

**ICEWEST-2015 [05th - 06th Feb 2015]****International Conference on Energy, Water and
Environmental Science & Technology****PG and Research Department of Chemistry, Presidency College (Autonomous),
Chennai-600 005, India****Effect of nanofiller on ionic conductivity of polymer
nanocomposite electrolyte for solar cell applications****Hari Hara Priya G¹, Suganya N¹ And Jaisankar V^{1*}****¹PG and Research Department of Chemistry, Presidency College(Autonomous),
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Abstract: The conversion of sunlight to electricity using dye-sensitized solar cells (DSSCs) is a most promising modern technology for future low cost power production from renewable energy source. The development of DSSC with potential efficiency is a recent research arena because of low fabrication cost, good stability and compatibility with flexible substrates. The performance of DSSCs is enhanced by synthesising new polymers or adding inorganic nanofillers. The present investigation deals with the synthesis of polymer nanocomposite electrolyte consisting of poly(methyl methacrylate)-poly(ethylene glycol) (PMMA-PEG)/n-ZnO/KI/I₂. Zinc oxide nanoparticle synthesised by sol-gel method is used as inorganic nanofiller. Polymeric nanocomposite was prepared by blending polymer with ZnO nanoparticle using solvent casting technique. The dispersion of nanoparticles in the polymer matrices is not only to improve the ionic conductivity but also to enhance the mechanical strength and stability of the polymer electrolyte. ZnO nanoparticles and polymer nanocomposite were characterised by Ultraviolet-Visible (UV-Vis) spectroscopy, Fourier Transform Infra Red (FTIR) spectroscopy, X-Ray Diffraction (XRD) analysis and Field Emission-Scanning Electron Microscopy (FE-SEM). The ionic conductivity of polymer electrolyte and its nanocomposite electrolyte was evaluated by electrochemical impedance spectroscopy. The synthesised polymer nanocomposite electrolyte has its practical application in the fabrication of DSSC.

Keywords: Nanofiller, sol-gel method, polymer nanocomposite electrolyte, ionic conductivity.

Introduction

Dye-sensitized solar cells (DSSCs) developed by Gratzel *et al.*^{1,2} have been extensively studied in recent years because of their low cost, simple structure and easy fabrication procedure. The liquid electrolyte usually employed in the DSSC is I⁻/I₃⁻ redox couple dissolved in an organic solvent, and is sandwiched between photo anode and cathode material³. The liquid electrolytes have drawbacks such as leakage, corrosion, poor long-term stability and solvent evaporation⁴. This leads to a decrease in efficiency of the solar cell. Therefore, attempts have been made to substitute the liquid electrolytes with ionic liquids⁵, solid polymer electrolytes⁶, polymer gel electrolytes⁷ and organic hole transport materials⁸. Among these species, the quasi-solid-state polymer gel electrolytes have been attracting a great deal of interest because of their nonflammability, negligible vapor

pressure, good contact with the nanocrystalline TiO₂ anode and Pt counter electrode⁹. However, DSSCs employing polymer gel electrolytes have exhibited low cell efficiency. In order to improve the efficiencies of quasi-solid-state DSSCs, many efforts on modification of gel electrolyte have been made through synthesizing new polymers¹⁰, or adding inorganic nanofillers^{11,12}. Researchers have reported that the addition of nanoscale ceramic fillers (i.e., TiO₂, SiO₂, Al₂O₃, ZnO)^{13,14} and clays¹⁵ into polymer electrolytes will form polymer nanocomposite electrolyte which not only improved the ionic conductivity but also enhanced the mechanical strength and stability of the polymer electrolyte. The enhancement in the conductivity is predominantly due to the increase of amorphous region in the polymer as a consequence of the dispersal of the filler particles.

Several polymers used for gel polymer electrolytes (GPEs), such as poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA), poly(ethylene glycol) (PEG) and poly(vinylidene fluoride-co-hexafluoro propylene) (PVDF-co-HFP)^{16,17} have been investigated for DSSCs. Among the copolymers, PMMA is of special interest because it provides a high transparency, good gelatinizing properties, high solvent retention ability and excellent compatibility with the liquid electrolytes. In addition, it has an excellent environmental stability¹⁸. Polyethylene glycol (PEG) is a photochemical stable polyhydric linear polymer, it was used as both reactant and plasticizer¹⁹ and prevents the PVP volatilizing and leaking to form a stable polyblend electrolyte.

Shenet *et al.* compared different alkali metal iodides for PEO polymer in DSSC and concluded that KI salt is a more suitable iodide salt for DSSCs as it costs relatively less and has better chemical stability²⁰. Stergiopoulou *et al.*²¹ introduced TiO₂ into poly(ethylene oxide) matrix of the electrolyte of a DSSC, and this led to an outstanding overall conversion efficiency for the cell. Effects of the addition of TiO₂ into the electrolyte of a quasi-solid-state DSSC on the performance of the cell were also studied by Kang *et al.*²². Scully *et al.*²³ employed layered silicate nanoparticles as additives to the DSSC and obtained increased performance of the cell.

ZnO in many different nanostructural forms were used as photoanode. ZnO has shown a great deal of research interest in DSSCs due to some of its fascinating properties. Nanostructured ZnO has unique properties like high isoelectric point, transparent n-type semiconductor with direct wide band gap (3.37 eV), biocompatibility, nontoxicity, high chemical stability and high electron transfer capability²⁴. Inorganic ZnO nanofiller particles are a good candidate to prevent recrystallization and increase the amorphicity of the polymer.

In the present work, zinc oxide nanoparticles have been used as nanofiller to polymer electrolyte containing PMMA-PEG-KI-I₂ to form polymer nanocomposite electrolyte and the influence of this nanofiller on ionic conductivity have been investigated.

Experimental

Materials

All chemicals used were of analytical grade and have been used without purification. Zinc nitrate (Zn(NO₃)₂) and sodium hydroxide (NaOH) were purchased from SD fine chem., India. Acetonitrile and acetone were purchased from Merck. Iodine (I₂) and potassium iodide (KI) were purchased from Himedia. PMMA and PEG (Mw 6000) were obtained from Aldrich.

Synthesis of nano-zinc oxide (n-ZnO)

To the 100 ml of hot 1M NaOH solution, 100 ml of 0.5 M Zn(NO₃)₂ was slowly added in drops with stirring. The precipitated ZnO was stirred for 2 h. Then the precipitate was washed with deionized water several times and dried at 100°C for 24 h to obtain n-ZnO powder.

Synthesis of gel polymer electrolyte

The gel polymer electrolyte (PE) was prepared as per a previously described method in the literature²⁵, by which PMMA was dissolved in acetone by stirring at 70°C for 1 h to obtain homogeneous solution. At the same time PEG was dissolved in acetonitrile at 70°C for 1 h under continuous stirring and then added to the above solution. The mixture was continuously stirred for another 2 h. After that, KI (0.2 M) and I₂ (0.02M) were added. Finally the homogeneous solution were stirred at room temperature in a sealed glass vessel for 24 h to form polymer electrolyte and then the glass vessel is unsealed to evaporate the solvent until a viscous gel was obtained.

Synthesis of polymer nanocomposite electrolyte

In order to improve the properties of gel polymer electrolyte, the prepared n-ZnO(10 wt%) was added to the prepared gel polymer electrolyte. The mixture was stirred vigorously at room temperature in a sealed glass vessel for 24 h in order to disperse n-ZnO to form polymer nanocomposite electrolyte (PNE).

Characterisation

The prepared n-ZnO, gel polymer electrolyte and gel polymer nanocomposite electrolyte were characterized by UV-Vis spectra, IR spectra, XRD and SEM. The UV-Vis absorption spectra of the samples were recorded in the range of 200-400 nm by UV-Vis spectrophotometer. IR spectra were recorded to confirm the formation of polymer electrolyte using a PerkinElmer IR spectrometer in the range of 400 cm^{-1} to 4000 cm^{-1} . The samples were embedded in KBr pellets. For XRD analysis a Siemens D 500 diffractometer with $\text{CuK}\alpha$ filtered radiations was used for assessing the structure and crystallinity. The samples were scanned over the 2θ range from 10° to 90° . The crystallite size (D) of the nanoparticles was calculated from XRD using the Scherrer equation:

$$D = \frac{0.89\lambda}{\beta \cos \theta}$$

The structure and morphology were studied using aF E I Quanta FEG 200 - High Resolution Scanning Electron Microscope (HRSEM). The conductivity of gel polymer and polymer nanocomposite electrolyte was measured by electrochemical impedance spectroscopy and compared.

Results and Discussion

UV-Vis Spectra

Absorption spectroscopy is a powerful non-destructive technique for exploring the optical properties of semiconducting nanoparticles. The absorption spectra of n-ZnO in the UV range are presented in Figure 1.

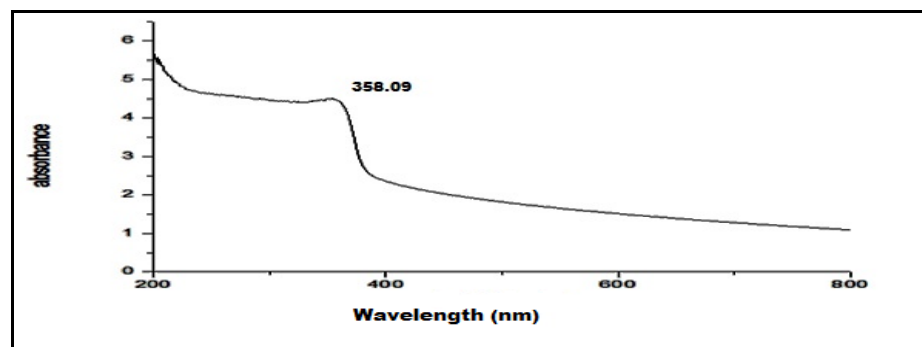


Fig. 1 UV-Vis spectra of n-ZnO

ZnO nanoparticles showed strong absorption band of λ_{max} at 358 nm, which is blue shifted with respect to the bulk absorption edge appearing at 380 nm. The absorption edge systematically shifts to the lower wavelength or higher energy with decreasing size of the nanoparticle.

Fourier-Transform Infrared (FTIR) spectroscopy

FTIR spectra recorded for n-ZnO, PE and PNE are presented in Figure 2.

Figure 2 shows the FTIR spectrum of the ZnO nanoparticles synthesized by sol-gel method. The characteristic absorption peak at 476 cm^{-1} due to Zn-O vibration authenticates the presence of ZnO. The IR spectra of PE and PNE are also shown in Figure 2. It was observed that the stretching frequency at 1736 cm^{-1} , corresponding to CO group of pure PMMA is shifted to 1730 cm^{-1} and 1732 cm^{-1} in PE and PNE respectively confirms the formation of electrolyte. The peaks observed at 3024 cm^{-1} and 2887 cm^{-1} are assigned to O-CH₂ asymmetric stretching and -CH₂ stretching vibration. 1112 cm^{-1} is assigned to C-O-C stretching, 3451 cm^{-1}

corresponds to O-H stretching and 427 cm^{-1} corresponds to presence of metal oxide in nanocomposite. The shift of n-ZnO observed in the spectrum confirms the formation of polymer nanocomposite.

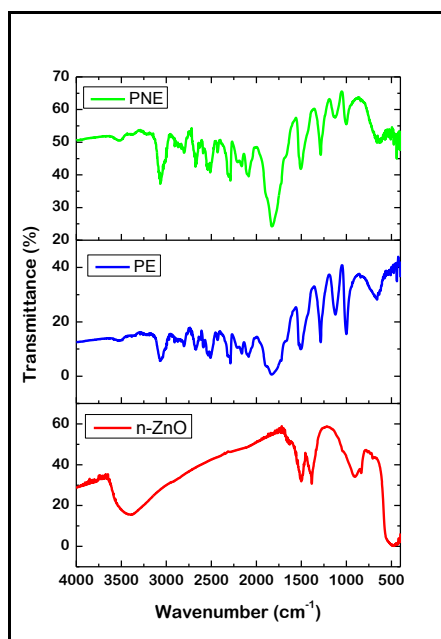


Fig. 2 FTIR spectrum of pure ZnO nanoparticles, PE and PNE

X-Ray diffraction analysis

The X-ray diffraction analysis is a powerful tool to determine the structure and crystallization of the polymer matrices. In order to investigate the effect of blending, XRD analysis was performed. The diffraction patterns of the n-ZnO, PE and PNE were shown in Figure 3.

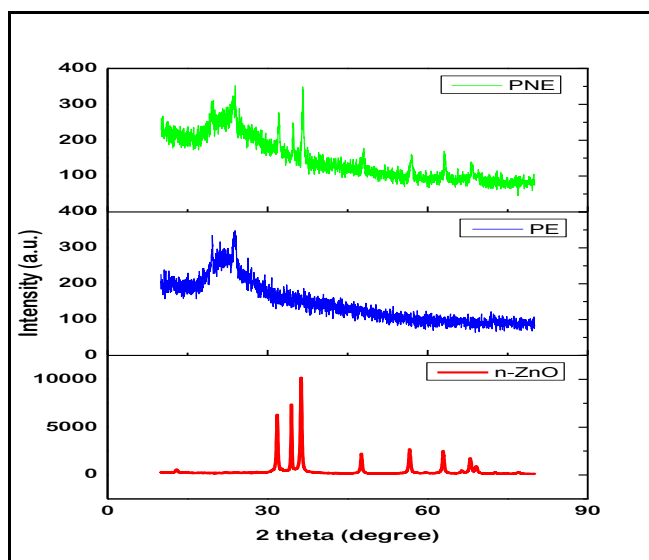


Fig. 3 X-ray diffraction patterns of the n-ZnO, PE and PNE

The particle size of n-ZnO was calculated from the XRD using Scherrer formula and was found to be around 35-45 nm. XRD of the PE shows peak at $2\theta=24^\circ$. XRD of the gel polymer nanocomposite electrolyte shows a broad peak at $2\theta=24^\circ$ and also some new peaks, which implies that all ingredients (I_2 , KI, PEG, PMMA, and n-ZnO) were mixed properly to form a gel, indicating the amorphous nature of the electrolyte. The presence of n-ZnO increased the amorphous nature of the electrolyte. It is well known that amorphous state of the polymeric gel is desirable for the carrier transport and the ionic conductivity.

Scanning Electron Microscopy (SEM)

SEM images of the n-ZnO, polymer electrolyte without and with ZnOnanofiller (PE and PNE) are provided in Fig. 4.

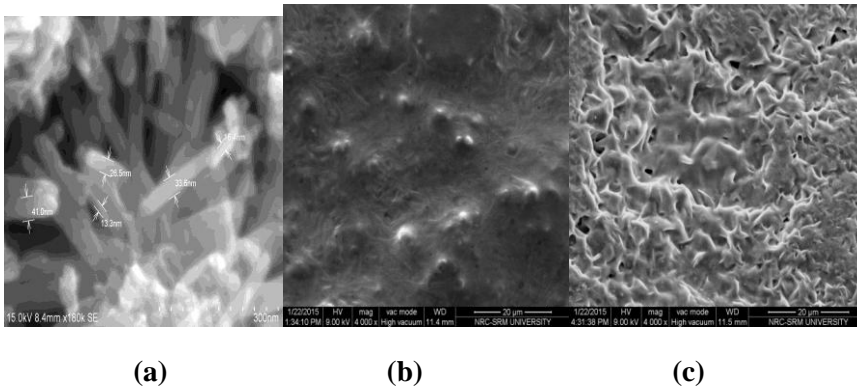


Fig. 4 SEM images of (a) n-ZnO, (b)PE and (c)PNE

Figure 4(a) shows the SEM morphology of the synthesized n-ZnO particles. It demonstrates clearly the formation of ZnOnanorods. The SEM of n-ZnO particles have smooth surfaces and are crystalline with size 15-45 nm. Figure 4(b) shows the SEM morphology of the synthesized PE. Figure 4(c) shows the SEM morphology of the synthesized PNE. From Fig 4(c) it can be seen that the introduction of the n-ZnO into the polymer matrix produces dramatic morphological changes to the host polymer structure. In the case of an electrolyte without ZnOnanofiller (PE), the polymer tends to crystallize at room temperature. However in the presence of ZnO (PNE), the crystallinity of polymer decreases considerably. The existence of two distinct phases was confirmed, the first phase corresponds mainly to the original polymer matrix, and is crystalline, the second phase is an amorphous area consisting of polymer subunits held together forming straight long chains along which ZnO particles of about 20 nm are distributed. Therefore, the polymer chains separated by the ZnO are arranged in a three-dimensional stable network that creates free space and voids into which the iodide/triiodide anions can easily migrate.

Conductivity study of PE and PNE electrolyte

The ionic conductivity of PE and PNE was calculated using impedance plots obtained from electrochemical impedance spectroscopy. The bulk resistance (R_b) value is given by the intercept obtained on the real axis in the plot of real versus imaginary component of impedance. The conductivity (σ) of the polymer electrolyte was calculated using the relation,

$$\sigma = t / A \times R_b$$

where t is the thickness of the polymer electrolyte and A is the contact area of the sample.

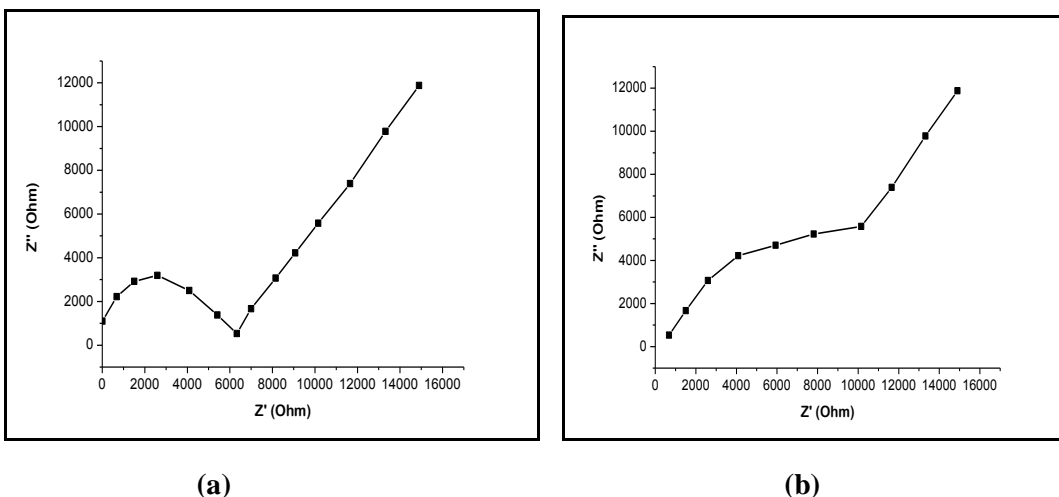


Fig. 5 Nyquist plots of (a) PE and (b) PNE

The ionic conductivities of polymer electrolyte and polymer nanocomposite electrolyte were found to be $2.31 \times 10^{-6} \text{ S cm}^{-1}$ and $3.28 \times 10^{-5} \text{ S cm}^{-1}$ respectively. The increase in conductivity of polymer nanocomposite electrolyte was due to the presence of n-ZnO.

Conclusion

A gel polymer nanocomposite electrolyte (PNE) based on PMMA-PEG-n-ZnO was prepared by solvent casting method. The addition of n-ZnO enhances the degree of porosity and decreases the degree of crystallinity and degree of self-aggregation to the polymer. FTIR confirms the presence of n-ZnO in the prepared polymer nanocomposite electrolyte. XRD analysis reveals the amorphous nature of the polymer nanocomposite electrolyte. The amorphous state of the PNE is due to n-ZnO and desirable for the carrier transport and the ionic conductivity. SEM analysis of PNE shows that the polymer chains are separated by n-ZnO that creates free space and voids into which the iodide/triiodide anions can easily migrate and thereby increase in conductivity. The maximum value of ionic conductivity of PNE was measured to be $3.28 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. The synthesized gel polymer nanocomposite electrolyte can be used in DSSCs to increase the energy conversion efficiency.

References

1. O'Regan B, Grätzel M, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature.*, 1991, 353: 737-740.
2. Gratzel M, Photoelectrochemical cells. *Nature.*, 2001, 414: 338-344.
3. Hagfeldt A, Grätzel M, Light-Induced redox reactions in nanocrystalline systems. *Chem. Rev.*, 1995, 95: 49-68.
4. Nogueira A F, Durrant J. R, De Paoli M-A, Dye-Sensitized nanocrystalline solar cells employing a polymer electrolyte, *Adv. Mat.*, 2001, 13: 826-830.
5. Yang H, Yu C. Z, Song Q. L, Xia Y. Y, Li F. Y, Chen Z. G., Li X.H, Yi T, Huang C.H. High-Temperature and long-term stable solid-state electrolyte for dye-sensitized solar cells by self-assembly. *Chem. Mater.*, 2006, 18: 5173-5177.
6. Paruthimal Kalaignan G, Kang M-S, Kang Y.S, Effects of compositions on properties of PEO-KI-I₂ salts polymer electrolytes for DSSC. *Solid State Ionics.*, 2006, 177: 1091-1097.
7. Wang P, Zakeeruddin S. M, Moser J. E, Nazeeruddin M. K, Sekiguchi T, Gratzel, A stable quasi-solid-state dye-sensitized solar cell with an amphiphilic ruthenium sensitizer and polymer gel electrolyte. *Nat. Mater.*, 2003, 2: 402-407.
8. Bach U., Lupo D., Comte P., Moser J. E., Weissortel F., Salbeck J., Spreitzer H., Gratzel M, Solid-state dye-sensitized mesoporous TiO₂ solar cells with high photon-to-electron conversion efficiencies. *Nature.*, 1998, 395: 583.
9. Nei de Freitas J, Nogueira A.F, De Paoli M.-A, New insights into dye-sensitized solar cells with polymer electrolytes. *J. Mater. Chem.*, 2009, 19: 5279-5294.
10. Chen X, Li Q, Zhao J, Qiu L, Zhang Y, Sun B, Yan F, Ionic liquid-tethered nanoparticle/poly(ionic liquid) electrolytes for quasi-solid-state dye-sensitized solar cell, *J. Power Sources*, 2012, 207: 216-221.
11. Kim J.H, Chi Y.S, Kang T.J, Optimization of quasi-solid-state dye-sensitized photovoltaic fibers using porous polymer electrolyte membranes. *J. Power Sources.*, 2013, 229: 84-94.
12. Yang Y, Hu H, Zhou C.-H, Xu S, Sebo B, Zhao X.-Z. Novel agarose polymer electrolyte for quasi-solid state dye sensitized solar cell. *J. Power Sources.*, 2011, 196: 2410-2415.
13. Baxter J, Nanoscale design to enable the revolution in renewable energy. *Energy Environ. Sci*, 2009, 2: 559-588.
14. Byrne M.T, Gun'ko Y. K. Recent advances in research on carbon nanotube-polymer composites. *Adv. Mater.*, 2010, 22: 1672-1688.
15. Kim S, Hwang E.J, Jung Y, Han M, Park S.J, Ionic conductivity of polymeric nanocomposite electrolytes based on poly(ethylene oxide) and organo-clay materials. *Colloids Surf. A.*, 2008, 313-314: 216-219.
16. Yang H, Huang, M, Wu J, Lan Z, Hao S, Lin J, The polymer gel electrolyte based on poly(methyl methacrylate) and its application in quasi-solid-state dye-sensitized solar cells. *Mater. Chem. Phys.*, 2008, 110: 38-42.

17. Suryanarayana V, Lee K.M, Ho W.H, Chen H.C, Ho K.C, A comparative study based on PVDF-HFP and liquid electrolytes, containing imidazolium ionic liquids of different carbon chain lengths in DSSCs. *Sol. Energy Mater. Sol. Cells.*, 2007, 91: 1467–1471.
18. Ahmad S, Bohidar H.B, Ahmad S, Agnihotry S.A, Role of fumed silica on ion conduction and rheology in nanocomposite polymeric electrolytes. *Polymer.*, 2006, 47: 3583–3590.
19. Cha D.K, Park S.M, Electrochemical studies of polyethylene glycols as solid polymer electrolytes. *J. Electroanal. Chem.*, 1998, 459: 135.
20. Singh P. K, Kim K. W, Rhee H. W, Quantum dot doped solid polymer electrolyte for device application. *Electrochem Commun.*, 2009., 11: 1247-1250.
21. Stergiopoulos T, Arabatzis I.M, Katsaros G.P, Falaras. Binary polyethylene oxide/titania solid-state redox electrolyte for highly efficient nanocrystalline TiO₂ photoelectrochemical cells. *Nano Lett.*, 2002, 2: 1259–1261.
22. Kang M.S, Ahn K.S, Lee J.W, Quasi-solid-state dye-sensitized solar cells employing ternary component polymer-gel electrolytes. *J. Power Sources.*, 2008, 180: 896–901.
23. Scully S.R, Lloyd M.T, Herrera R, Giannelis E.P, Malliaras G.G. Dye-sensitized solar cells employing a highly conductive and mechanically robust nanocomposite gel electrolyte. *Synth. Met.*, 2004, 144: 291–296.
24. Ji L.-C, Huang L, Liu Y, et al. Optical and electrical properties of zinc oxide/indium/zinc oxide multilayer structures. *Thin Solid Films.*, 2011, 519: 3789–3791.
25. Zhao X.G., Jin E.M., Gu H.B., Increased charge transfer of PVDF–HFP based electrolyte by addition of graphite nanofiber and its application in dye sensitized solar cells, *Appl. Surf. Sci.*, 2013, 287: 8–12.
