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An innovative TiO_2 nanoparticle/nanofibre/nanoparticle, three layer composite photoanode for efficiency enhancement in dye-sensitized solar cells

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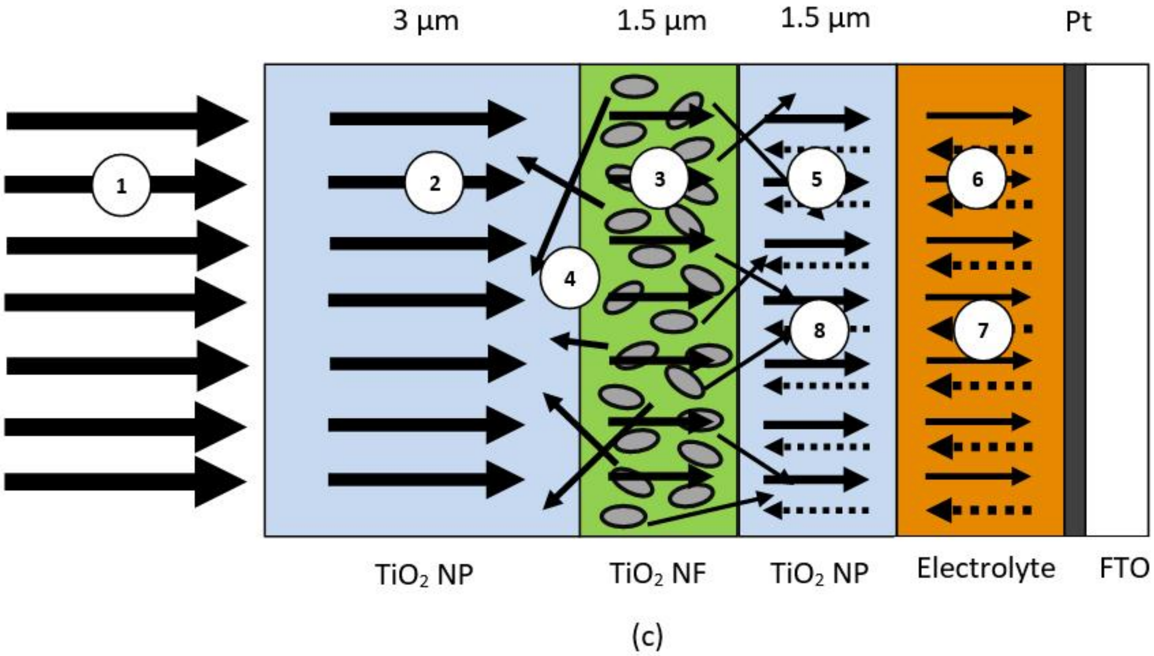
Graphical abstract



Research Highlights

- An innovative type of composite photoanode consisting of a TiO_2 nanofibre (NF) layer sandwiched between two TiO_2 nanoparticle (NP) layers has been fabricated and tested in dye sensitized solar cells.
- DSSCs fabricated with the TiO_2 NP/NF/NP composite three layer photoanode sensitized with N 719 dye showed the highest efficiency of 7.09 % where as the DSSC with TiO_2 nano particle photoanode with same thickness and the same electrolyte showed an efficiency of 5.38 %.
- The increased efficiency has been attributed to enhanced light harvesting due to scattering within the TiO_2 nanofibre structure.
- The composite photoanode with an electrolyte with two iodide slats increased the DSSC efficiency to 8.80% representing an impressive overall efficiency enhancement by 64% compared to a corresponding DSSC made with conventional TiO_2 nanoparticle (NP) photoanode and an electrolyte with the single iodide salt Pr_4NI.

Abstract

An innovative type of composite photoanode consisting of a TiO_2 nanofibre (NF) layer sandwiched between two TiO_2 nanoparticle (NP) layers has been fabricated and tested in dye sensitized solar cells. After sintering, the nanofibres in the layer have turned to an elongated bead type nanostructure. DSSCs fabricated with the TiO_2 NP/NF/NP composite three layer photoanode sensitized with N 719 Ruthenium dye and a electrolyte solution consisting of tetrapropylammonium iodide and iodine dissolved in acetontrile and ethylene carbonate co-solvent showed the highest efficiency of 7.09% where as the DSSC with TiO_2 nano particle photoanode and the same electrolyte showed an efficiency of 5.38%. The increased efficiency has been attributed to enhanced light harvesting due to scattering within the TiO_2 nanofibre structure. The efficiency of the highest efficiency DSSC has been further enhanced by using the "mixed cation effect" where the single iodide salt, Pr_4NI, in the electrolyte has been replaced by two iodide salts KI and Pr_4NI resulting an efficiency of 8.80%. The combined use of the TiO_2 three layer composite photoanode and the mixed cation iodide salt containing electrolyte represents an impressive efficiency enhancement by 64% compared to a corresponding DSSC made with TiO_2 nanoparticle (NP) photoanode and an electrolyte with the single iodide salt Pr_4NI.

Keywords: TiO_2 photoanode, nanofibre, dye sensitized solar cells, mixed cation electrolyte

1. **Introduction**

Dye-sensitized solar cells (DSSCs) have received a great deal of attention in recent years as an emerging competitor to traditional thin film solar cells mainly because of lower fabrication cost [1,2]. A typical DSSC consists of a dye sensitized, nanoporous, nanoparticle TiO_2 photoanode and a Pt counter electrode separated by a electrolyte solution or a gel electrolyte containing a I^-/I_3^- redox couple. The energy conversion efficiency of electrolyte solution based DSSCs has reached around 11% and recent research efforts have been directed towards further improving their efficiency as well as the long term stability [3]. Several directions of research are being focused on developing efficient and stable DSSCs. Improving the redox electrolyte, enhancing the density and mobility of photogenerated electrons within the TiO_2 photoanode and structural modifications to the photoanode for efficient light harvesting are some of these [4,5,6]. Although widely used TiO_2 nanoparticle photoanodes have a high surface area for the attachment of the sensitizing dye molecules, inherently limited light absorption and high light transmission may limit the number of photogenerated electrons thereby reducing the photocurrent density and the efficiency. Therefore, in order to increase the efficiency of DSSCs, one possible approach is to develop TiO_2 structures that possess favorable characteristics such as enhanced light harvesting by scattering, faster electron transport rate, high porosity and larger surface area compared to widely used TiO_2 nanoparticles. Several groups have reported enhancement of efficiency in DSSCs from improved alternate TIO_2 nano structures[7,8]. Nanofibre based electrodes [9], nanowire based composite electrodes [10,11], nanorods-nanoparticle based composite electrodes [12], rice grain shaped nano beads from nanofibres [13], nanofibre-nanoparticle composite electrodes [14], nanoparticle-nanowire composite electrodes [15], TiO_2 nanowires [16] and highly ordered TiO_2 nanotube arrays [17] are some of these attempts which have shown positive efficiency enhancement by modification of the TiO_2 electrode nanostructure. However, the attachment of dye molecules to most of these nanostructures has found to be somewhat lower than that of the TiO_2 nanopowder based electrode widely used in DSSC research. Another problem to be overcome in designing novel TiO_2 electrodes is the poor harvesting of light with wavelengths greater than 600 nm due to the high transmission of incident light through the widely used nanoporous, single layer TiO_2 photoanode. TiO_2 nanofibre membrane is one of the available nanosize structures having a great potential to be used in the fabrication of DSSC photoanodes. Recently, the electrospinning method has been used successfully for the fabrication of TiO_2 nanofibers to be used in DSSCs because of the possibility of controlling the nanofibre diameter and their shape and also the thickness of nanofibre membranes [18].

In the present study an innovative type of composite photoanode structure consisting of an electrospun TiO_2 nanofibre layer sandwiched between two TiO_2 nanoparticle layers has been fabricated and used successfully to enhance the efficiency of DSSCs by improved light harvesting. The increase in light harvesting appears to be due to scattering of light by the "elongated bead like" nanostructure, resulting from the optimized TiO_2 nanofiber network within the composite photoanode. As a result of this study, it has been found that, under the same preparation conditions and the same TiO_2 photoanode thickness, DSSCs made from TiO_2 nanopartice/nanofiber/nanoparticle three layer composite photoanode exhibits significantly improved cell efficiencies by as much as 32 % higher, compared to DSSCs with photoanodes made from TiO_2 nanoparticles alone. In addition we have also been successful in using the "mixed cation effect" in the electrolyte to further enhance the efficiency of DSSCs fabricated with the novel composite photoanode [19,20,21,22]. The overall improvement in efficiency by using both the novel TiO_2 nanopartice/nanofiber/nanoparticle three layer composite photoanode along with the electrolyte solution containing mixed cation iodide salts is found to be an impressive 64% compared to a corresponding DSSC made with conventional TiO_2 nanoparticle photoanode and an electrolyte with a single iodide salt.

2.. Experimental

2.1 Preparation of the TiO_2 nanoparticle/nanofibre/nanoparticle composite photoanode

A TiO_2 film of thickness about 3.0 µm was prepared by spreading commercial (Solaronix D) titania paste on a pre-cleaned FTO glass plate (2.0 cm x 2.0 cm) using the doctor blade technique and sintered at 250 ^oC for 30 min to obtain a thin, porous TiO_2 layer prior to depositing the TiO_2 nanofibre layer by electrospinning. A mixture containing 1.5 g poly(vinylacetate) (PVA), 3 g titanium(IV) isopropoxide (TiP) and 1.2 g of acetic acid as a catalyst for sol-gel reaction in 19 ml of N,N-dimethylformamide (DMF) was subjected to magnetic stirring for 4 h prior to electrospinning. This mixture was used to electrospun TiO_2 nanofibres on to the first TiO_2 nanoparticle layer using a NaBond electrospinner (NaBond Technologies, Hong Kong). For electrospinning, a 15 kV DC voltage was applied between the spinneret and the drum collector. The syringe tip to drum collector distance was fixed at 6.5

cm. Several grounded conducting glass substrates, were electrically grounded and attached to the drum collector. The flow rate of the polymer solution was adjusted to 2 ml/h by using a syringe pump. The electrospun TiO_2 nanofibre membrane was deposited directly on to the first TiO_2 nanoparticle layer while the drum collector was rotating at a speed of 270 rpm. The thickness of the nanofiber membrane was varied by varying the duration of electrospinning as 10 min, 15 min, 20 min, 25 min and 30 min. The thickness of the electrospun TiO_2 nanofibre layer optimized for the highest DSSC efficiency corresponds to an electrospinning time of 20 min and a thickness of about 1.5 μm. The electrospun TiO_2 nanofibre membranes were kept in air for about 1 h prior to sintering in order to remove the solvent residues. The sintering was carried out in air stepwise at each temperature as: 100 ^{o}C (15 min), 150 ^{O}C (15 min), 325 ^{o}C (5 min) and 450 ^{o}C (1h). Subsequently, another commercial (Solaronix D) titania paste was coated on the electrospun TiO_2 nanofibre membrane by the doctor blade technique to a thickness of about 1.5 μm and the composite TiO_2 photoanode structure was sintered in air at 450 ^{o}C for 45 min. The resulting TiO_2 nanoparticle/TiO_2 nanofibre/TiO_2 nanoparticle composite photoanode (abbreviated as TiO_2 NP/NF/NP photoanode) with an estimated total thickness of 6.0 μm was used to fabricate the DSSCs. DSSCs were also made by using a normal TiO_2 nanoparticle (NP) photoanode of thickness 6.0 μm for comparison purpose. FTO glass substrates with TiO_2 NF layer coated on TiO_2 NP layer were separately prepared and sintered to be used for the SEM imaging.

From our previous experience and measurements on doctor bladed TiO_2 layers taken using a profiliometer and also the SEM images taken for the present study, the thickness of the first TiO_2 nanoparticle layer made from Solaronix TiO_2 and doctor bladed on FTO glass substrate can be estimated to be about 3.0 μm. From the SEM images of the cross-section the thickness of the electrospun TiO_2 nanofibre layer (20 mts electrospinning time) after sintering can be estimated to be about 1.5 μm. From the SEM images, the thickness of the final TiO_2 nanoparticle layer made from Solaronix paste and gently doctor bladed on sintered TiO_2 nanofibre layer can be estimated to be about 1.5 μm. Therefore, the combined total thickness of the TiO_2 NP/NF/NP three layer photoanode could be about 6.0 μm. This was used to compare the efficiencies of DSSCs fabricated with the novel three layer composite photoanode and the conventional TiO_2 nanoparticle photoanode with similar thickness.

2.2 Preparation of the electrolyte

For the preparation of the electrolyte samples the starting chemicals with purity > 98% (Fluka) were used. For testing the TiO_2 NP/NF/NP composite photoanode in a DSSC made with a single iodide salt containing electrolyte, an electrolyte solution was prepared by dissolving tetrapropylammoniummiodide(Pr_4NI), iodine and ethylene carbonate in acetonitrile. For testing a similar DSSC made with a mixed cation electrolyte, potassium iodide (KI) and tetrapropylammonium iodide (Pr_4NI) were used as the two iodide salts in the electrolyte solution. KI was selected as the iodide salt with a smaller size cation(ionic radius of K^+ is 0.152 nm) and Pr_4NI with chemical formula $C_{12}H_{28}IN$ was used as the iodide salt with a bulky cation (Pr_4N^+). Pr_4NI is a hygroscopic, quaternary ammonium iodide salt with a cationic radius of 0.460 nm. Ethylene carbonate (EC; MW 88.06 g / mol, dielectric constant (ε) 89.6) was used as the plasticizer as well as the solvent. A series of electrolyte solutions were prepared by keeping the amount of EC (3.6 ml, volume measured after melting at 38 ^oC) and acetonitrile (1.0 ml) unchanged and varying the relative amounts of $Pr_4N^+I^-$ and KI according to Table 1 by keeping the total weight of the two salts at 0.738 g. The amount of iodine added was fixed at 0.1 times the total number of moles of salts ($Pr_4N^+I^-$ + KI) in the electrolyte. Initially, the appropriate weights of EC, acetonitrile and the salts (KI, Pr_4NI) were mixed in a closed glass bottle by continuous stirring for about 3 h. Subsequently, iodine was added to the mixture and the stirring was continued for about 24 h until a homogeneous solution was obtained. The compositions of the electrolytes containing the mixed cation iodide salts are shown in Table 1.

Table 1 Here…..

2.3 Cell assembly

The TiO_2 NP photoanode and the TiO_2NP/NF/NP three layer, composite photoanode were both sensitized separately by soaking each of them in 3 ml of ethanolic solutions of N719 Ruthenium dye
[2-(4-carboxypyridin-2-yl)pyridine-4-carboxylate;ruthenium(2+);tetrabutylazanium;
diisothiocyanate] of 0.3 mM initial concentration at room temperature. After soaking for 48 h the electrodes were removed from the dye solutions and the remaining dye solutions were diluted by adding 15 ml of absolute ethanol. The optical absorbance of the dye solutions was measured by using the double beam UV-Visible spectrometer (Shimadzu UV 2450). For

performance comparison, optical absorbance measurements were obtained for a reference dye solution. Several sets of DSSCs were assembled by sandwiching the electrolyte solution in between the Glass/FTO/TiO_2 composite photoanode and the platinized (Pt) FTO glass counter electrode for different thicknesses TiO_2 NF layer. A similar DSSC was fabricated usingb the same electrolyte solution and normal TiO_2 NP photoanode of thickness 6.0 μm.

2.4 Characterization

The morphology of the electrospun TiO_2 nanofiber membranes were observed by the Scanning Electron Microscope (SEM Zeiss Model EVO LS15). Photovoltaic characteristics of the DSSCs were measured by using a solar simulator which was coupled to a Keithly 2000 multimeter with Potentiostat/galvanostat HA-301 under the illumination of 1000 Wm^{-2} using a Xenon 500 lamp with an AM 1.5 filter. The incident light intensities were calibrated using a standard Si photodiode.

3.. Results and Discussion

3.1 Morphology of Electrospun TiO_2 membranes

Figure 1 shows a schematic diagram of the TiO_2 nanoparticle/nanofibre/nanoparticle composite electrode.

Fig. 1 here….

Figure 2 (a) shows a SEM image of a cross sectional view of the TiO_2 NP/NF/NP three layer composite photoanode, before sintering. The upper and lower parts show the TiO_2 NP layers while the middle part shows the TiO_2 nanofibre layer. Figure 2(b) shows a SEM image of TiO_2 nanofibre layer electrospun on the pre-TiO_2 nanoparticle layer coated on FTO plate after sintering**.**

Fig. 2(a) Here……

Fig. 2(b) Here……

From Figure 2 (b) it can be clearly seen that the electrospun TiO_2 nanofibres during the process of sintering and thermal removal of the polymer (PVA), have changed into a series of elongated and poorly interconnected beads of diameter around 50 nm and length around 200-400 nm, randomly distributed, providing a more open network structure compared to a film with only TiO_2 nanoparticles.

3.2 UV-Visible spectroscopy

A comparison of the UV-Visible absorption spectra of the original dye solution and the two dye solutions remaining after dye loading of the TiO_2 composite NP/NF/NP photoanode (20 min electrospun NFs) and the normal TiO_2 NP photoanode, both having the same total thickness of 6.0 μm, are shown in Figure 3. It can be inferred from the absorption spectra that the dye solution remaining after dye loading of the TiO_2 NP electrode contains a relatively lower concentration of the dye compared to the dye solution remaining after dye loading of the TiO_2 NP/NF/NP composite electrode. This result confirms that the dye loading of the composite electrode is slightly lower than that of the conventional TiO_2 NP electrode suggesting that the increase in J_{sc} of the DSSCs with composite photoanode is quite unlikely to be due to the effect of the adsorbed dye.

This can be due to the reduction of the effective surface area of TiO_2 "elongated beads" of larger size (diameter 50 nm and length 200-400 nm) in the composite photoanode, compared to the spehrical TiO_2nano particles (commercial Degussa P25, size 25 nm) in the NP photoanode. Similar results with regard to slightly reduced dye uptake has been reported by Joshi et al [14] and by Tan et al [15] for their DSSCs with TiO_2 nanofiber–nanoparticle composite photoanodes. As we have discussed in subsequent sections, the small reduction in dye loading in the composite TiO_2 electrode has been more than compensated for by the scattering induced increase in light harvesting by the elongated bead structure.

Fig. 3 Here…..

3.3 Photovoltaic performance

The short-circuit photocurrent density (J_{SC}), the open-circuit voltage (V_{OC}), the fill factor (*FF*) and the energy conversion efficiency (η) of five different solar cells fabricated with TiO_2 nanofibre membrane of five different thicknesses (different electrospun times) along with corresponding parameters for the solar cell with normal TiO_2 nanoparticle photoanode of thickness 6.0 μm (corresponding to zero electrospinning time) are shown in Table 2. These solar cells were fabricated with a electrolyte solution consisting of 0.738 g of tetrapropyl ammonium iodide, 0.06 g of iodine, 3.6 ml of ethylene carbonate (heated to melt) and 1.0 ml of acetonitrile.

Figure 4 shows the photocurrent-voltage curves correspond to the six DSSCs shown in Table 2

Fig. 4 Here…..

It can be seen from Table 2 that all six DSSCs using tetrapropyl ammonium iodide based electrolyte solution, show energy conversion efficiencies of more than 5%. The photocurrent density J_{sc}, gradually increases and exhibits maxima for 20 and 25 min electrospun films. The open circuit photovoltage V_{OC}, exhibits lower values at these film thicknesses. Both these trends agree well with the mechanisms expected from "mixed cation effect" described in section 3.5.

Table 2 Here…..

According to Table 2, the maximum efficiency (η) of 7.09% with J_{SC} of 15.75 mA cm^{-2}, V_{OC} of 714.6 mV and *FF* of 63.0% was obtained for the cell with composite TiO_2 NP/NF/NP electrode fabricated using TiO_2 NF film with 1.5 μm thickness (20 minute electrospinning time). The next higher efficiency of 6.96% with highest J_{sc} of 16.14 mA cm^{-2}, V_{oc} of 712.3 mV and *FF* of 60.5% was obtained for the cell with composite TiO_2 electrode fabricated with electrospinning time of 25 minutes. The major contribution to the efficiency enhancement in these two DSSCs appears to come from the improved J_{sc}. The small difference in efficiency between these two best cells evidently comes from the difference in their fill factors. In comparison, the DSSC made with TiO_2 nanoparticles alone (NP layer thickness 6.0 μm, electrospinning time "0" in Table 2) had a J_{sc} of 11.24 mA cm^{-2}, V_{oc} of 710.6 mV and an efficiency of 5.38%.

Table 2 Here…..

The reduction in the J_{sc} and efficiency of DSSCs with TiO_2 NP/NF/NP composite electrode having thicker TiO_2 nanofibre membranes (electrospinning times 30 min) could possibly be due to the lower light harvesting by scattering effect by more densely distributed nanofibre beads. More densely distributed bead structure can have a blocking effect on scattered light masking a significant number of scattering centres, thereby limiting the number of photogenerated electrons.

3.4 Enhanced light harvesting by scattering

The presence of the TiO_2 elongated "bead like" network structure formed from the TiO_2 nanofibre layer after sintering affects the specific surface area, porosity, light scattering and electron transport rate in the TiO_2 composite photoanode. As already explained, the increased J_{sc} in the cells with composite electrode is very unlikely to come from the effect of dye adsorption. Increased electron transport also can be ruled out as the nanofibre structure, after sintering has lost most of the interconnected network structure as seen from the SEM picture (Fig. 2(b)). The resulting beads have diameters of about 50 nm and lengths about 200 – 400 nm and are randomly distributed. They can scatter the incident light effectively resulting a substantial increase in light absorption by TiO_2 particles in the two adjacent TiO_2 NP layers. Therefore, the enhanced J_{sc} values are quite likely due to the improved light harvesting by multiple scattering events by the TiO_2 elongated bead structure in the composite anode. According to Zhu et al, the "rice grain" shaped TiO_2 nanostructure obtained in their work is somewhat similar to what we have obtained in our work as "elongated bead shaped" nanostructure[13]. These authors also suggest that the efficiency enhancement in their DSSCs made with "rice grain shaped" TiO_2 nanobeads is due to improved light harvesting by scattering. Similar improvement in light harvesting by scattering by a composite TiO_2 electrode consisting of a mixture of nanofibres and nanoparticles has been discussed in detail by P. Joshi et al [14].

The novel feature in our composite photoanode, compared to the TiO_2 nanofibre based photoanodes reported by Zhu et al [13], Joshi et al [14] and Tan et al [15] is that our TiO_2 NP/NF/NP three layer sandwiched structure enables more efficient light trapping due to positioning of the two NP layers on either side of the scattering layer. To the best of our knowledge this is a novel three layer design for the TiO_2 photoanode not reported by any other group so far. The advantage of this type of sandwich structure is that the light entering the photoanode can be utilized most effectively due to the multiple scattering effects by the elongated TiO_2 beads as shown schematically in Figure 5.

The action of the three layer TiO_2 photoanode reported here can be explained based on the Figure 5 as follows. Light rays incident on the first NP layer after going through the FTO glass plate go through the first NP layer while partly undergoing absorption by dye molecules attached to TiO_2 particles. After entering the middle TiO_2 NF layer, most of the light undergoes multiple scattering events by “elongated TiO_2 beads” making more light photons to enter the two adjacent TiO_2 layers where they contribute to the generation of photoelectrons. Remaining light goes through the second NP layer and partly get absorbed by the dye molecules and partly incident on the Pt film. Light rays then get reflected back from the Pt film, and again goes through the TiO_2 particle layer and enters the middle NF layer to contribute to scattering events. Thus, the middle layer with elongated TiO_2 beads makes an impressive contribution through scattering for the efficient generation of photoelectrons by the sensitized dye molecules in the two NP layers..

Figure 5 Here….(Figure with light rays)

Figure 6 shows the variation of photocurrent density and efficiency of DSSCs as a function of electrospinning time (assumed to be proportional to the thickness of the electrospun TiO_2 NF layer). For these measurements, the electrolyte solution with tetrapropyl ammonium iodide was used. It is clear from this figure that the variation of both, the photocurrent density and the efficiency with the thickness of the TiO_2 nanofibre membrane essentially follows the same trend, suggesting that the enhancement of photocurrent density, J_{sc} is largely responsible for the enhancement of efficiency in these solar cells. The J_{sc}, to a large extent is determined by the amount of light absorbed by the dye coated, composite photoanode structure.

Fig. 6 Here…..

3.5.. Mixed cation effect

The enhancement of efficiency in DSSCs with normal TiO_2 nanoparticle photoanodes due to the “mixed cation effect” of using two iodide salts with dissimilar cations is now rather well established [19,20,21,22,23,24]. In order to study whether the mixed cation effect would enhance the photocurrent and the efficiency in DSSCs made with TiO_2 NP/NF/NP three layer, composite photoanode also, six different electrolyte samples were prepared using KI and Pr_4NI as the two iodide salts according to the compositions given in Table 1 and six different DSSCs, A, B, C, D, E and F were fabricated using the composite TiO_2 NP/NF/NP photoanode having optimized TiO_2 nanofibre layer thickness (1.5 μm and 20 minutes electrospinning time). The current-voltage characteristic curves of the six DSSCs obtained under the irradiation of 1000 Wm^{-2} are shown in Figure 7. The short-circuit photocurrent density (J_{SC}), open-circuit voltage (V_{OC}), the fill factor (*FF*) and the energy conversion efficiency (η) of these cells are shown in Table 3.

Fig. 7 Here…..

It can be noted that all six DSSCs fabricated with TiO_2 NP/NF/NP composite photoelectrode exhibit energy conversion efficiencies higher than 7% and the highest energy conversion efficiency of 8.8% is shown by the cell that containing the electrolyte sample D which consists of the iodide salt mixture with 60.0 wt% of KI and 40.0 wt% of $Pr_4N^+I^-$. The J_{SC}, V_{OC}, and FF of this solar cell are 24.22 mA cm^{-2}, 624.2 mV and 58.21% respectively. The two electrolytes with 100% $Pr_4N^+I^-$ and 0% KI (sample A) and 100% KI and 0% Pr_4N^+ I^- (sample F) which correspond to the two end members of the composition series have shown the lowest efficiencies of 7.09% and 7.69% respectively.

Table 3 Here…….

As shown in Figure 8 the efficiency and the J_{SC} as a function of KI% (w/w) follow a similar trend, exhibiting initially an increase with increasing KI wt% (or molar iodide ion concentration) and reach the maximum at 60.0 wt% KI, followed by a steep decrease. This correlation between η and J_{SC} is interesting as it clearly shows that the efficiency in these solar cells is governed predominantly by the short circuit photocurrent density, J_{sc}. A similar variation has been reported by us and other groups for DSSCs containing other mixed cation electrolytes and with normal TiO_2 nanoparticle based photoelectrodes [19,20,21,22,23,24].

Fig. 8 Here…..

It can be clearly noticed that due to the presence of the mixed cation iodide salts, the solar cell efficiency has been enhanced by a factor of about 14% compared to the higher efficiency end member and by about 24% compared to the lower efficiency end member. The cations in the electrolyte/semiconductor interface can show a negative or positive influence on the DSSC parameters such as V_{OC}, J_{SC}, η and *FF* depending on their nature, type and size [25,26,27,28,29]. Creation of deeper electron-trapping states and a positive shift of the flat band potential of the semiconductor have to be considered in order to understand the effects of the cations on the electron transport process through TiO_2 to the current collector. Cation adsorption shifts the acceptor states in TiO_2 to more positive potentials resulting in favourable energetic for interfacial charge injection from dye to TiO_2. Small-radius cations can deeply penetrate into the mesoporous dye-coated nanocrystalline TiO_2 film. A detailed discussion of the cation adsorption in TiO_2 anode and the effect of a binary iodide salt mixture with two dissimilar cations in enhancing the efficiency of DSSCs can be found in several papers [19,20,21,22]. We expect the effect of cation adsorption by the TiO_2 NP/NF/NP composite photoanode structure also to be similar to the case of normal TiO_2 photoanode.

3.6 Influence on V_{OC}

Due to the cation adsorption, the conduction band edge move to the positive side (downward shift) independent of the cation charge density. The movement is higher for the small size cations like K^+ as compared to the bulky cations like Pr_4N^+ as the number of adsorbed small sized cations per unit area of nano titania grain surface would be much greater.

The open circuit voltage (V_{OC}) of the DSSCs is determined by the relative positions of the flat band potential and the redox potential of the electrolyte. Therefore, adsorption of the cations on the surface of the TiO_2 composite photoanode structure results in a drop in V_{OC} of the solar cell and the amount of the decrease in V_{OC} depends on the type, size and the number of cations. As the ionic radius of the K^+ ion and Pr_4N^+ ion are 0.138 nm and 0.460 nm respectively, more K^+ ions can get adsorbed per unit area of TiO_2 and the resulting drop in V_{OC} would be greater compared to the adsorption of bulky Pr_4N^+ ions. Therefore, one would expect a gradual decrease in V_{OC} as the relative concentration of KI in the electrolyte increases from 0 wt% KI (samples A) to 100 wt% KI (sample F). This expected voltage drop can clearly be seen in Table 3 and Figure 8 confirming that the variation of the V_{OC} is determined essentially by the relative concentration of the small radius cation (K^+) in the electrolyte.

Fig. 9 Here…..

3.7 Influence of J_{SC} on efficiency

Although V_{OC} deceases with the positive shifting of TiO_2 conduction band edge, the increased height of the downward potential hill will increase the driving force for electron injection leading to a higher J_{SC}. Some research groups have studied the influence of cation charge density on the photovoltaic performance of DSSCs by using Li^+, Na^+, K^+ and dimethyeimidazolium (DMI^+) ions [27,28,29]. These results show that, from DMI^+ to Li^+ the short circuit current density (J_{SC}) increases due to the increase in electron injection rates with increase in cation charge density. This is consistent with the results obtained for the two end members in our study where the J_{SC} values are 15.75 mA cm^{-2} for the 100 wt% Pr_4NI system and 20.47 mA cm^{-2} for the 100 wt% KI system.

The variation of J_{SC} with adsorbed cation concentration is also related to the rate of dye regeneration. A faster dye regeneration reaction is also very important for the reduction of back electron transfer [27]. According to some reports the reduction rate of the oxidized state of the dye strongly depends upon the nature of the cation and for instance the total recovery time for the oxidized dye is high, in the presence of bulky cation [26]. Also, the intercalation of the cations to the trapping sites of TiO_2 network results a lowering of the conduction band edge of the TiO_2 and enhance the electron transfer dynamics at the semiconductor/dye interface as well in addition to the increase in the electron diffusion rate through the TiO_2 and hence the higher J_{SC}. This effect is seen to be higher for small radius cations compared to bulky cations. In addition, the cations in the electrolyte can efficiently screen the photo-injected electrons on the TiO_2 film, ensuring that electro-neutrality is maintained throughout the TiO_2 network.

The combined effect of the positive influences described above and exhibited by the presence of two dissimilar cations evidently enhances the overall performance of DSSCs made with a mixed cation iodide mixture in the electrolyte. This mixed cation effect, already demonstrated in several DSSC systems with TiO_2 nanoparticle photoanode, appears to work equally well for the present DSSC system fabricated with the TiO_2 NP/NF/NP composite photoanode.

Conclusions

In this work we have fabricated and tested an innovative type of composite photoanode for dye sensitized solar cells. It consists of a TiO_2 nanofibre layer sandwiched between two TiO_2 nanoparticle layers. After sintering the nanofibres in the layer have turned to an elongated bead type nanostructure. DSSCs fabricated with the TiO_2 NP/NF/NP composite photoanode of total thickness 6.0 μm and sensitized with Ru N 719 dye and a electrolyte solution consisting of tetrapropylammonium iodide and iodine dissolved in acetontrile and EC showed the highest efficiency of 7.09% where as the DSSC with TiO_2 particle photoanode of thickness 6.0 μm and the same electrolyte showed an efficiency of 5.38%. The increased efficiency has been attributed to enhanced light harvesting due to scattering within the TiO_2 nanofibre structure. The efficiency of the highest efficiency DSSC has been further enhanced by using the "mixed cation effect" where the single iodide salt, Pr_4NI, in the electrolyte has been replaced by two iodide salts KI and Pr_4NI resulting an efficiency of 8.80%. This represents an overall efficiency enhancement of 64% compared to a corresponding DSSC made with conventional TiO_2 nanoparticle photoanode and an electrolyte with the single iodide salt, Pr_4NI.

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Figure Captions

Fig.1: Schematic diagram of the TiO_2 nanoparticle/nanofibre/nanoparticle composite photoanode.

Fig.2(a): SEM image of the cross sectional view of the TiO_2 NP/NF/NP three layer composite photoanode, before sintering. From the top: FTO glass plate (dark band); thin SnO_2 layer; commercial TiO_2 nanoparticle layer (about 3.0 μm thick); Electrospun TiO_2 nanofibre layer (about 1.5 μm thick); commercial TiO_2 nanoparticle layer (about 1.5 μm thick).

Fig. 2(b): SEM image of TiO_2 nanofibre layer electrospun on the pre-TiO_2 nanoparticle layer coated on FTO plate after sintering**.** The small "elongated bead like" structure with nano size beads of diameter around 50 nm and length about 200-400 nm formed after sintering of the TiO_2 nanofibre can clearly be seen in this SEM image.

Fig. 3: UV-Visible absorbance by original dye solution, remaining dye solution after dye absorption by TiO_2 nanoparticle electrode and remaining dye solution after dye absorption by TiO_2 NP/NF/NP composite photoanode made with TiO_2 nanofibre layer of 20 minute electro deposition time.

Fig. 4: Photocurrent-voltage curves for DSSCs fabricated with TiO_2 NP/NF/NP composite photoanodes with different thicknesses of TiO_2 nanofibre membranes. The electrolyte solution used was made of tetrapropyl ammonium iodide, iodine and ethylene carbonate dissolved in acetonitrile.

Fig. 5 Schematic diagram of the TiO_2 NP/NF/NP three layer photoanode showing the effect of scattering of ligh. (1) light rays incident on the first NP layer after going through the FTO glass plate, (2) light rays going through the first NP layer while partly undergoing absorption by dye molecules attached to TiO_2 particles, (3) and (4) light transmitted and scattered by "elongated TiO_2 beads" while traversing through the middle TiO_2 NF layer, (5) direct light entering the second NP layer, (6) direct light incident on the Pt film and (7) light rays reflected back from the Pt film, and (8) scattered light from NF layer, entering the second NP layer. Multiple scattering events in the middle NF layer make many light photons to be directed to the two adjacent TiO_2 NP layers for efficient generation of photoelectrons by the sensitized dye molecules.

Fig. 6: Variation of photocurrent density and efficiency of DSSCs fabricated as a function of electrospinning time used to deposit TiO_2 nanofibres for the composite photoanode.

Fig. 7: Photocurrent density vs cell voltage for the six different DSSCs (with optimized TiO_2 NP/NF/NP composite electrode) fabricated using EC (heated)/acetonitrile/ (KI: $Pr_4N^+I^-$) electrolytes under irradiation of 1000 W m^{-2} light. The DSSCs are labelled using the salt percentage in the electrolyte as given in Table 3.

Fig. 8: The variation of efficiency and photo current density as a function of KI % (w/w) for DSSCs fabricated with six different electrolytes (shown in Table 6) and optimized TiO_2NP/NF/NP composite electrode.

Fig. 9: Variation of V_{OC} as a function of KI % (w/w) for the DSSCs for the series of electrolyte solutions shown in Table 3.

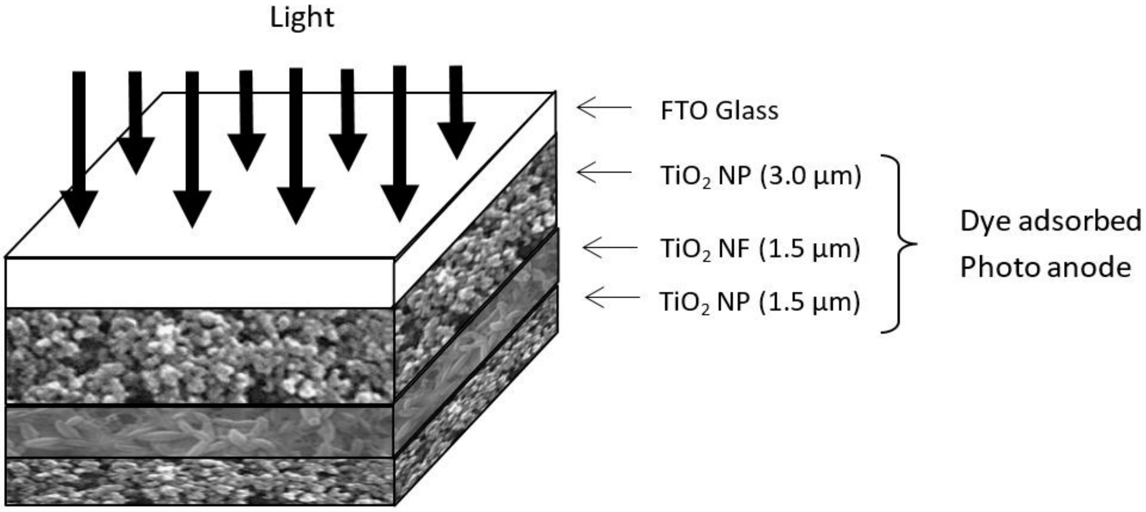

Light
FTO Glass
TiO_2 NP (3.0 µm)
TiO_2 NF (1.5 µm)
TiO_2 NP (1.5 µm)
Dye adsorbed
Photo anode

Fig. 1: (above)

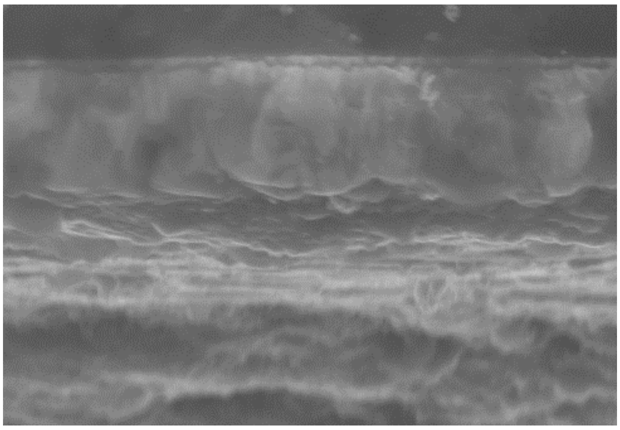


Fig. 2(a): (above)

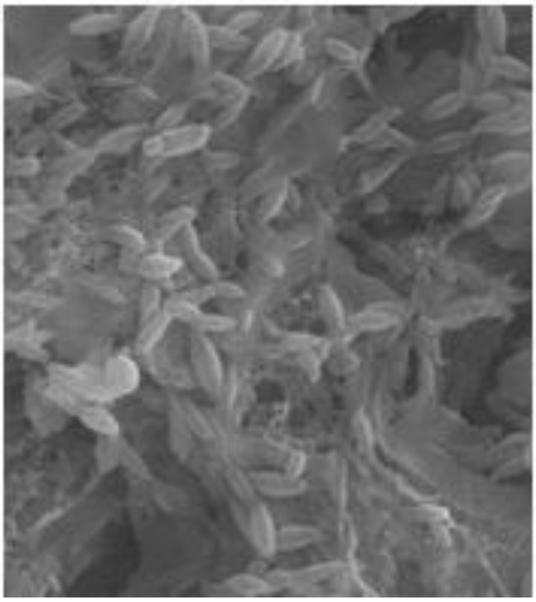


Fig: 2(b): (above)

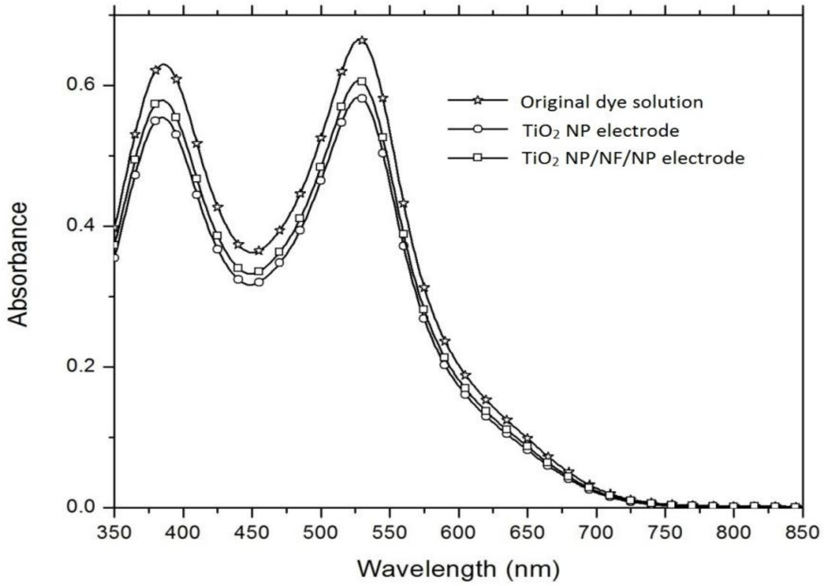

Absorbance
0.0
0.2
0.4
0.6
Wavelength (nm)
350
400
450
500
550
600
650
700
750
800
850
Original dye solution
TiO₂ NP electrode
TiO₂ NP/NF/NP electrode

Fig.3: (above)

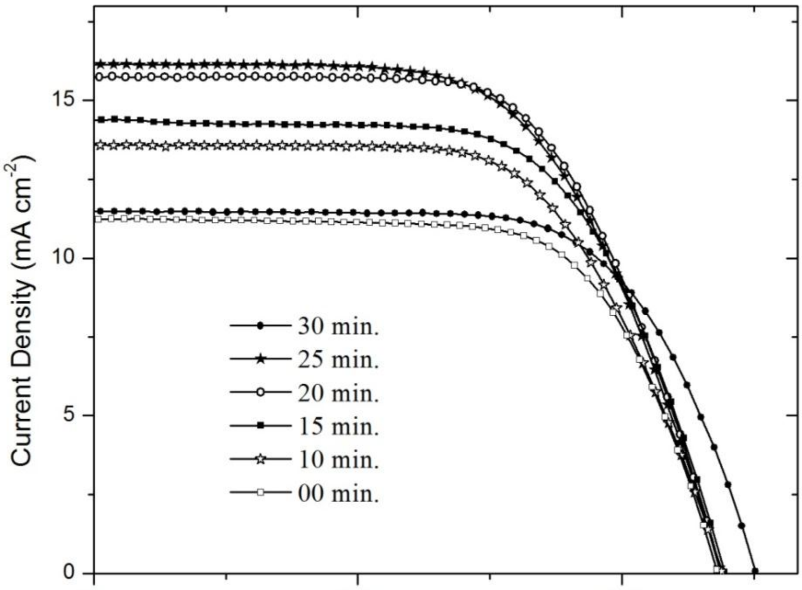

Current Density (mA cm^{-2})
0
5
10
15
Voltage (mV)
0
300
600
30 min.
25 min.
20 min.
15 min.
10 min.
00 min.

Fig. 4: (above)

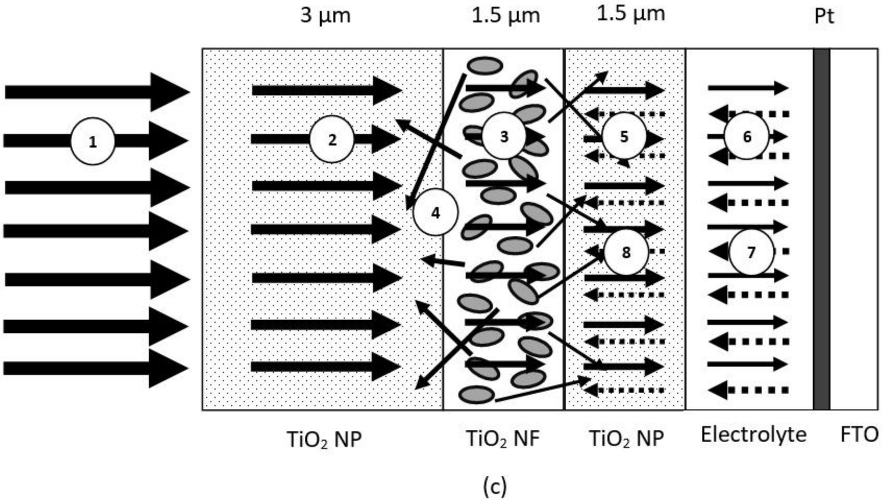
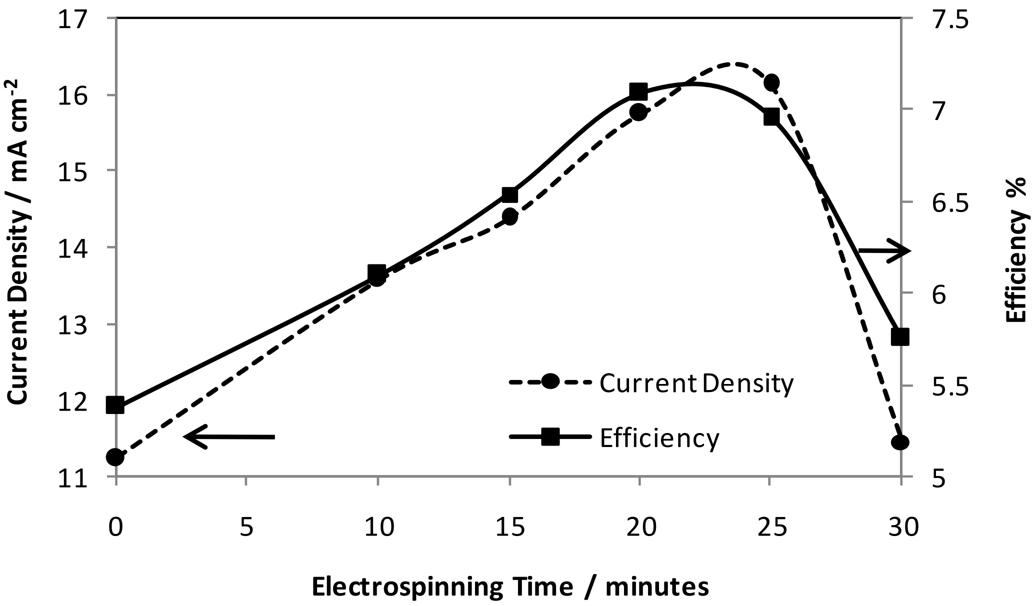


Fig. 5 (above)



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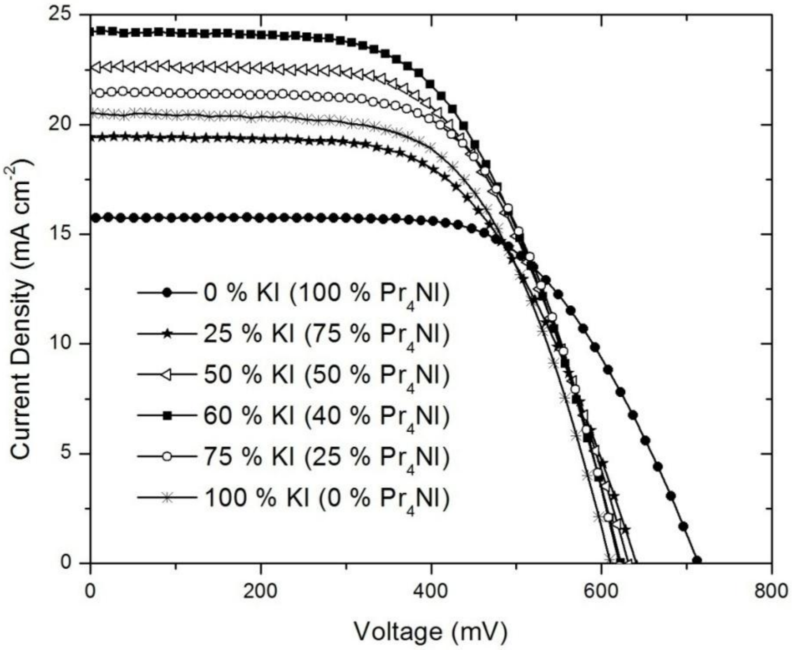

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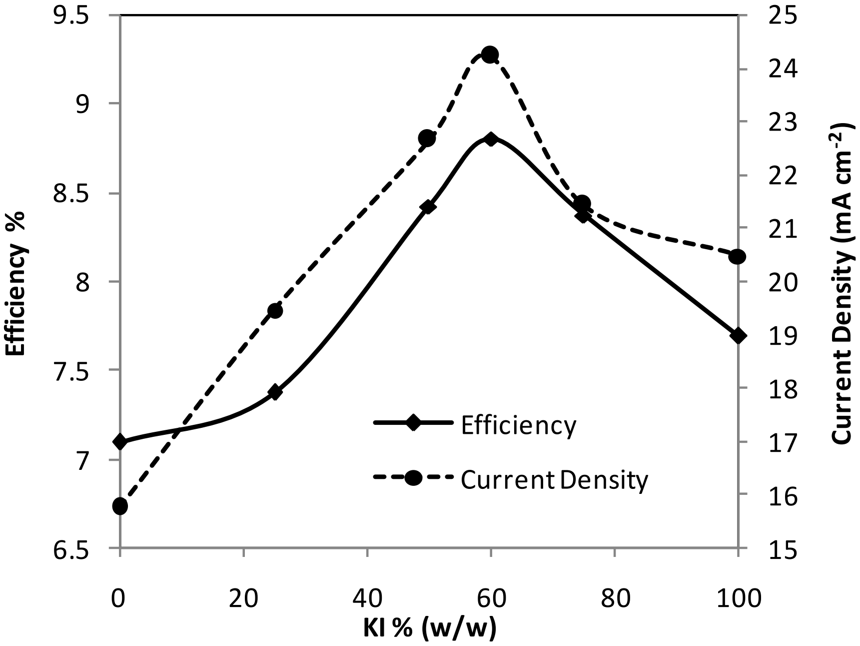

Fig.8: (above)

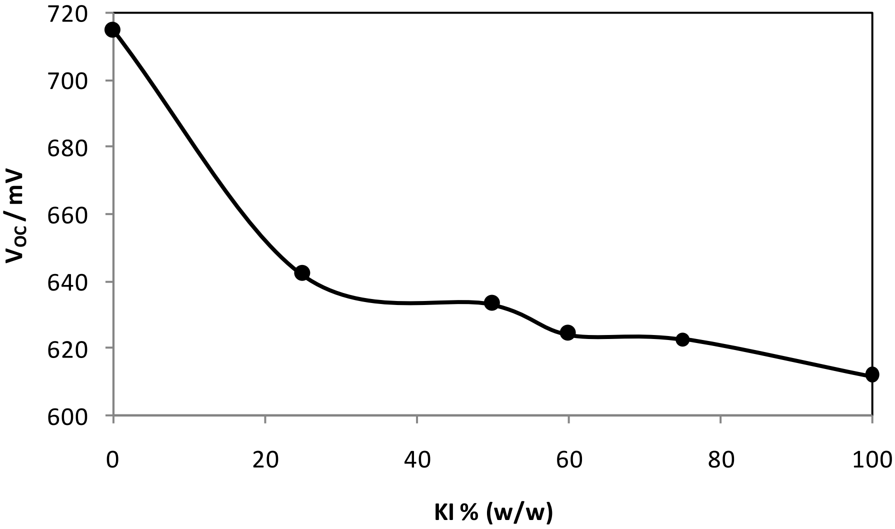

Fig.9: (above)

Table 1. Electrolyte solution compositions, where the amounts of EC and acetonitrile were kept unchanged at 3.6 ml and 1.0 ml respectively and the amounts of KI and Pr4$_4$N$^+$I$^-$ were varied by keeping the total weight as 0.738 g. The relative weight ratios of the two iodide salts (*x* %) are also shown.

Electrolyte		A	B	C	D	E	F
KI/ g		0.0000	0.1845	0.3690	0.4428	0.5535	0.7380
Pr$_4$N$^+$I$^-$ / g		0.7380	0.5535	0.3690	0.2952	0.1845	0.00
I$_2$ / g		0.0600	0.0682	0.0700	0.0783	0.0913	0.1128
Salt % (w/w)	KI	0	25.0	50.0	60.0	75.0	100.0
	Pr$_4$N$^+$I$^-$	100.0	75.0	50.0	40.0	25.0	0.0

Table 2: Photovoltaic parameters of the Ru 719 dye based DSSCs with different TiO_2 nanofibre layer thicknesses (different electrospinning times) while keeping the total composite electrode thickness as constant at ~6.0 μm. Time 0 min corresponds to the solar cell fabricated with normal TiO_2 nanoparticle photoanode with the same thickness. Electrolyte solution consists of 0.738 g of tetrapropyl ammonium iodide, 0.06 g of iodine, 3.6 ml of ethylene carbonate and 1.0 ml of acetonitrile.

Electrospinning Time (min.)	J_{SC} (mA cm^{-2})	V_{OC} (mV)	*FF* (%)	Eff (%)
00	11.24	710.6	67.3	5.38
10	13.58	715.5	62.6	6.10
15	14.38	718.7	63.2	6.54
20	**15.75**	**714.6**	**63.0**	**7.09**
25	**16.14**	**712.3**	**60.5**	**6.96**
30	11.45	753.5	66.4	5.75

Table 3. The performance of DSSCs prepared using electrolytes containing different KI and $Pr_4N^+ I^-$ compositions (given in Table 3) and the TiO_2 NP/NF/NP composite electrode.

Electrolyte	J_{SC} / mA cm^{-2}	V_{OC} / mV	*FF* / %	Efficiency / %
A	15.75	714.6	63.0	7.09
B	19.46	642.0	59.0	7.37
C	22.65	633.2	58.7	8.42
D	**24.22**	**624.2**	**58.2**	**8.80**
E	21.42	622.8	62.7	8.37
F	20.47	611.7	51.4	7.69