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Photoanode Engineering Using TiO_2 Nanofibers for Enhancing the Photovoltaic Parameters of Natural Dye Sensitised Solar Cells

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Dye Sensitized solar cell (DSSC) have been looked upon as having the potential to modernize photovoltaic as a cost effective technology. Especially nanostructured DSSC is proposed to have the capability to boost the efficiency by limiting charge recombination, thereby increasing the charge transportation which affects the overall conversion efficiency favourably. In the present work we discuss the effect of nanofibers as photo anode for increasing the efficiency of a dye sensitized solar cell. As we know nanostructured metal oxides have paying much attention in the field of photovoltaics due to their physical properties and dimensionality. This type of geometry provides direct and spatially separated charge transport channels for electrons and holes. TiO_2 single-crystalline nanofibers of different diameter are prepared by electrospinning process and TiO_2 nanoparticles by doctor blade technique are used for fabricating the device using natural sensitizers.

Keywords: DSSC, Natural sensitizers, Electrospinning, Nanofibers, Nanopowder.

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1. INTRODUCTION

Dye sensitized solar cell (DSSC) [1] is inspired by the energy and electron transfer mechanisms in natural photosynthesis. The major parts of a dye sensitized solar cell [3] are working electrode or photo anode, electrolyte and counter electrode. The sensitizer [4] is also plays an important role to harvest the photons and all the parts have relevance in the photovoltaic properties. Dye-sensitized solar cells [2] have attracted extensive academic and commercial interest during the last 20 years due to their potential for low cost solar energy conversion. When the light incident on the photo anode the dye molecules from the photo anode got excited from the HOMO layer to the LUMO layer. The counter electrode plays an important role of gathering electrons that are generated at the photo-anode [5] and delivered through the external circuit, back to the electrolyte. Since the electrolyte is corrosive the counter electrode requires a high reaction rate to reduce the iodine in the electrolyte to an iodide ion. The importance of counter electrode [6] to gather electrons that are generated at the photo-electrode is substantial. Over the past few years nanostructured TiO_2 materials have attracted particular attention as electrodes in dye sensitised solar cells [7] due to their promising physical properties [8]. Several techniques are developed by researchers for the synthesis of TiO_2 nano structures. Research on the creation of nanofibers has centred on the fabrication of the fibers using different techniques. They are thermal evaporation, template growth, self assembling, electrospinning and strong alkali treatment. Of the given techniques electrospinning has the advantages of flexibility, simplicity, ease of fabrication of fibres at laboratory level and controllability. Electrospinning is the only process in which we can effectively control the dimension of the fiber during the synthesis. So we can optimise the size of the fiber easily by this technique. Recently, one dimensional nanomaterial such as nanotubes, nanowires and nanofibers have been projected to swap the nanoparticles used in DSSCs, since 1D nanomaterials can recover the electron transport and hence increase the electron collection efficiency in the devices. [9-11].

2. EXPERIMENTAL

2.1 Electro Spinning Process of Nanofiber

Electrospinning unit contains a high voltage power supply, a stand to hold the syringe with very small diameter and a collector. In electrospinning process the nanofibres of metal oxides are produced from a liquid droplet of liquid polymeric solution under the influence of electrostatic forces. The droplet overcomes the surface tension force holding the droplet because of the increased electric force and allows the drop to falls on the conductive collector. The high voltage difference between the needle tip and the collector helps the droplet to be drawn in to a fiber in the form of a jet. The fiber diameter and morphology can be changed by controlling the electric field and injection rate. It also depends on the viscosity of the polymeric solution. In the present study we prepared one dimensional nanofibres with different diameter of TiO_2 by changing the flow rate of the polymeric solution and can be used as photoanode for the DSSC application. DSSCs with different fiber diameter were prepared to optimise the conversion efficiency. The different photovoltaic parameters of the device are measured by Keithely electrometer. The calcinated TiO_2 nanofiber on FTO substrate was then dipped into the solution of natural dye Lawsone purchased from Sigma Aldrich for 12 hour. FTO glass was also used as the substrate for the counter electrode. Iodine based electrolyte is used. The DSSC is assembled by clamping a dye-sensitized photoelectrode with a Pt-coated FTO counter electrode to form a sandwiched-type structure whose schematic diagram is shown in Fig. 1.

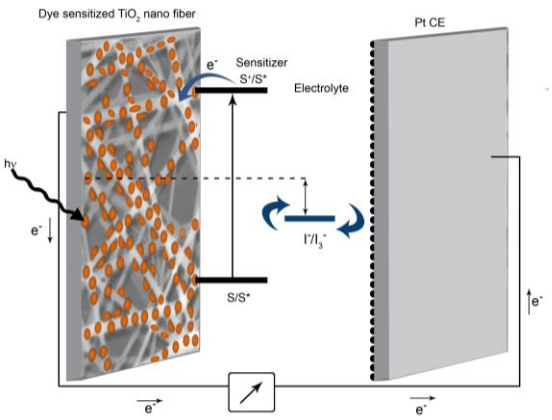

Fig. 1 – Structure of the fabricated device

2.2 Preparation of the Polymer Solution

2.5 g PVP (Poly Vinyl Pyrrolidone) is added in 50 ml ethanol (5 wt % ethanol solution of PVP) and is magnetic stirred well at room temperature. Then 27.5 ml ethanol, 27.5 ml acetic acid and 15.8 ml Titanium Tetra Isopropoxide is mixed with the 5 wt % ethanol solution of PVP. These two solutions are mixed well using magnetic stirrer.

2.3 Electro Spinning of TiO_2 Nanofiber

This solution is taken in a syringe tube of diameter 15.6 mm and placed in the electro spinning apparatus. Cleaned FTO glass plate which is masked by using scotch tape is fixed on the aluminium foil in the apparatus. Measure the distance between the needle tip and the glass plate. Set the values of duration and flow rate. By applying proper voltage, TiO_2 Nanofiber will start to form on the glass plate.

2.4 Preparation of the Counter Electrode

The counter electrode is prepared using the cleaned FTO glass plates which must match with the size of Titania electrode being prepared. The FTO glass plate is masked 1.5cm using the scotch tape. Counter electrode is made by developing a thin film of platinum over FTO glass substrate. In the process, platinum is grown over the FTO glass plate by spin coating method. The film is dried at 1500 °C for 60 minutes.

2.5 Preparation of Electrolyte

0.3 g of Poly Ethylene Glycol (PEG) is dissolved in 2.5 ml acetonitryl solution 0.46 g of KI and is stirred well. Another 2.5 ml acetonitryl solution is now added to. Now one pellet of iodine is added to this solution which can be used as the electrolyte.

3. RESULT AND DISCUSSION

The dye-sensitized solar cells (DSSC) provide a technically and economically credible alternative concept to present day *p-n* junction photovoltaic devices. In contrast to the conventional systems where the semiconductor assume both the task of light absorption and charge carrier transport the two functions are separated here. Light is absorbed by a sensitizer, which is anchored to the surface of a wide band semiconductor.

DSSCs comprise a sensitized semiconductor (photoelectrode) and a catalytic electrode (counter electrode) with an electrolyte sandwiched between them. Here we used electrospinning technique for coating TiO_2 nanofibers over the FTO glass plate.TiO_2 nanofiber act as a scaffold to hold large numbers of the dye molecules in a 3-D matrix. Counter electrode is prepared by coating platinum layer over the FTO glass plate by spin coating method. Also an iodine based electrolyte is prepared. For the study of the working electrode we have done different characterisation techniques such as SEM, XRD and J-V characteristics and the details of the results are explained below.

3.1 SEM Analysis of TiO_2 Nanofibers

The Scanning Electron Microscopy analysis is conducted for the study of morphology of the mesoporous anatase TiO_2 nanofibers. From the SEM images it is clear that the fibers being composed of small anatase nano crystals. The deposition of titanium nano fibers on the surface of the films are found in the SEM images. Obviously confirmed the presence of fibers increases a number of necking point in a very porous TiO_2 frame work. The density of the closely packed nanocrystals facilitate the electron-hole transport and and thus suppress the electron-hole recombination.

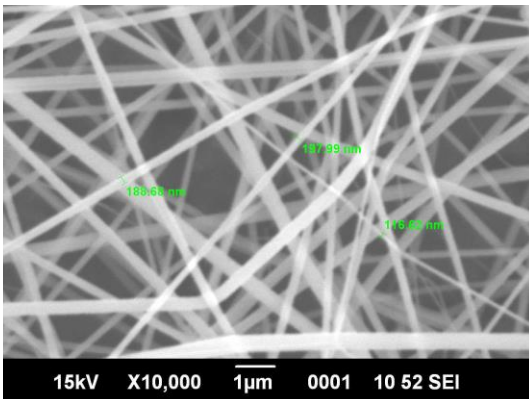

Fig. 2 – SEM images of titanium nano fibers with flow rate 0.5 ml/h

The SEM images give a clear picture about the polycrystalline structure of the TiO_2 nanofibers with crystalline size of the fiber diameter ranges from 106 to 166 nm before the calcinations. From the SEM images it is clear that the heat treatment does not affected the morphology of the fibers. Moreover the diameter of the fiber size decreases. The reason for this can be explained as the polymer and titanium isopropoxide will undergo decomposition under high temperature it may lead to decrease in fiber diameter. Another reason is that the titanium iso propoxide was uniformly distributed in the PVP matrix. So after the complete pyrolisis process of PVP the phase of TiO_2 was preserved better.

3.2 Current-Voltage Characteristics of the Fabricated Device

Photocurrent-voltage curves were measured using a Keithley Electrometer 2420. A solar simulator with

300 W Xe lamp with an AM 1.5 spectrum and an output power of 100 mW/cm² was used to illuminate the active area, 1 cm² of the photo electrode. Fig. 7 and Fig. 8 compares the photocurrent-voltage curve of DSSCs using the photo electrode by nanofibers of different diameter and nanoparticles sensitized by lawsone. Important physical parameters governing the efficiency of the DSSCs were determined from the photo- current-voltage curve, and the results are presented in Table 1.

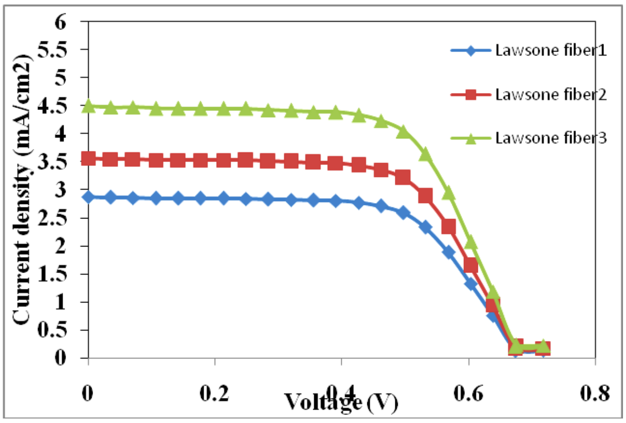

Fig. 3 – Current-voltage characteristics of fabricated device using TiO_2 nanofibers of different diameter

Fig. 3 gives the photovoltaic parameters of the fabricated device using nanofibers of different diameter as photoanodes. Nanofibers having small diameter gives better efficiency ie, for Lawsone fiber 3.

Table 2 – Photovoltaic parameters of the fabricated device using nanoibers

Sample	J_{sc} (mA/cm²)	V_{oc} (V)	FF	Efficiency (%)
Lawsone 1 -by doctor blade	2.21	0.70	0.61	0.95
Lawsone 2- by screen printing	3.8	0.70	0.62	1.66

The maximum current density we got is 4.5 mA/cm², fill factor and efficiency also increased. It is shown in Table 1. We also fabricated the devices using TiO_2 nanoparticles as semiconducting material by doctor blade technique and screen printing over the FTO glassplates and sintered at 450 °C respectively.

Table 3 – Photovoltaic parameters of the fabricated device using N719 dye

Sample	J_{sc} (mA/cm²)	V_{oc} (V)	FF	Efficiency (%)
N719 with nanoparticle	5.4	0.86	0.65	3.04
N719 with nanofiber	7.8	0.86	0.65	4.4

Fig. 4 shows the J-V characteristics of the device using nanoparticle over the FTO glass plate by doctor blade technique and screen printing. The dye sensitized solar cell using nanoparticle by screen printing gives the better efficiency than the other. The maximum current density obtained is 3.8 mA/cm².

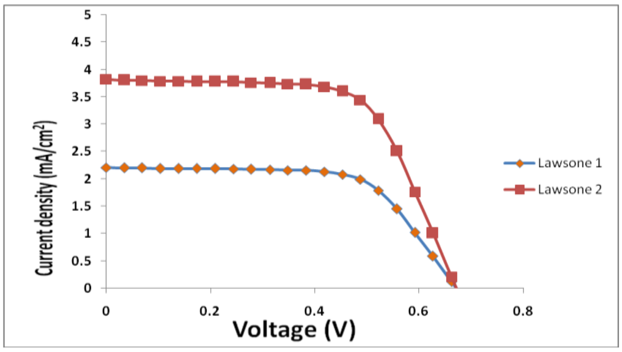

Fig. 4 – J-V characteristics of the fabricated device using nanoparticles doctor blade technique (Lawsone 1) and screen printing (Lawsone 2)

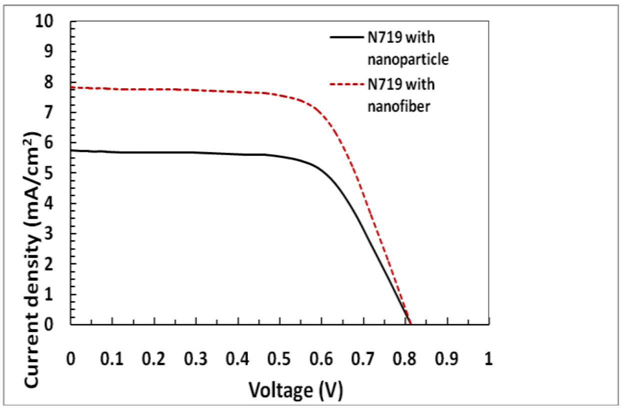

Fig. 5 – J-V characteristics of the fabricated device using N719 dye

Fig. 5 shows the J-V characteristics of the device fabricated using N719 dye. The best efficiency we got when nanofiber is used as the photoanode. The maximum current density obtained is 7.8 mA/cm². The photovoltaic parameters of the fabricated device using N719 dye is given in Table 3.

4. CONCLUSION

As we know the emerging problem of most of the developing countries are energy crisis, solar cells especially DSSCs which uses solar energy to generate electrical energy and since it can work in low light conditions, is a best remedy for the above problem. In our work we modified the photo anode using nanofibers of different diameter by changing the flow rate and viscosity of the polymer solution by electrospinning process and used natural sensitizers. The use of nanofibers with small diameter increases the surface area with volume and thereby increases the dye adsorption compared to that of nanoparticles. Electrical characteristics are plotted and photovoltaic parameters are measured. It is found that the photovoltaic parameters of DSSC with nanofibers found to be increased .Also the result is compared with that of N719 dye.

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