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A solvent-free composite polymer/inorganic oxide electrolyte for high efficiency solid-state dye-sensitized solar cells

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Abstract

A new solvent-free composite polymer electrolyte consisting of high-molecular mass polyethylene oxide (PEO) filled with titanium oxide and containing LiI and I_2 was developed. The introduction of the inorganic filler (TiO_2 Degussa P25) into the polymer matrix produces dramatic morphological changes to the host polymer structure. Upon addition of the inorganic oxide, the surface roughness increases, with respect to the original polymer and in parallel, the fractal dimension decreases. Both the thermograms and the atomic force microscope (AFM) pictures confirm the amorphicity of the composite electrolyte. The polymer sub-units are held together in a parallel orientation, forming straight long chains of about 500 nm in width, along which TiO_2 spherical particles of about 20–25 nm in diameter are distributed. The polymer chains separated by the titania particles are arranged in a three-dimensional, mechanically stable network, that creates free space and voids into which the iodide/triodide anions can easily migrate. All solid-state dye-sensitized solar cells fabricated using this composite electrolyte present high efficiencies (typical maximum incident photon to current efficiency (IPCE) as high as 40% at 520 nm and overall conversion efficiency (η) of 0.96% ($V_{oc} = 0.67$ V, $J_{sc} = 2.050$ mA/cm^2, FF = 39%)) under direct solar irradiation. Further improvement of the photovoltaic performance is expected by optimization of the electrolyte parameters and of the cell assembly.

Keywords: Composite PEO/titania/I^-/I_3^- electrolyte; TiO_2 films; AFM; All solid-state dye-sensitized solar cell

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1. Introduction

Owing to their high conversion efficiency and low production cost, dye-sensitized solar cells have attracted great scientific and technological interest as potential alternatives to classical photovoltaic devices [1]. The development of this low cost, new type photovoltaic solar cells is based on the optimization of several factors including: (i) the preparation of nanostructured, high surface area TiO_2 thin film electrodes [2,3]; (ii) the synthesis of light capturing antennas, (Ru^{II}-bpy or -terpy complexes) presenting broad and strong MLCT absorption bands and bearing functional anchoring groups [3,4]; and (iii) the use of the I^-/I_3^- redox couple in an appropriate medium. The cell's operation mechanism involves absorption of visible light by the chemisorbed dye, followed by electron injection from the excited sensitizer into the semiconductor's conduction band. The selection of a liquid electrolyte, usually containing an organic solvent such as acetonitrile or propylene carbonate, assures perfect regeneration of the dye by direct interaction between the dye oxidized state and the I^-/I_3^- redox couple and leads to impressively high solar-to-electrical conversion efficiencies (7–11%) [1,5,6]. However, the stability and long-term operation of the cell are affected by solvent evaporation or leakage. Thus, the commercial exploitation of these devices needs the replacement of the liquid electrolyte by a solid charge-transport medium, which not only offers hermetic sealing and stability but also reduces design restrictions and endows the cell with shape choice and flexibility. Several authors made efforts to replace the liquid electrolyte with room temperature molten salts [7,8], inorganic p-type semiconductors [9–12], ionic conducting polymers [13–19] and organic hole transport materials [20–22]. The above systems present high technological interest but their practical use encounters serious problems such as low conversion efficiencies or/and poor electric contact between the photoelectrode and the electrolyte.

On the other hand, recent researches on polymer electrolytes of the type polyethylene oxide (PEO)/LiX proved that the addition of inorganic fillers generally improves their transport properties, the resistance to crystallization and the

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electrode–electrolyte stability [23]. In fact, it has been discovered that the conductivity at room temperature could be enhanced ($\sim 10^{-5}$ S/cm) and this fact led to the production of efficient solid electrolytes for lithium batteries [24–28]. The increase in conductivity with respect to the corresponding unfilled electrolytes was attributed to the enlargement of the amorphous phase in the polymer matrix [29]. Some research groups focused their investigation on the characterization of these polymer electrolytes. Very recently, crystallography has been used to study the structure of PEO/MX electrolytes (without the addition of any filler) [30–34]. Scrosati [35] and Croce and Scrosati [36] found out that the structure of the solid composite PEO/LiX filled with Al_2O_3 is similar with that of the liquid electrolytes consisting of low-molecular weight polyethylene glycol–lithium salt solutions.

Thus, in order to overcome the problems encountered with polymer electrolytes, in this paper we report on the assembling and performance of a solid-state dye-sensitized solar cell using a composite electrolyte consisting of PEO with an inorganic oxide (commercial TiO_2 Degussa P25) as the filler, in the presence of the I^-/I_3^- redox couple. Such a composite material is particularly attractive because it permits excellent ionic mobility of the iodide/triodide anions in its solid-state matrix. The obtained efficiencies of the corresponding dye-sensitized cells are very encouraging for this type of solvent-free composite polymer electrolyte.

2. Experimental

2.1. Preparation of the TiO_2 films

Opaque, thin nanostructured TiO_2 films (5 μm in thickness) were prepared using the doctor-blade technique [5,37] on TEC 15 conductive glass substrates (purchased from Hartford Glass Co. Inc.), ultrasonically cleaned in ethanol prior to use. A viscous paste was first prepared by grinding 0.5 g TiO_2 powder (Degussa P25) with 1 ml of water containing 0.1 ml acetylacetone. The paste was then diluted by very slow addition of 1.7 ml of water where finally, one drop of Triton X-100 was added. The resulting dispersion is smeared onto the TEC 15 substrate by a glass rod. An adhesive tape strip on the conductive glass determines the film thickness (typically 5 μm and uniform all over the film's extension as determined by surface profilometry). The layer is dried in air at room temperature for 15 min, followed by treatment at a temperature of 150 °C for 15 min. Than the film is heated at 450 °C at a rate of 20 °C/min and left at 450 °C for 30 min. Finally, thin film electrodes typically 0.2 cm^2 in geometric area were determined by using a diamond cutter.

2.2. Dye attachment—surface modification

The dye, $Ru(dcbpy)_2(NCS)_2$ (where dcbpy is 4,4′-dicarboxylic acid-2,2′-bipyridine) was purchased from Solaronix. Surface derivatization of the titanium oxide was achieved by immersing the TiO_2 thin film electrodes overnight in a 10^{-4} M ethanolic solution of the complex. The TiO_2 films were heat-treated for 30 min at 120 °C before immersion, in order to eliminate physisorbed water. Noteworthy that a red coloration colour was developed imminently after immersion, implying that a chemical reaction takes place (chemisorption) and confirming the dye grafting on the semiconductor surface. After completion of the dye adsorption the modified materials were thoroughly washed with ethanol and dried under Ar. Thus, any dye in excess (physically adsorbed) was eliminated and a monolayer coverage of the titanium oxide surface was assured.

2.3. Preparation of the composite polymer inorganic oxide electrolyte

Special care was taken to prevent the re-crystallization and avoid phase discontinuities [38]. Of great importance is the percentage (5–15%) of the filler added in the electrolyte. For the composite electrolyte preparation, 0.0383 g of TiO_2 Degussa P25, dried for about 24 h at 250 °C, were first dispersed in acetonitrile (CH_3CN). To this dispersion, the I^-/I_3^- redox couple was incorporated. Then, the (PEO, molecular weight = 2,000,000) was added under continuous stirring. To improve homogeneity, the mixture was sonicated for about half an hour and then stirred for another 24 h. The final product was placed in an oven at 70 °C to evaporate the solvent.

2.4. Cell assembly

The counter-electrode is a TEC 8 transparent conductive glass (purchased from Hartford Glass Co. Inc.) on which very small platinum layer is deposited to give a catalytic effect on the electron donor reduction. The electrolyte was sandwiched between the photoelectrode and the platinized SnO_2 counter-electrode by firmly press. An adhesive tape (approximately 50 μm, 3M Scotch) was placed between the photoelectrode and the counter-electrode to avoid short-circuiting.

2.5. Physical measurements, characterization

Fourier transform IR measurements were carried out using a Perkin-Elmer 1600 spectrometer, the sample being in the form of KBr pellets. The thermal properties of the composite polymer electrolyte were investigated on samples of about 10 mg, using a TA Instruments 2920 DSC. Before the measurements, the materials were placed in a desiccator for two days. Then, they were heated from −120 to 100 °C with a rate of 5 °C/min under nitrogen atmosphere. The morphology of both the TiO_2 electrodes and composite electrolyte was examined with an atomic force microscope (AFM, Nanoscope III, Digital Instruments, operated in the tapping mode). Film thickness, determined by surface profilometry

(Sloan Dektak II Stylus Profilometer), was typically 5 μm and was uniform all over the film's extension.

Photoelectrochemical experiments were performed using a Vinci Technologies P/G STAT Z_1 potensiostat. Illumination was provided by a 300 W Xe arc light source (Oriel) coupled to a 1/8 holographic grating monochromator (Oriel). A cut-off filter was used to exclude wavelengths $\lambda < 400$ nm preventing the generation of electron–hole pairs through direct TiO_2 band gap excitation. *I–V* measurements were performed by connecting the cell to a variable resistor together with a microampere meter in series and a voltmeter in parallel. The lamp radiant flux was measured using an 28-0925 Ealing research radiometer–photometer operating in conjunction with a 28-0982 silicon detector and a 28-0727 flat response filter. In the case of sun illumination, a 10:1 (DO = 1) neutral density filter was interposed in order to avoid saturation and measure its direct irradiance (mW/cm^2).

3. Results and discussion

All solid-state dye-sensitized solar cells of the type:

$$\mathrm{TEC15/TiO_2-dye//electrolyte//Pt/TEC8}$$

were fabricated using the $PEO/TiO_2/I^-/I_3^-$ composite electrolyte. The photoelectrochemical properties of these cells were investigated under short circuit conditions. By using the 300 W Xe lamp, typical maximum incident photon to current efficiencies (IPCE) as high as 40% were obtained at 520 nm, only two times lower than that obtained with liquid electrolytes [5]. It is worth mentioning that the dye was excited through the conducting glass sheet serving as support for the opaque TiO_2 film and that the given value is not corrected for reflection and absorption losses of the conducting glass (3 mm thick), which are estimated to be at least 15% in the visible region of the spectrum.

Fig. 1 exhibits the current–voltage characteristics of such a typical dye-sensitized solar cell employing the $PEO/TiO_2/I^-/I_3^-$ composite polymer electrolyte, measured at a direct sunlight irradiance of 55.8 mW/cm^2 (which is approximately 50% of the standard AM1.5 irradiance). The optimum performance was obtained under normal illumination, yielding a fill factor (FF) of 39%, a short circuit current density (J_{sc}) of 2.05 mA/cm^2, an open-circuit voltage (V_{oc}) of 0.67 V and an overall efficiency (η) of 0.96%. For an all-solid-state device, such overall conversion efficiency value is considered to be sufficiently high [17,39], especially if one takes into consideration that for both the composite polymer electrolyte preparation and the cell assembly no special precaution was taken.

In order to better understand the above behavior and explain the obtained high conversion efficiency, the cell components (especially the composite electrolyte and the semiconductor thin film) were characterized. The nature of the electrolyte was first controlled by FT-IR spectroscopy. The sample did not show any presence of C≡N vibrations and confirmed that it is exempt of acetonitrile, Fig. 2. However, the electrolyte prepared present perfect uniformity and maintains an excellent elasticity and plasticity probably due to its amorphous character. The above properties assure a good

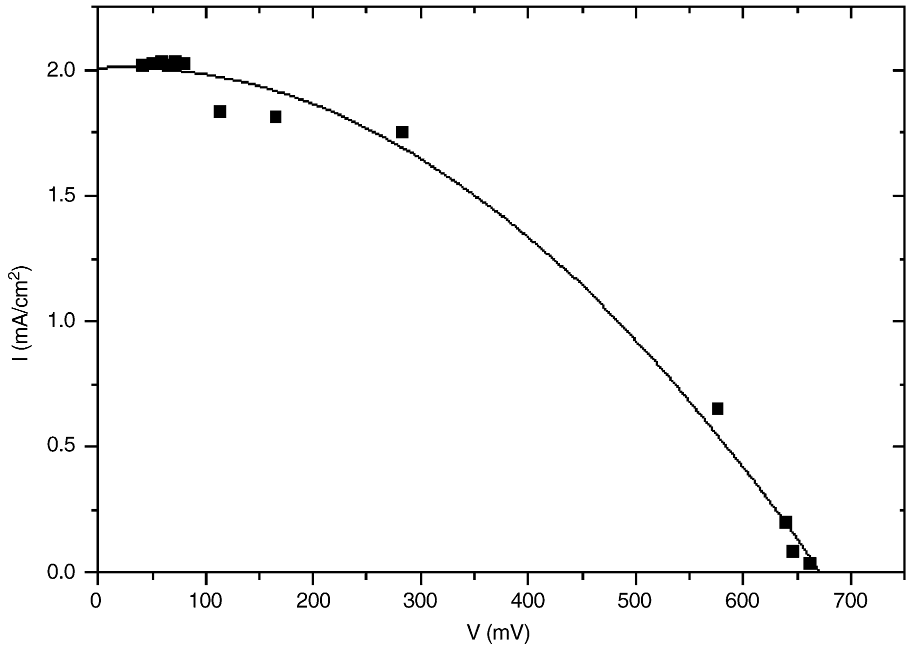


Fig. 1. Photocurrent–voltage (*I–V*) curve characteristics of the TiO_2 (Degussa P25)/Ru535 dye sensitized solar cell using the $PEO/TiO_2/I^-/I_3^-$ composite polymer electrolyte. Temperature: 20 °C, area: 0.2 cm^2, solar irradiance: 55.8 mW/cm^2. $V_{oc} = 0.67$ V, $I_{sc} = 0.406$ mA ($J_{sc} = 2.050$ mA/cm^2), FF = 39%, $\eta = 0.96\%$.

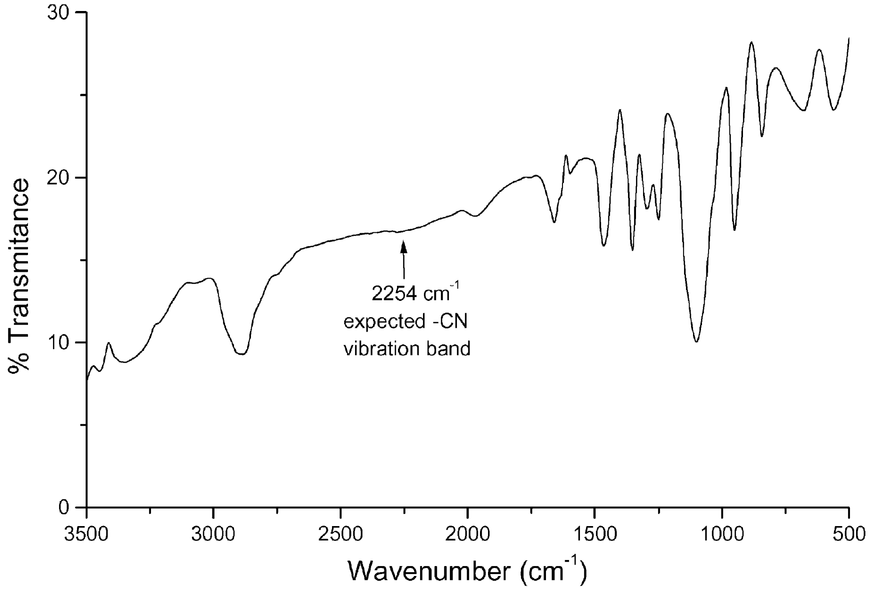


Fig. 2. FT-IR spectrum of the PEO/TiO_2/I^-/I_3^- composite electrolyte.

wetting of the photoelectrode pores and result in a good electric contact between the cell components.

The thermal properties of the polymer inorganic matrix were also investigated. From the DSC thermograms the glass transition temperature (T_g), the melting temperature (T_m) and the melting enthalpy (ΔH_m) were determined. T_m was taken as the peak of the melting endotherm and T_g as the inflection point. The obtained results for the pure PEO (figure not shown) and for the PEO/TiO_2/I^-/I_3^- composite electrolyte (Fig. 3) are summarized in Table 1. Before the

Table 1
Glass transition temperature (T_g), melting temperature (T_m), melting enthalpy (ΔH_m) and crystallinity (X_c (%)) for PEO and PEO/TiO_2/I^-/I_3^- composite electrolyte

	T_g (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)
PEO	−58.79	65.15	114.20	76.9
PEO/TiO_2/I^-/I_3^-	−52.52	31.27	10.61	8.6

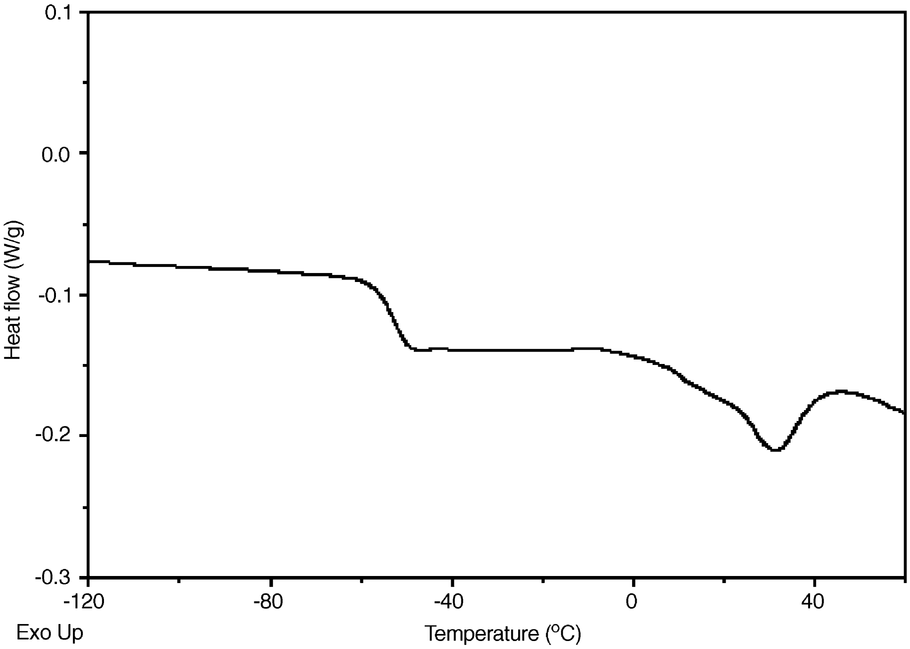


Fig. 3. DSC curve for the PEO/TiO_2/I^-/I_3^- composite electrolyte.

measurements, the materials were placed in a desiccator for 2 days. Then, they were heated from −120 to 100 °C with a rate of 5 °C/min under nitrogen atmosphere. The slight increase of the glass transition temperature observed for the composite polymer inorganic electrolyte is expected. In fact, according to the literature [40], the addition of small inorganic oxide particles stiffens the polymer chains causing in that way a slight increase in the T_g. The decrease of the crystallinity is expected due to the steric hindrance effect. After heating the polymer electrolyte over the melting temperature, the large surface area of the titania particles prevents the PEO chains to re-crystallize [25].

From the melting enthalpy values the crystallinity of the samples were calculated according to the Eq. (1):

$$X_c = \frac{\Delta H_m}{\Delta H_{m,c}} f_{PEO} \tag{1}$$

where ΔH_m is the melting enthalpy which is experimentally measured, $\Delta H_{m,c}$ (=196.4 J/g) is the melting enthalpy of 100% crystalline PEO and f_{PEO} is the weight fraction of polyethylene oxide in the polymer electrolyte [41]. The obtained values, $X_c = 76.9\%$ for the pure PEO and $X_c = 8.6\%$ for the PEO/TiO_2/I^-/I_3^- material, respectively, confirm that the composite electrolyte can be considered as an almost amorphous material.

To investigate the morphological characteristics of both TiO_2 photoelectrodes and composite electrolyte, AFM in the tapping mode has been used. The titanium dioxide films consist of interconnected grain particles, with an average grain diameter of about 20–25 nm, fused together and forming high mountains and deep valleys, Fig. 4. The films present important roughness resulting from surface features of important height. The height histogram of surface characteristics (not shown) has a Gaussian-like distribution with a maximum at 100 nm. The fractal analysis has shown that the prepared films exhibit also self-affine scaling character over a significant range of length scales as a consequence of a "chaotic" dynamic deposition process. It is clearly evident that the effective surface area in this case is several times greater than the one of a flat "Euclidean" non-fractal surface. As a result, the TiO_2 films are endowed with a high real surface extension, which readily favors the photosensitization process. In fact, such a surface not only permits the adsorption of a greater number of dye molecules, but also creates a rough environment where multiple light reflection can occur, thus considerable increasing the amount of the adsorbed photons. Furthermore, such a rough photoelectrode surface permits a better "wetting" of the film by the composite electrolyte and finally results in a perfect penetration of the I^-/I_3^- redox couple into the film pores, which in turn favor the interaction between the oxidized dye and regeneration of the sensitizer's ground state.

Fig. 5a shows the three-dimensional surface plot of the original polymer film (PEO of molecular weight 2×10^6). The material presents a crystallized network of regular spherulites developing spirals and branches of well-distributed surface contours. The network is characterized by relatively low roughness and high complexity, as indicated by the corresponding values of Rms and fractal dimension D_f (a parameter which accounts for the geometric surface complexity) values, Table 2.

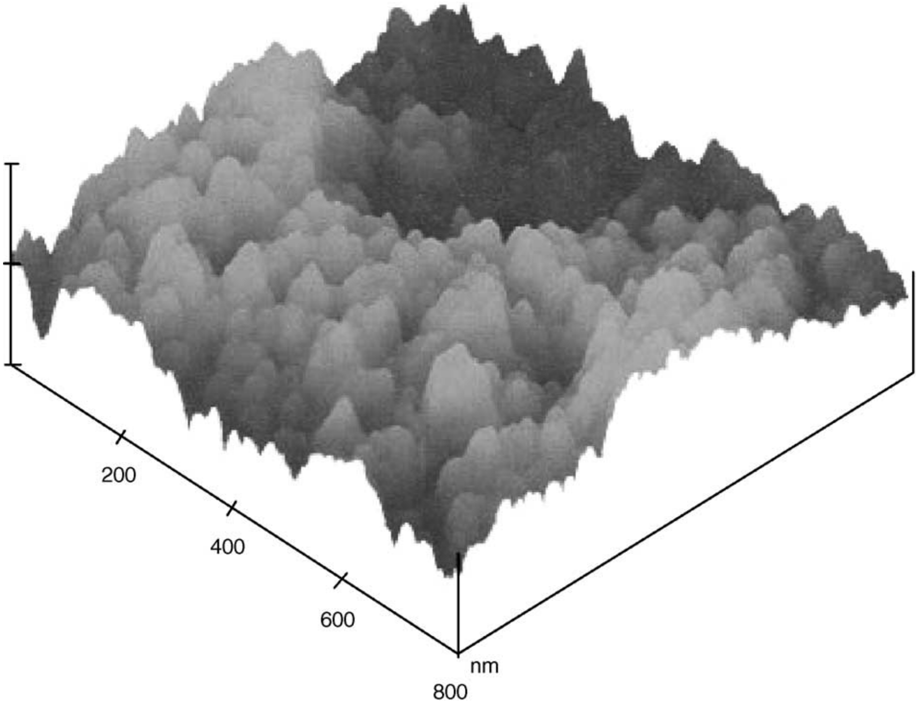
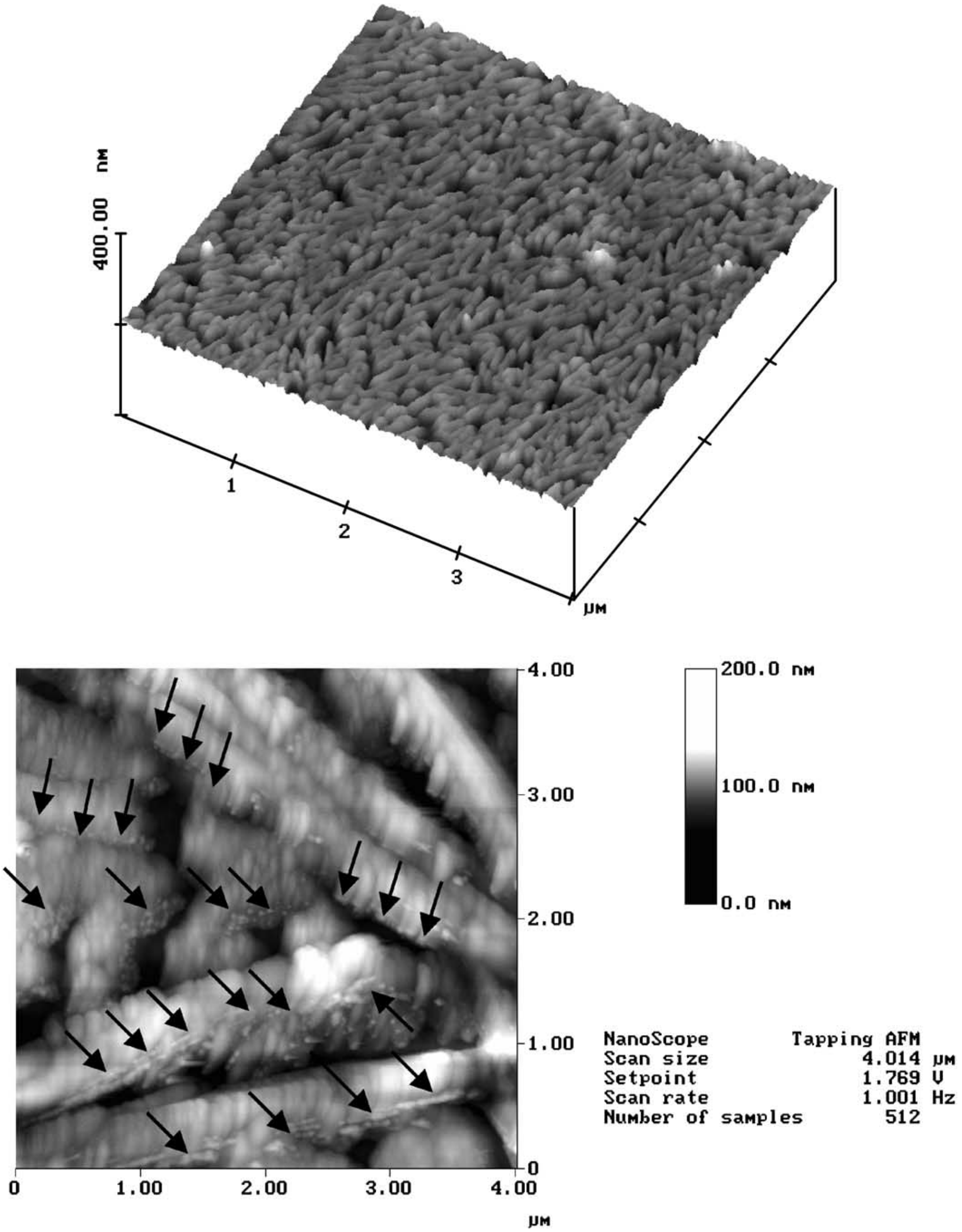


Fig. 4. Three-dimensional AFM picture (surface plot) of the nanocrystalline TiO_2 film.



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NanoScope           Tapping AFM
Scan size              4.014 µM
Setpoint               1.769 V
Scan rate              1.001 Hz
Number of samples        512
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Fig. 5. Top-view AFM pictures of the PEO (a) and of the PEO/TiO_2/I^-/I_3^- (b) composite polymer electrolyte. The arrows indicate the distribution of titania particles.

Table 2
Roughness (Rms) and fractal dimension (D_f) values of the original polymer and the composite polymer electrolyte

	Rms (nm)	D_f
PEO	4.9	2.31
PEO/TiO_2/I^-/I_3^-	14.5	2.19

The introduction of the inorganic filler into the polymer matrix produces dramatic morphological changes to the host polymer structure. The AFM top-view image of the composite electrolyte (Fig. 5b), reveals that in the presence of the titania filler the crystallinity of the PEO considerably decreases, in excellent agreement with the DSC results. The image shows that the polymer sub-units are held together in a parallel orientation, forming straight long chains of about 500 nm in width, along which TiO_2 spherical particles (indicated by arrows) of about 20–25 nm in diameter are distributed. The polymer chains separated by the titania particles are arranged in a three-dimensional, mechanically stable network, that creates free space and voids into which the iodide/triodide anions can easily migrate. It is worth mentioning that upon addition of the inorganic oxide, the surface roughness increases, with respect to the original polymer and that in parallel, the fractal dimension decreases (Table 2).

In the above composite system the inorganic filler acts as a support matrix for the polymer so that even at high temperatures, the electrolyte remains solid. Subsequently, at the microscopic level, it maintains a "liquid" like structure, which is important for sufficient conductivity. Furthermore, the filler particles, because of their large surface area, prevent the re-crystallization of the PEO when this is annealed at a temperature higher than T_m. In fact, with the addition of titania powders to the polymer both the thermograms and the AFM pictures have shown that the amorphicity of the polymer electrolyte was increased. The structure modification of the polymer electrolyte may be produced by a combination of steric hindrance effects or/and of acid–base interactions between the filler surface groups and the oxygen of the PEO. The Lewis acid character of the inorganic filler may favorite the formation of complexes with the PEO. In that way the filler may act as a cross-linking center for the PEO reducing the tension of the polymer for self-organization and promoting stiffness. It is believed that this structure provides the conducting pathways for the ions at the surface of the filler improving thus the conductivity [25]. On the other hand, acid–base interactions between the polar surface groups of the filler and the electrolyte ions probably favor the dissolution of the salt [26,42,43].

It is well established that the size of the filler particles plays an important role to the performance of such an electrolyte [44]. Our results indicate excellent "wetting" of the semiconductor TiO_2 film by the solid composite polymer electrolyte, which gives rise to a high penetration into the nanoporous structure of the film. This is probably due to the fact that for both the semiconductor film and the filler the same material (TiO_2 Degussa P25) was used. This allows a uniform particle distribution at the dye-coated semiconductor/electrolyte interface, which explains the high conversion efficiency of the corresponding solar cells.

In summary, we have presented a new type of solvent-free composite polymer electrolyte based on high-molecular mass PEO filled with titania (TiO_2) and containing LiI and I_2. The thermal properties of the polymer inorganic matrix were characterized. Surface features of the composite electrolyte were investigated by AFM. All solid-state dye-sensitized solar cells using this composite electrolyte were developed. Photoelectrochemical measurements indicate that the cells present high overall energy conversion efficiencies (0.96%) under direct solar irradiation. This is a very encouraging result and the cell is particularly attractive because of its solid-state nature. Long-term stability measurements of the cell are in progress. Further improvement of the photovoltaic performance is expected, as many parameters of the cell assembly and of the electrolyte (especially the polymer molecular weight as well as the nature and particle size distribution of the titania filler) had not been yet optimized.

Acknowledgements

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