl_4$ solution at 70ºC for 30 min, rinsed with water and ethanol afterwards. After the dip-coating, the TiO_2-electrodes were fired for 30 min at 450ºC again in a very slow heating rate. After the second heat treatment, the TiO_2 electrodes were immediately sensitized. The TiO_2-films were immersed into Ru 535 (N3) dye solution after cooling them down to 60ºC, typically the sensitization was done for 24 hours.

II. Preparation of the counter electrode

Drops of platisol solution (transparent platinum catalyst paint) were spread on clean TCO-substrate with a glass rod. The solvent evaporated at room temperature within a few minutes. Then the substrates were fired at 450ºC for 15-30 min in an air. Small clusters of catalytically highly active platinum are formed.

2.4. Assembly of quasi-solid DSSC

The polymer electrolyte was prepared by dissolving the polymer in acetonitrile under stirring at 70°C in a sealed glass for 1h and 0.5M KI and 0.5M I_2 were dissolved separately in a PC/EG mixture (9 : 1) by volume. The iodine mixture was added to the polymer solution, then 0.5M IMII and the mixture was stirred for another 1h in a sealed glass, the temperature was raised to 90°C and the glass was uncovered to evaporate the acetonitrile solvent, stirring was continued for 24hrs to get a homogeneous gel electrolyte. The polymer electrolyte was spread over the sensitized TiO_2 photo-electrode by using doctor blade technique. Finally, a Pt counter electrode was pressed on top of the front electrode with the help of two clamps. Polycarbonate spacer of thickness 50μm was used to separate the counter and photo electrodes in liquid and quasi-solid DSSCs.

3. Results and Discussion

3.1. Preparation and characterization of conductive polymers

Polyaniline was synthesized using more than one dopant (HCl and oxalic acids) and different oxidants (PPS and $KMnO_4$). It is known that properties of PAni differ and change greatly on using different dopants in the preparation step; such as polymer morphology, solubility, and electric conductivity. However, it was important to prepare PAni using either inorganic or organic dopants, and study the effect of dopant on the electric conductivity, processability of the formed polymer and consequently the performance of the DSSC.

3.1.1. Polyaniline synthesized using HCl/PPS system (PANI-1)

Polyaniline (PANI-1) was prepared by using ANI-HCl and equimolar ratio of PPS. The reaction proceeded for three days to ensure the complete conversion of the monomer. The polymer obtained is green powder, which is soluble only in high polar solvents such as

N-methylpyrilidone. The obtained polymer is a self doped conjugated polymer with the chemical structure shown in Figure 1. Oxidation of aniline yields polyaniline in or close to emeraldine form. The degree of oxidation may vary smoothly between fully reduced leucoemeraldine and completely oxidized pernigraniline [19, 20]. Both reduced and oxidized forms can be protonated in the presence of acids [21]. The imine nitrogens are believed to be protonated more easily than the amine nitrogens after treatment with acid. However, in some cases, it is difficult to attribute that the protonation occurred either on the imine or the amine or both [22]. So, it is assumed that using aniline hydrochloride will assess the protonation process more on the imine nitrogen than on the amine ones.

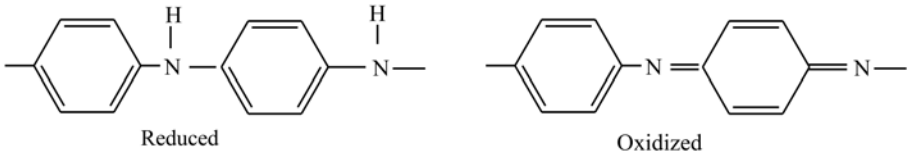


Figure 1. Chemical structure of PANI indicating the reduced and oxidized repeat units.

In order to enhance chemical properties and electrical conductivity of PANI-1, polyethylene oxide of different molecular weights (300 and 2000g/mol) were added during the polymerization reaction. Moreover, to increase the electrical conductivity of the prepared polymer, nanoparticles of ZnO or TiO_2 in different ratios were added during the polymerization process.

3.1.2. Fourier-transform infrared spectroscopy (FTIR)

The FTIR absorption spectra of the PANI-1 and its composite with PEO300 and PEO2000 are shown in Figure 2. Bands observed at $3300cm^{-1}$ is attributed to N–H stretching mode, while bands appear at

2921cm^{-1} is assigned for the aromatic C–H stretching. The band observed at 1614cm^{-1} is the stretching vibration of quinine ring. There is a red shift in this absorption band from PANI-1 to 1572cm^{-1} in case of PEO2000-PANI-1. The C–N stretching vibration appeared at 1313cm^{-1}. The increase in the intensity of the band at 1140cm^{-1} was attributed to charge delocalization on the polymer ring [23]. In acidic medium, an $N^{+}H^{-}$ structure is present. The positive charge on the polymer chain leads to a strong increase in the molecular dipole moment, resulting in a rapid increase in the intensity of all vibrational bands. In particular, the intensity of the band at 1140cm^{-1} increases upon doping. This band can be assigned to a vibrational mode $B\text{–}NH^{+} = Q$ structure [24, 25].

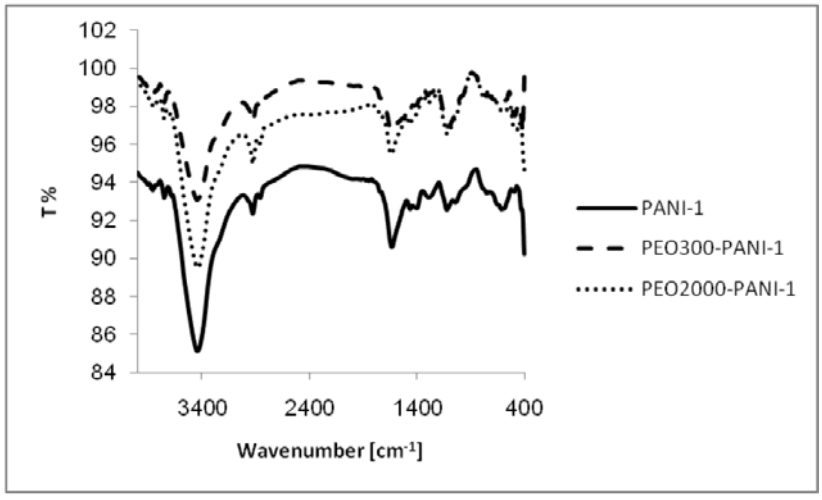


Figure 2. FTIR spectra of PANI-1, PEO300-PANI-1, and PEO2000-PANI-1.

The effect of doping of PANI-1 with ZnO or TiO_2 on the absorption bands of the polymers is represented in Figure 3. In case of 0.1 TiO_2-PANI-1, new peaks appeared at $618cm^{-1}$, $501cm^{-1}$, and $411cm^{-1}$, which are characteristic peaks of TiO_2 (anatase). In the spectrum for ZnO-PANI-1, a sharp characteristic peak for ZnO can be observed at $441cm^{-1}$.

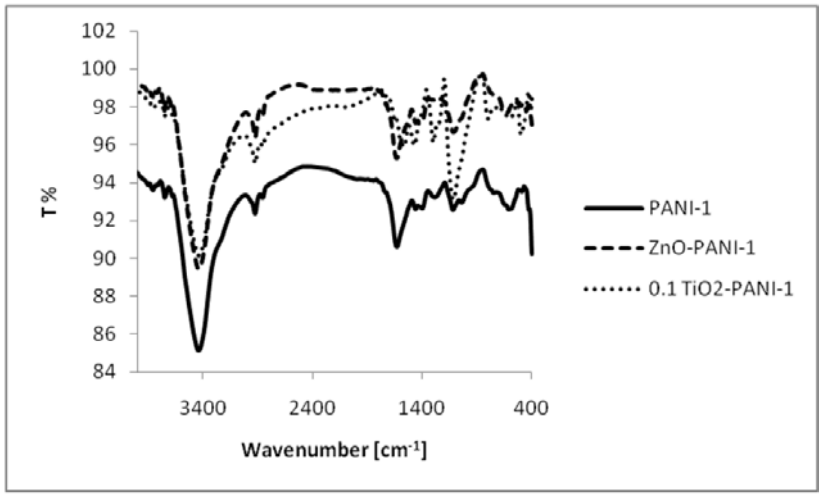


Figure 3. FTIR spectra of PANI-1, ZnO-PANI-1, and 0.1 TiO_2-PANI-1.

3.1.3. Electronic spectra

The polyaniline polymer samples were dissolved in DMSO to record the electronic absorption spectrum of the solutions. Figure 4 reveals the UV characteristics of PANI-1 and its hybrids with PEO300 and PEO2000. PANI-1 has two characteristic bands at 336nm and a broad one around 800nm owing to radical cation (polaron) state formed on PANI backbone [26]. Absorption at 336 in PANI-1 is due to π-π^* transition of aniline and/or anilinum radicals [26-28], which is shifted to 342nm and 344nm in PEO300-PANI-1 and PEO2000-PANI-1, respectively. π-π^* transition of quinine-imine groups [28] at 632nm of

PANI-1 was bathochromic shifted to 646nm in PEO2000-PANI-1, while in PEO300-PANI-1 was broadened and overlapped with the broad band at 800nm to become a very broad one band.

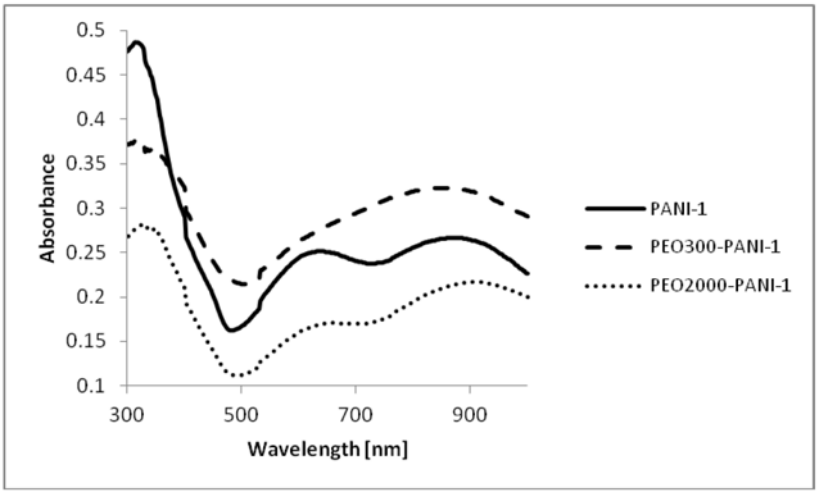


Figure 4. Electronic spectra of PANI-1, PEO300-PANI-1, and PEO2000-PANI-1.

In Figure 5, PANI-ZnO, 0.1 TiO_2-PANI-1, and 0.5 TiO_2-PANI-1 compared with parent PANI-1. They are almost the same, but a red shift occurred compared with the parent PANI-1 due to the presence of nano-oxides bonded to the polymer. It is assumed that bonding of nano-oxides to PANI decreases the band gab and hence lowers the required energy [26]. It is worth to mention that the difference in absorbance from sample to another as in case of 0.1 TiO_2-PANI-1 and 0.5 TiO_2-PANI-1 is due to concentration of the sample in the solvent during measurement.

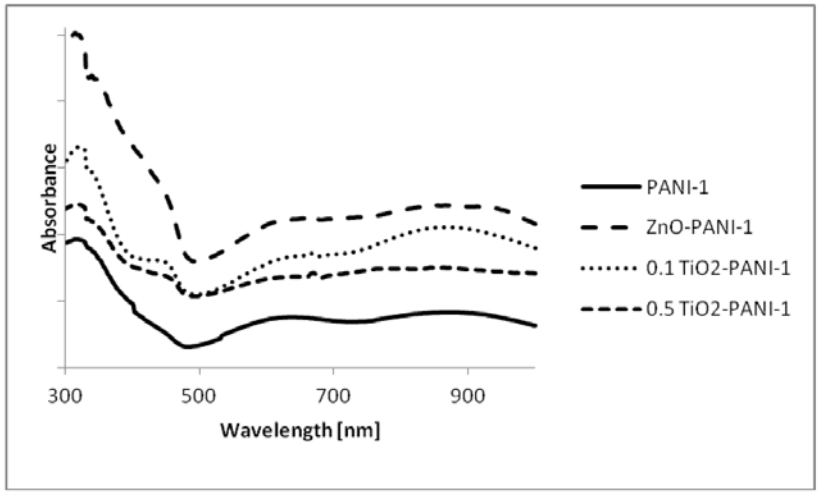
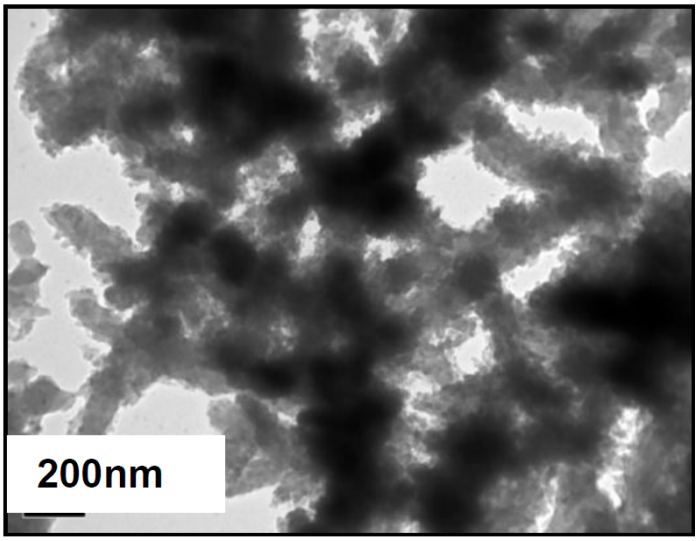


Figure 5. Electronic spectra of PANI-1, ZnO-PANI-1, 0.1 TiO_2-PANI-1, and 0.5 TiO_2-PANI-1.

3.1.4. Transmission electron microscope (TEM)

The morphology of PANI-1 and its blends with PEO 300, PEO 2000 is studied and the images are shown in Figure 6. Comparing TEM photos of the blends with the pure polymer, one can notice that PEO is dissolved into the PANI-1 chains and this lead to the losing of PAN-1 morphology to some extent.



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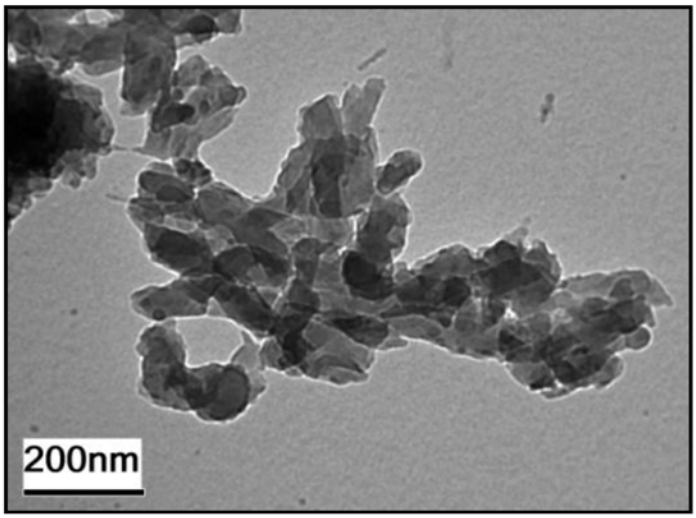

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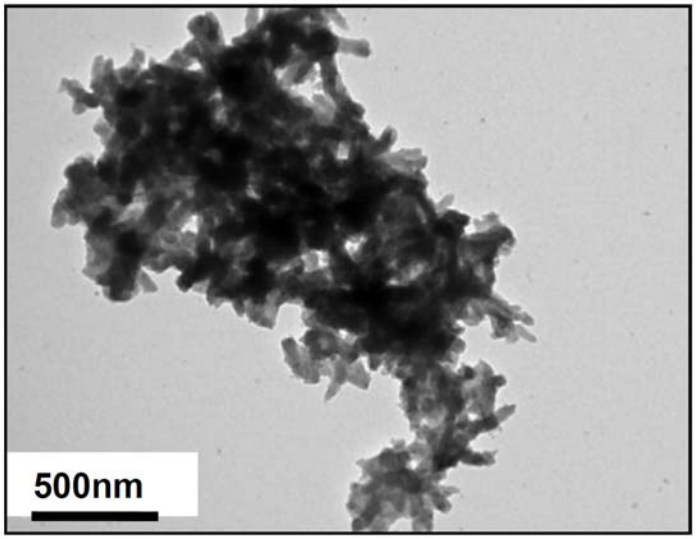
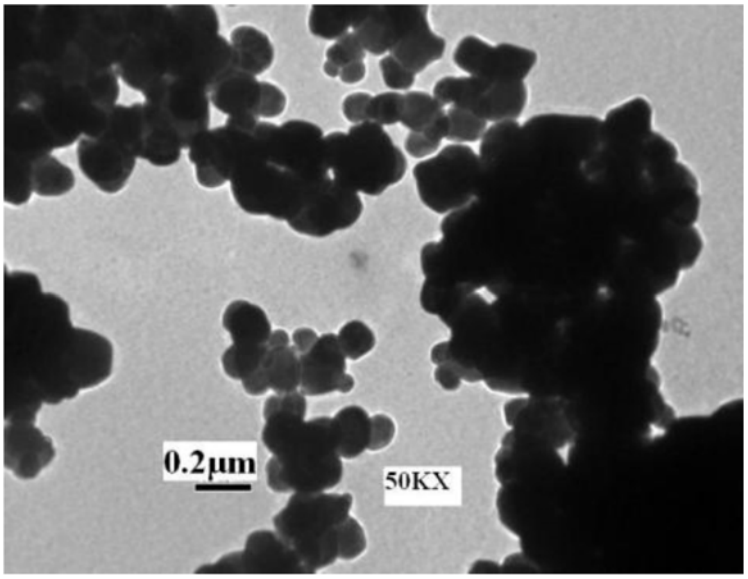


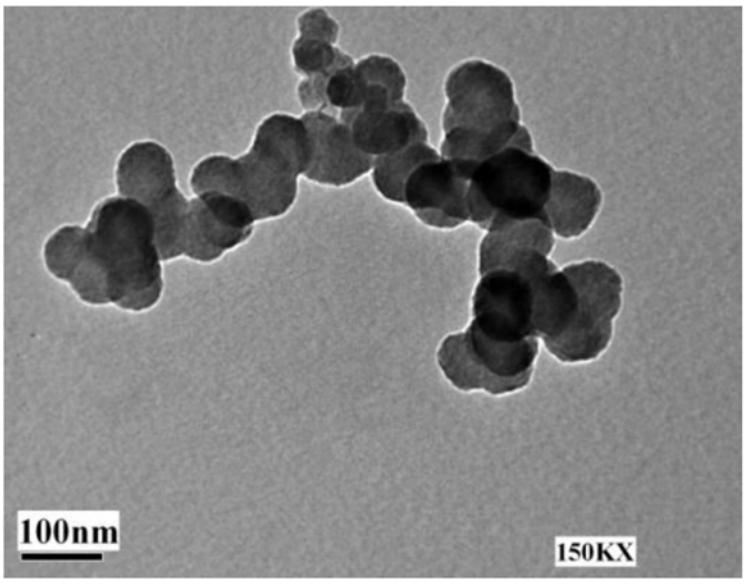
(c)

Figure 6. TEM of (a) PANI-1; (b) PEO300-PANI-1; and (c) PEO2000-PANI-1.

TEM images were taken to pure purchased TiO_2 (Figure 7(a)) and prepared ZnO (Figure 7(b)) nanoparticles indicating that the average particle size of TiO_2 is 100nm, while the average particle size of prepared ZnO is 60nm. Figures 7(c) and 7(d) depict TEM photos of 0.1 TiO_2-PANI-1 and 0.5 TiO_2-PANI-1, respectively. The TiO_2 nanoparticles can be observed on the PANI fibers but on using higher mount of TiO_2 in the composite, aggregates of TiO_2 nanoparticles appear very obviously on the fibers. On adding ZnO to the polymer, the morphology of the polymer changes completely from nanofibers to layered structure as shown in Figure 7(e), and the crystallinity of the polymer increases significantly as noticed from diffraction pattern in Figure 7(f).



(a)



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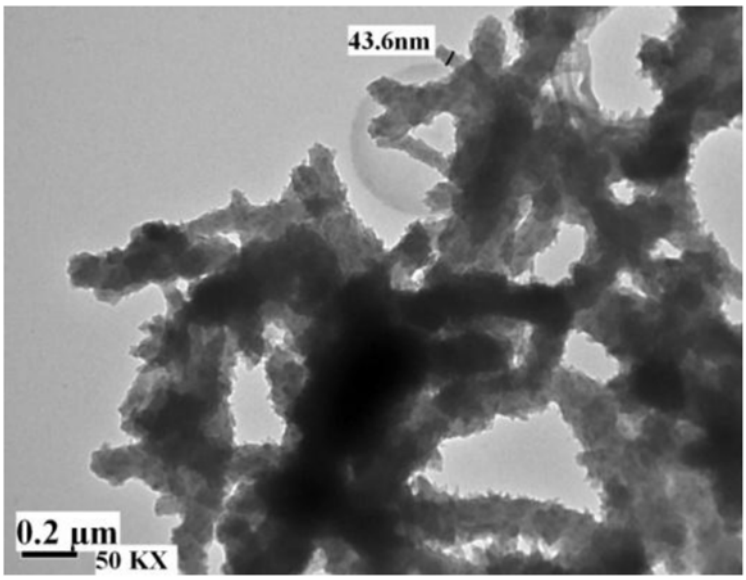

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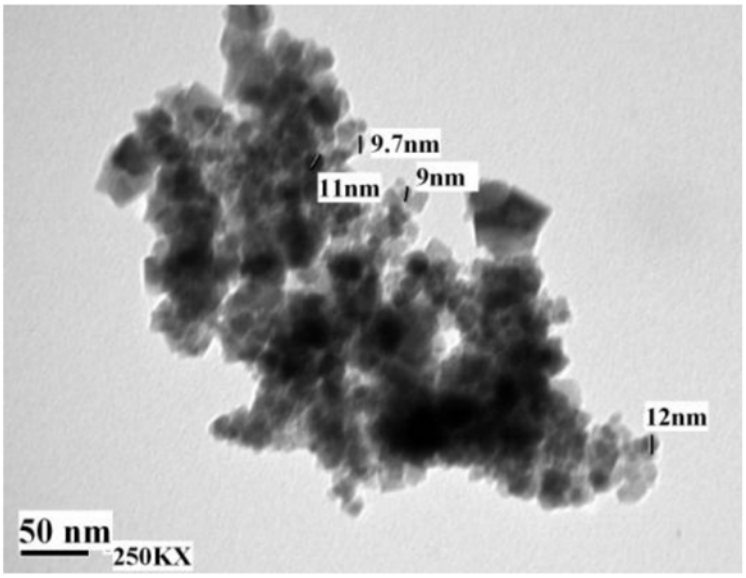

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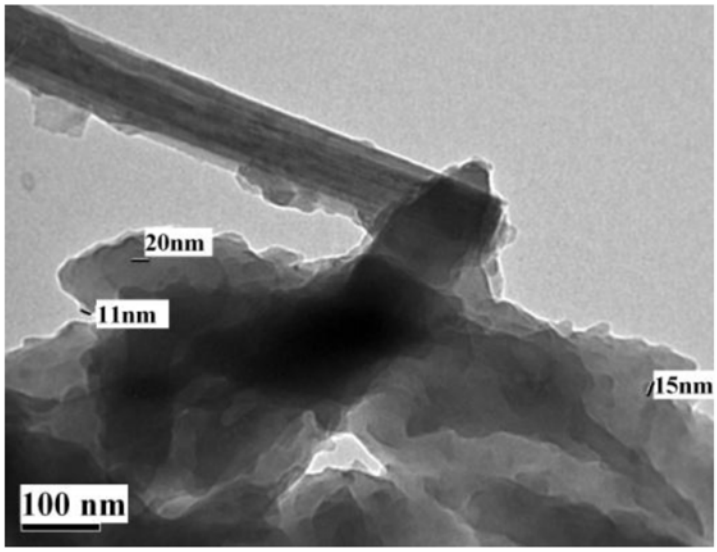
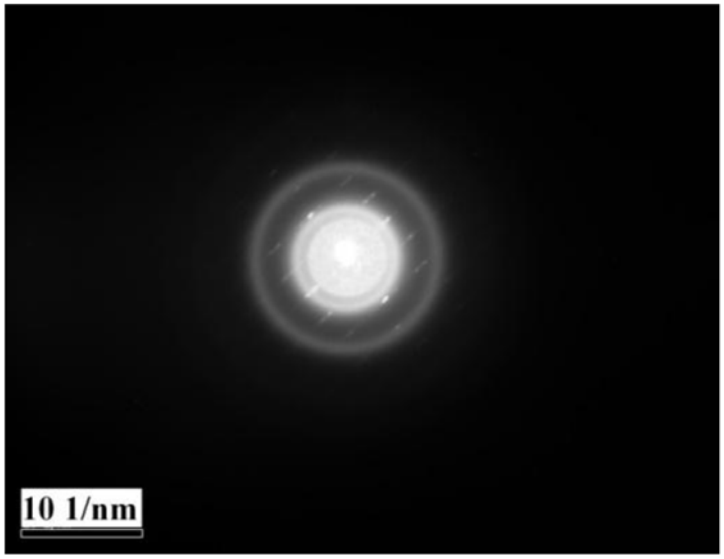


(e)



(f)

Figure 7. TEM of (a) pure anatase TiO_2; (b) pure ZnO; (c) 0.1 TiO_2-PANI-1; (d) 0.5 TiO_2-PANI-1; (e) 0.1 ZnO-PANI-1; and (f) 0.1 ZnO-PANI-1 diffraction pattern.

3.1.5. Electrical conductivity

The electrical conductivity was measured and the results were given in Table 1. The results reveal that pure polyaniline has the lowest conductivity value while doping of the polymer with polyethylene oxide increases the electrical conductivity significantly. Addition of 0.1% of TiO_2 to the polymer increases its electrical conductivity. However, when the amount of TiO_2 is increased to 0.5%, the electrical conductivity decreases sharply since presence of aggregates in the polymer obstacle the mobility of charge carriers and hence decreases conductivity. The electrical conductivity for 0.1 ZnO-PANI-1 is very high in comparison with both pure polymer and 0.1 TiO_2-PANI-1 since the size of ZnO is very small compared with TiO_2 and does not tend to form aggregates, which lead to sharp increase in the electrical conductivity.

Table 1. Electrical conductivity values for polyaniline samples and their composites

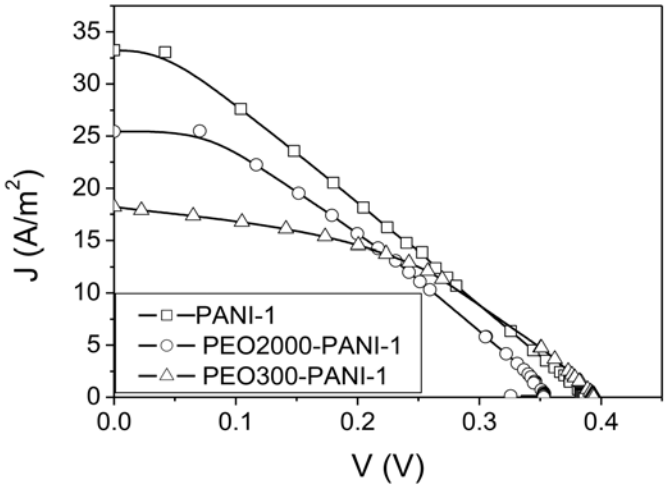
Polymer sample	$\sigma(S.cm^{-1})$
PANI-1	1.15×10^{-4}
PEO300-PANI-1	10.0×10^{-2}
PEO2000-PANI-1	5.4×10^{-2}
0.1 TiO_2-PANI-1	3.35
0.5 TiO_2-PANI-1	3.8×10^{-2}
0.1 ZnO-PANI-1	20
PANI-2	0.56×10^{-2}
PEO2000-PANI-2	1.51×10^{-2}

3.2. Fabrication and characterization of DSSC

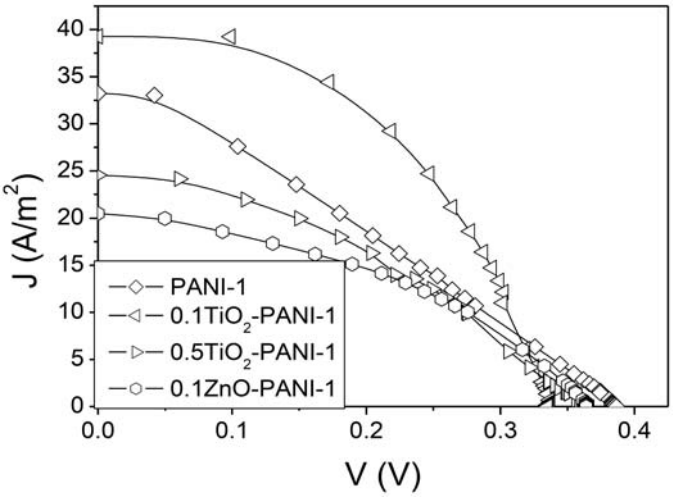
The cells were fabricated by incorporating the polymer gel electrolyte between the photo and counter electrodes. Factors affecting the DSSCs performance were studied to get the most optimized conditions. These factors are divided into these related to TiO_2 layer and factors related to electrolyte composition. Thin layer of TiO_2 paste prepared from TiO_2 of particle size less than 25nm is applied. The small particle was chosen since it has the ability to enhance the overall cell efficiency, moreover, application of thick layers of TiO_2 hinder the motion of electrons for the long path to reach the other electrode through the external circuit. Triton X-100 is added during the paste preparation as a surfactant for TiO_2 particles. PEO is added as a binder, it is burned and evaporated at 150°C leaving behind holes, which improves the dye ability to penetrate into the TiO_2 layers. Conductive glass is treated with $0.2M\ TiCl_4$ solution for 30 min at 70°C in order to increase contact between TiO_2 layer and conductive glass, since $TiCl_4$ prevent bad contact of the electrolyte with the ITO layer.

3.3. Current-voltage characterization curves

The photocurrent-voltage $(I - V)$ curves were measured by using two highly sensitive multimeters under direct sunlight. It could not be the same for all cells due to changing of natural solar intensity with the day time. Current-voltage curves ($I - V$ characteristics) are depicted in Figures 8 and 9 for cells fabricated using different polyaniline electrolyte systems. These curves give short-circuit photocurrent (I_{sc}) and open-circuit voltage (V_{oc}), which are used to calculate the cell FF and η. In general, all DSSC cells showed a smooth uniform trend, with a comparative low fill factor, which is mainly related to the measuring equipments rather than the cell mechanics.



(a)



(b)

Figure 8. Current-voltage curves for solar cells using (a) PANI-1, PEO300-PANI-1, and PEO2000-PANI-1; (b) PANI-1/nanoparticles as polymer electrolytes.

Figure 9 shows the superior polymer electrolyte system based on oxalic acid doped polyaniline. Presence of carboxylate group as conjugate anion in PANI-2 increased its water solubility also this group is bonded strongly with TiO_2 via chelation, which means better absorption of polyaniline on the TiO_2 layer, this was reflected obviously on I*sc* and V*oc*.

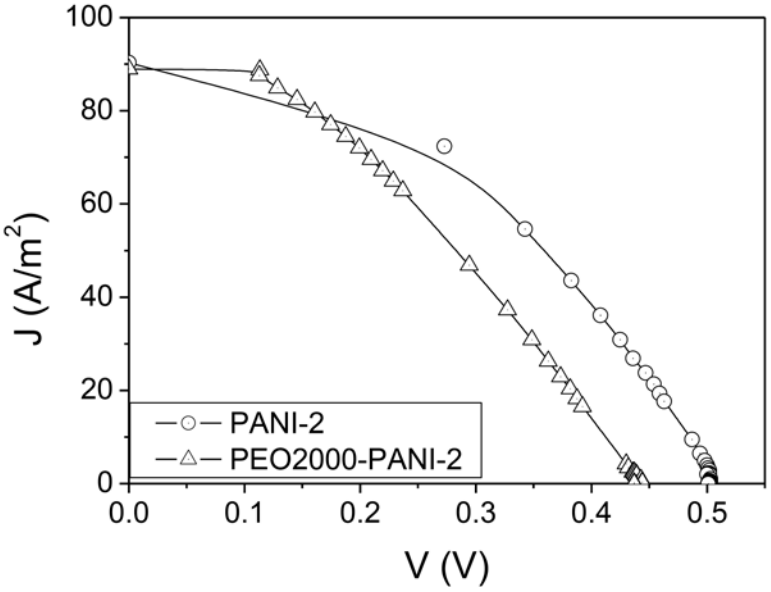


Figure 9. Current-voltage curves for solar cells using PANI-2 and PEO2000-PANI-2 as polymer electrolytes.

Table 2 presents and summarizes the performance of the DSSCs fabricated of these polymer systems in the form of different cell parameters, (I*sc*), (V*oc*), fill factor (FF), and energy conversion efficiency (η). The results showed that the polymer electrolyte systems studied, inserted between both the photo-and counter electrodes, work efficiently in deoxidizing reduced dye and promote electron transfer across the cell. Obviously, the efficiency is highly affected by the polymer composition, dopants, and morphology. Moreover, it is related to the degree of interaction with the TiO_2 photoelectrode, the ability and velocity of generating and transferring charges across the cell and also

the degree of conductivity affects as well. Without referring to FF, the efficiency in case of PANI-1 is higher than its blends with PEO-300 and PEO-2000, although PEO2000-PANI-1 has the highest electrical conductivity. Moreover, nanofillers have a noticeable effect in enhancing the cell efficiency. TiO_2 increases the polymer conductivity and consequently the cell efficiency. It can be explained by the fact that adding TiO_2 nanofiller in the polymer electrolyte increases the concentration of electrons in the electrolyte relative to the substrate electrode because, it acts as a cross-linking center for the polymer, which increases the mobility of electrons. Furthermore, it avoids maximum electron-hole recombination; as a result, the stability of fabricated solar cell is increasing [29]. On the other hand, increasing the ratio of TiO_2 decreases the overall cell efficiency this is due to formation of aggregates, which leads to disconnected or weakly connected parts of the fractal network [29, 30]. Using ZnO-PANI-1 in the cell reduces its efficiency. This can be attributed to the high ability of ZnO to transfer charges faster than the polymer charge generation. Also, the high electrical conductivity of the polymer decreases the distance between HOMO and LUMO of the polymer and consequently increases the electrons-holes recombination.

Table 2. Photo-electrochemical properties of DSSC fabricated using polymer electrolyte systems and N3 as sensitizer under direct sunlight

Polymer	Isc (A/m^2)	Voc (V)	P_{max} (W/m^2)	FF	η (%)	Solar intensity (W/m^2)
PANI-1	33.24	0.39	3.71	0.29	0.57	650
PEO300-PANI-1	18.20	0.39	3.13	0.44	0.52	600
PEO2000-PANI-1	25.44	0.35	3.13	0.35	0.45	700
0.1 TiO_2-PANI-1	39.28	0.34	6.38	0.49	0.91	700
0.5 TiO_2-PANI-1	24.56	0.36	3.32	0.37	0.47	700
ZnO-PANI-1	20.48	0.36	3.01	0.40	0.50	600
PANI-2	90.32	0.49	19.75	0.44	2.63	750
PEO2000-PANI-2	88.96	0.44	14.89	0.38	1.99	750

3.4. DSSC stability

PANI-2 polymer electrolyte system DSSC was chosen for studying DSSCs stability by measuring I*sc* and V*oc* of the cell over under direct sunlight (active area $0.25cm^2$), Figure 10 shows the change in current density (J*sc*) with time. The figure depicts that the highest value for current density is $124.4A/m^2$, it should be noted that the change in current intensity with time was varied significantly due to the change in the intensity of sunlight from day to another. Generally, the decrease in J*sc* was not large until day 10, after that the change was more obvious. Using of polymer electrolytes in DSSC affect the performance of the cell since an interaction between the nitrogen atoms in the PANI structure and the acid cites of TiO_2. This interaction shifts the Fermi levels, which affect the electron occupancy of TiO_2 film, consequently, the value of J*sc* changes and can not be compared with the cells assembled with even liquid polymer electrolytes. It is worth to mention that other polymer electrolytes gave similar performance as PANI-2.

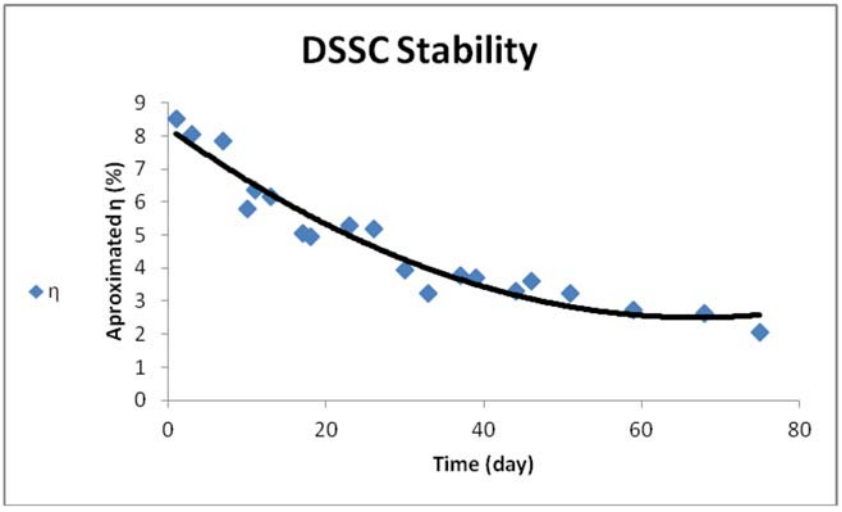


Figure 10. DSSC stability measurement with time using PANI-2 as a polymer electrolyte.

4. Conclusion

This study is concerned with improving the performance of DSSC cell by replacing the liquid electrolyte with a polymer gel electrolyte based on conductive polymer to get a highly stable cell. Two series of polyaniline families were synthesized simply by chemical oxidative polymerization and are used as electrolytes. Cell parameters of the fabricated DSSC are measured and the results showed that polyaniline doped with organic dopant is the best candidate as electrolytes in the DSSC due to its moderate conductivity and better solubility. The stability of the fabricated cells using PANI-2 is studied through measuring photocurrent with time under direct sun intensity. The results showed slow decrease in current density value with time in the first 10 days.

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