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Dye-Sensitized ZnO fibers from Electrospinning and Photovoltaic Cells

NSF Summer Undergraduate Fellowship in Sensor Technologies
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Abstract

Dye-Sensitized Solar Cells (DSC) have been studied because of the ability to transform solar into electrical energy at low cost. The system that DCS uses is a photo-electrochemical system based on a semiconductor sandwiched between a photosensitized anode and cathode, both immersed in an electrolyte. First it was important to develop a semiconductor for the DSC. Zinc oxide is a good semiconductor, and its synthesis is neither difficult nor expensive. Zinc oxide was produce using Poly(ethylene oxide), zinc acetate, water and anhydrous ether. Then we used the electrospinning technique with the solution to obtain fibers. These fibers were heated at 650^{o}C for 6 hours. For the characterization of the fibers we used Optical Microscope, Scanning Electron Microscope (SEM), and Raman Spectrometry. With the optical microscope we conclude that with the solution fibers could be made. By the shape of the fibers in the pictures taken with the SEM we could say that the fibers look like zinc oxide fibers. Finally with the Raman Spectrometry analyses we conclude that the fibers were compose by zinc oxide.

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1. Introduction

With the high cost of petroleum, new sources of energy must be developed in order to reduce the cost of living. With this in mind the scientific community has created and developed new power sources, which would help to reduce costs. An example of these sources is the Dye Sensitized Solar Cells (DSC). Recently, DSCs have come to the attention of the science community because is a way of generating energy without petroleum. The only problem with solar cells is that the production is expensive. A solar cell is a device for converting energy from the sun into electricity [1]. Modern DSCs are based on the application of semiconductor physics. They are basically just P-N junction photodiodes with a very large light-sensitive area. The photovoltaic effect, which causes the cell to convert light directly into electrical energy, occurs in the three energy-conversion layers [2]. This solar cell is expensive and is not accessible to everyone. This is why solar cells have to be modified to reduce the cost and increase efficiency. Because of the properties of the DSC, new materials could be used to produce them. It has been demonstrated that zinc oxide is a good semi-conductor, which could be used for DSC [3,4].

Zinc oxide micro and nanoscopic fibers can be obtained using the electrospinning technique, which is not expensive. The electrospinning technique has been recently adopted by materials scientist and electrical engineers as a convenient technique for the inexpensive production of nano-fibers. In the electrospinning process a high voltage is used to create an electrically charged jet of polymer solution or melt, which dries or solidifies to leave a polymer fiber. One electrode is placed into the spinning solution or melt and the other attached to a collector. Electric field is applied to the end of a capillary tube that contains the polymer fluid held by its surface tension. This induces a charge transfer to the surface of the liquid [5]. Also to obtain crystalline, solid zinc oxide, the material obtained in the electrospinning process must be oxidized. Heating the solution at a high temperature to decompose the precursors and finally oxidizing the zinc, this usually results in a complete oxidation.

In DSC, the semiconductor must have a particular orientation because the electric current path must be continuous. The electrospinning technique is random; it doesn't have any deposition order, that is why the fibers must be deposited in a oriented form. There are different types of electrospinning setups (e.g. vertical electropinning setup, side electrospinning setup, aligned fiber electrospinning setup). The best way to deposit zinc oxide is using the aligned fiber setup, this will make easier the heating and characterization process.

2. Background

2.1 Dye Sensitized Solar Cells (DSC)

Dye-sensitized solar cells (DSC) are a relatively new class of low-cost solar cell. These cells are based on a photoelectroquemical system (Figure 1). A photoelectrochemical system is based on a semiconductor placed between a photosensitized anode and cathode, both submerged in an electrolyte. These cells are very promising because they are made with low-cost materials.

DSC cells effectively separate the two functions of the silicon used in traditional solar cells. In traditional solar cells the silicon gives the source of photoelectrons, and provide the potential barrier to separate the charges and create a current. In DSC, the semiconductor is used only to separate the charges, the photoelectrons are provided from a photosensitive dye. Although the charges are not provided completely by the semiconductor, it is provide by the combination of it and an electrolyte [6].

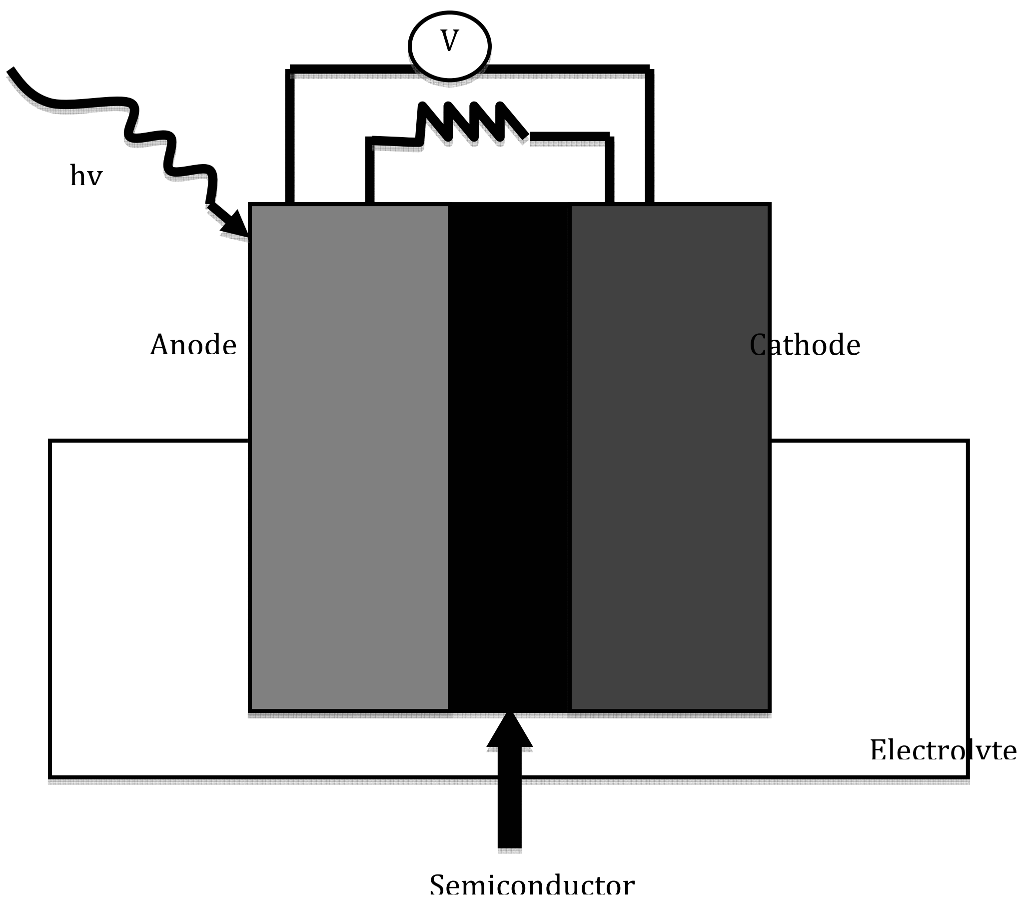

Figure 1

2.1.1Principle

Solar cells are based generally in converting light into energy by converting this light into heat or by the photovoltaic effect. DSC are based on the photovoltaic effect, which occurs when light falling on a two-layer semiconductor material produces a potential difference, or voltage, between the two layers. The voltage produced in DSC is capable of conduct a current through an external electrical circuit that can be used to power up electrical devices [7].

2.2 Zinc Oxide

Zinc Oxide is an amorphous white or yellowish powder that is insoluble in water and in organic solvents but soluble in acid and alkali. Zinc oxide particles may be spherical, acicular or nodular depending on the developing process. The particle shape is important for getting good physical properties. The zinc oxide UV Spectrum shows that absorbs virtually all ultra violet light radiation at wavelengths below 360 nm and provides binders outstanding protection, this is important for the characterization of zinc oxide [8]. Also zinc oxide is known to be a good semiconductor.

Zinc oxide is a versatile material; it has medical, sensors and electrical applications. The most studied application is electrical. The most common of the electrical applications are in laser diodes and light emitting diodes since it has exciton and biexciton energies of 60 meV and 15 meV, respectively [9].

2.2.1 Precursors

Zinc oxide can be obtained from many different processes, but the most common with the electrospinning process are organo-metallics , and then by the application of heat. To perform the electrospinning technique a solution has to be made. This solution has a mixture of zinc acetate in water and Poly(ethylene oxide) in anhydrous ether. After that the fibers are electro-spun and finally oxidized [10].

2.2.2 Characterization

In order to know if the synthesis of zinc oxide is completed, a characterization step is needed. Because zinc oxide is a well-studied material its characterization is simpler. The most common way to characterize zinc oxide is by IR and by Raman spectroscopy. In IR Spectroscopy, zinc oxide shows three peaks; one nearly the 1,100 cm^{-1} region, one nearly the 900 cm^{-1} region, and one nearly the 800 cm^{-1} region. In Raman Spectroscopy, zinc oxide shows two peaks; one intense peak at 440 cm^{-1}, and one less intense peak at 335 cm^{-1} [11]. These peaks are related to the relative motion of the atoms in the material, when excited by the light source.

2.2.2.1 Raman Spectroscopy

Raman spectroscopy is a technique used in solid state physics and chemistry to study vibrational, rotational, and other low-frequency modes. This technique relies on inelastic scattering usually from a laser in the visible, near infrared, or near ultraviolet light spectrum. The laser light interacts with the phonons or other excitations in the system, resulting in the energy of the laser photons being shifted in an up or down direction. The shift in energy gives information about the phonon modes in the system not like IR spectroscopy. IR spectroscopy yields similar, but complementary information is obtained (i.e., functional groups, orientation in space and substitution pattern).

2.3 Electrospinning Technique

The electrosipinning technique is the process that uses a high voltage to create an electrically charged jet of polymer solution or melt, which dries or solidifies to leave a polymer fiber. One electrode is placed into the spinning solution or melt and another one is attached to a collector.

An electric field is applied to a needle that has the solution. When there is a pendant droplet, the electric field induces a charge at the droplet and a jet forms. This jet travels to the collector. In the way, the solvent evaporates and when the solution hits the collector it solidify (Figure 2). This solid is known as a polymer fiber, and is really small. In order to see these fibers a microscope is needed. The most common microscope is the Scanning Electron Microscope.

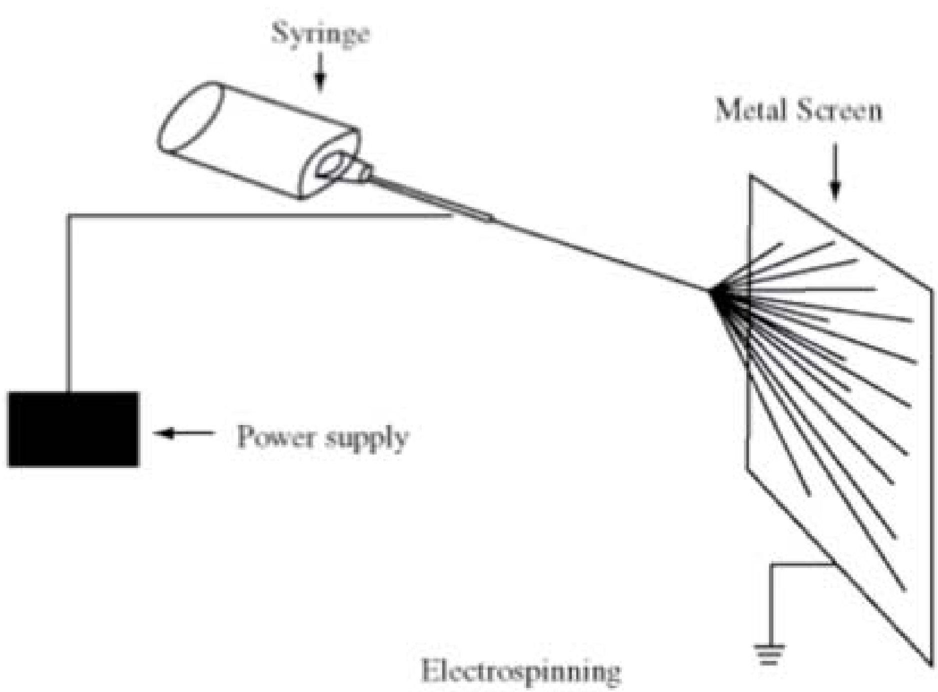

Figure 2.

2.3.1 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface (i.e. topography, composition) and other properties such as electrical conductivity.

3. Materials and Experiment

3.1 Overview

A methodology was developed to make zinc oxide fibers, due some problems the methodology was changed. A zinc acetate/Poly(ethylene oxide) solution was made and used for the electrospinning process. The fibers were heated to complete the oxidation process. Then they were characterized with a Raman Spectrometer. Finally the fibers were imaged in a Scanning Electron Microscope.

3.2 Experiment

In order to obtain zinc oxide, a precursor solution needs to be made. To produce the Zinc Oxide fibers 1.25g of Zinc Acetate will be mixed and stirred with 2.5mL of DI water. The composition will be a mixture of 20% (by weight) Poly(Vinyl Alcohol) (PVA) and water, which was heated and mixed overnight. Then the electro-spinning was performed to get nano-fibers in different orientations for the study, which is the best method in order to obtain stochiometry values close to the desired ones.

Due to problems discussed later on this paper the methodology was changed.

3.3 Changes

The changes were basically changing the solvent and the polymer. First a solution of 19% by weigh of zinc acetate in water was made. Then a solution of 13% by weight of Poly(ethylene oxide) (900,000 MW) in ether anhydrous was added to the first solution. This final solution was mixed over night.

When the solution was ready, it was placed in a syringe. This syringe was positioned in the aligned fibers electrospinning setup. In order to study the fibers, different voltage and different solution rates were used. The fibers were collected in silicon plates.

After the electrospinning process the fibers collected were heated from $400^{o}C$ to $700^{o}C$ with an increasing rate of $240^{o}C$ per hour for 6 hours. For the characterization, the fibers were studied using an Optical Microscope, a Scanning Electron Microscope and Raman Spectrometry.

4. Results

The solution in part 3.2 was made successfully. When the electrospinning process was tried no fibers were obtained. The concentration was changed, the rate was changed and the voltage was changed, but no fibers were obtained. Then the materials were changed.

The solution in part 3.3 was successfully made, and then the electrospinning process was performed. After the electrospinning process, fibers were obtained. Different voltages and different rates were used in this process. The fibers obtained were very good fibers, although no alignment was seen. For this last matter, different distances between the needle of the syringe and the collector were varied, but no alignment was obtained. After that pictures were taken using a Scanning Electron Microscope (Figure 3, 4, 5).

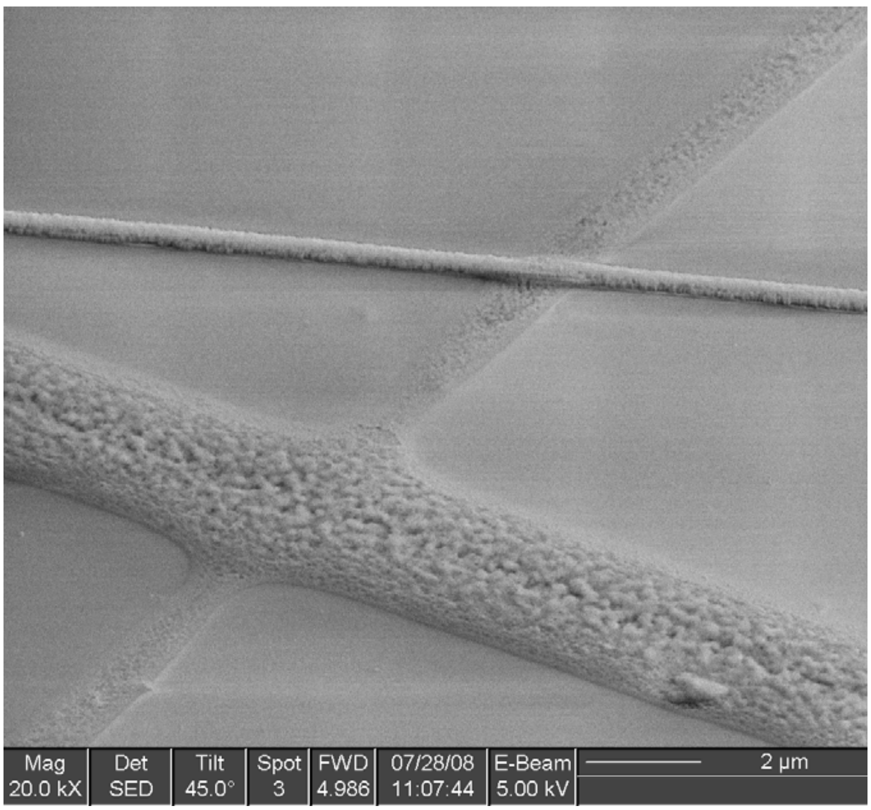

Figure 3

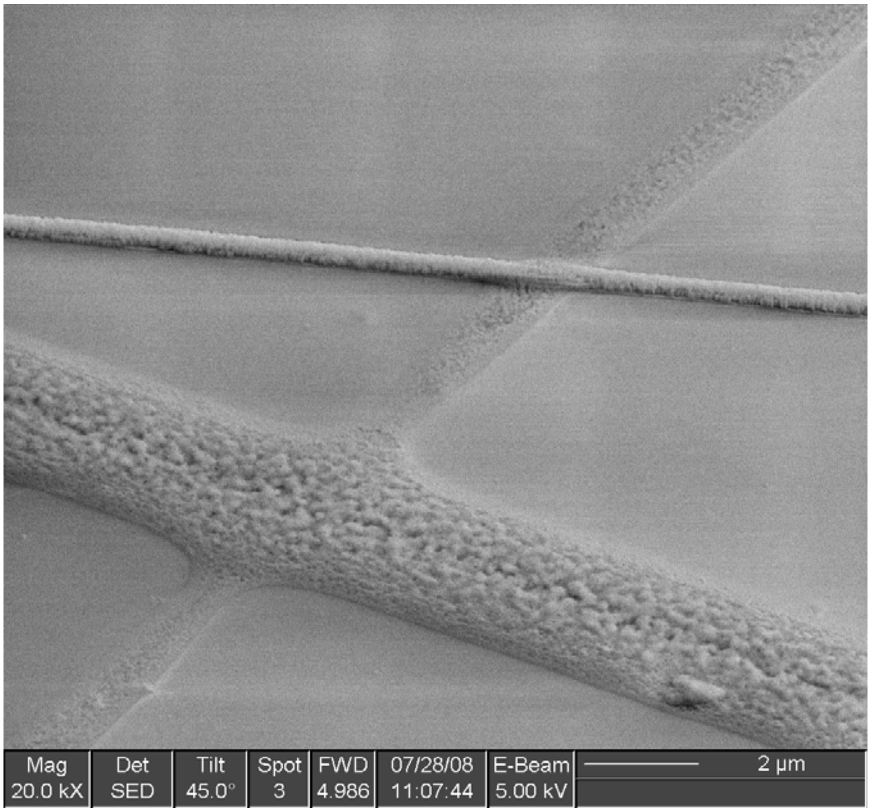

Figure 4

Figure 5

The fibers were heated at 650°C for 6 hours, after that pictures were taken using an Optical Microscope (Figures 6, 7, 8, 9) and using a Scanning Electron Microscope (Figures 10, 11, 12, 13).

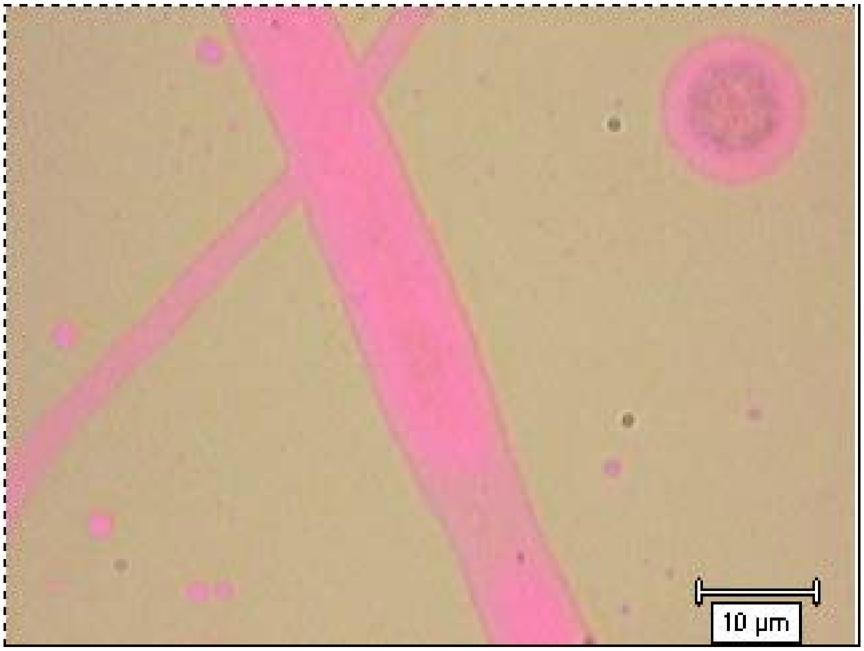

Figure 6

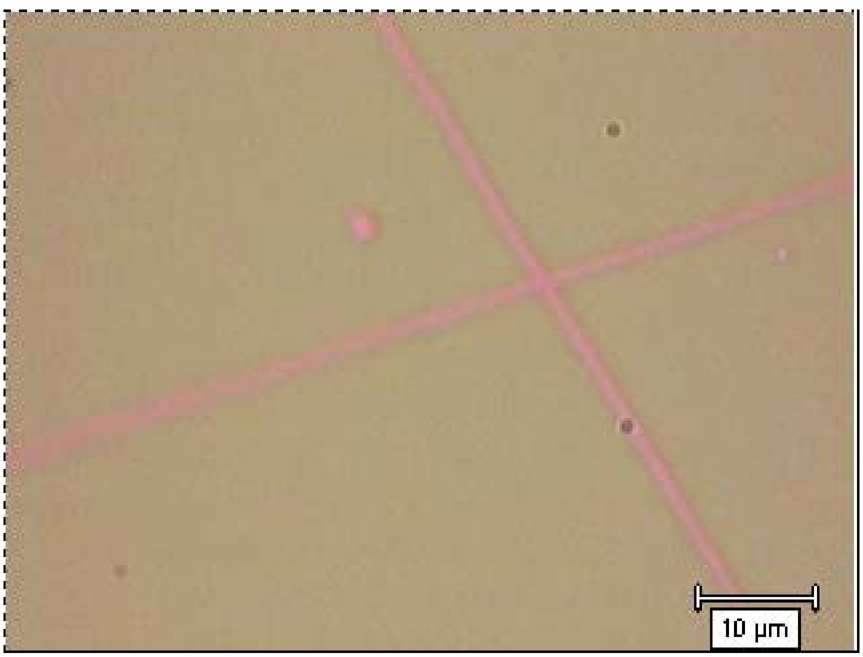

Figure 7

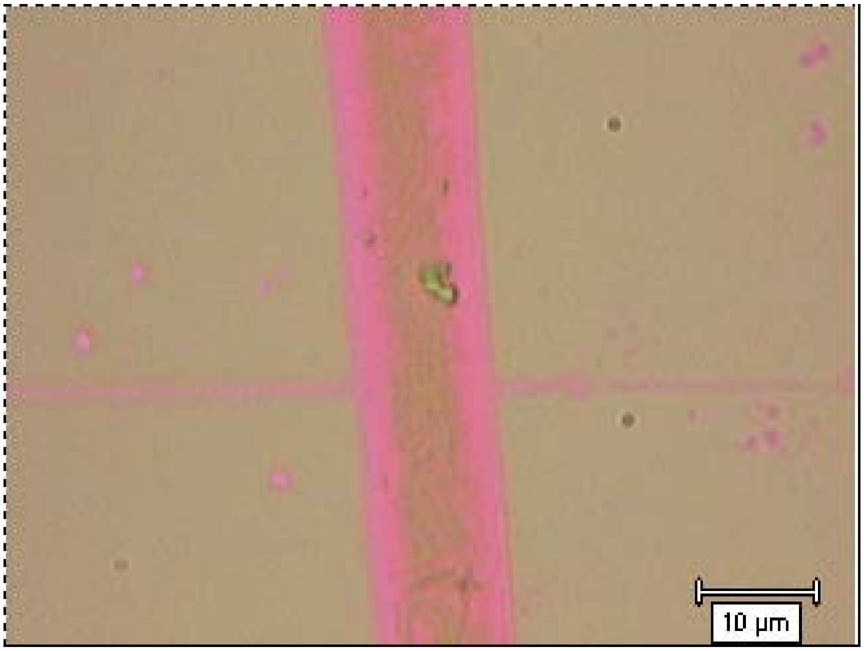

Figure 8

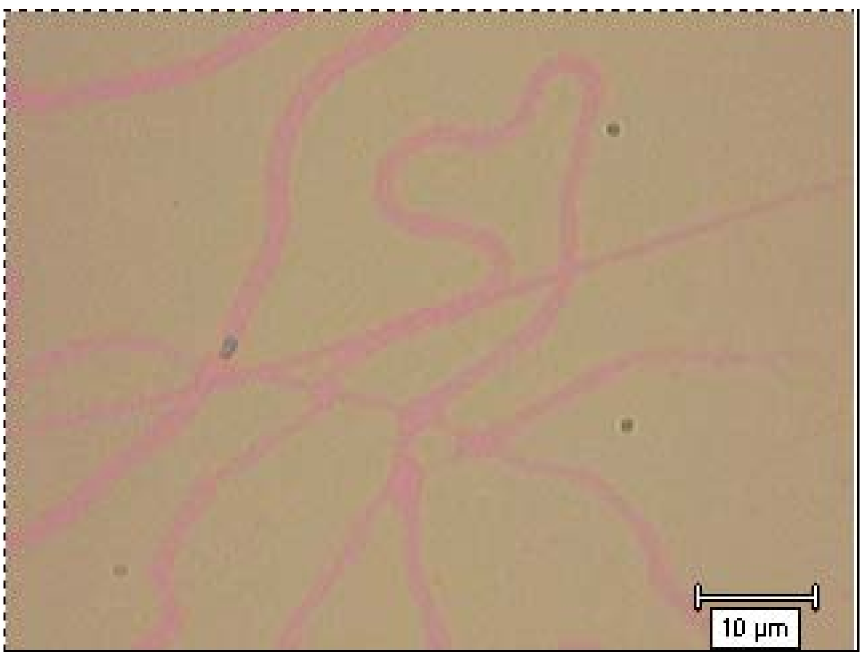

Figure 9

By the pictures obtained with the optical microscope, we can tell that after heating the fibers there were fibers and that is possible that they are zinc oxide fibers.

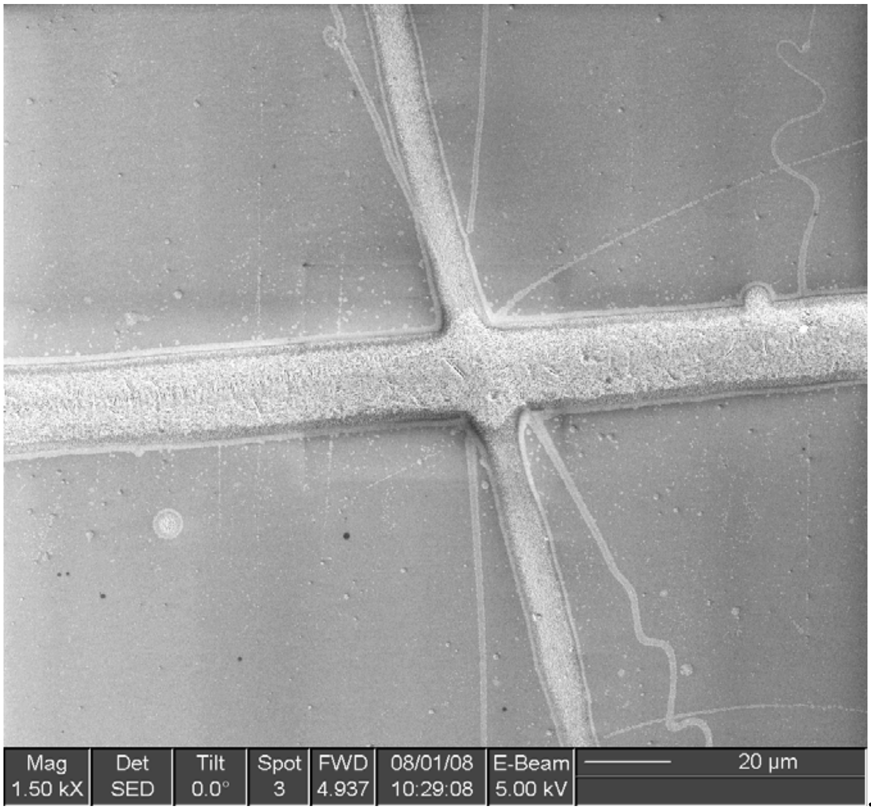

Figure 10

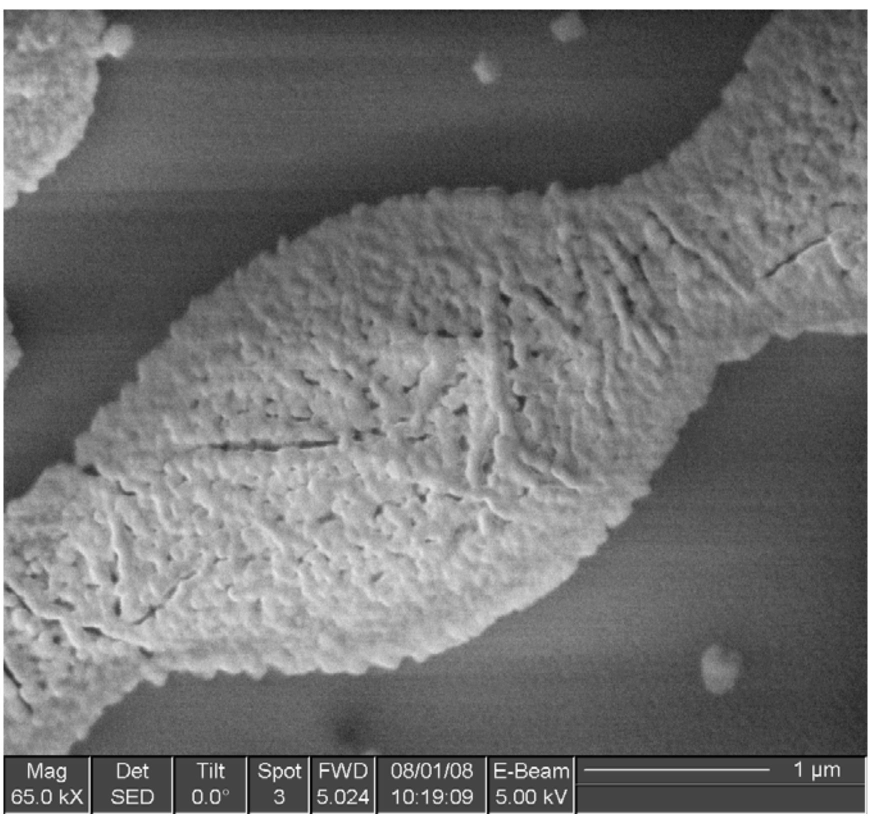

Figure 11

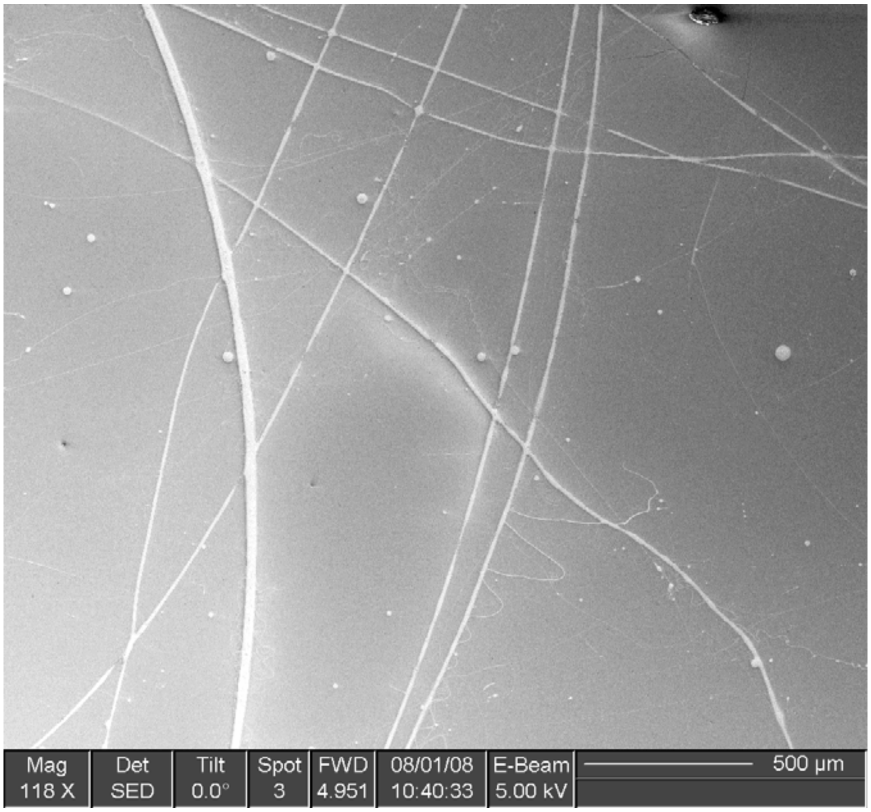

Figure 12

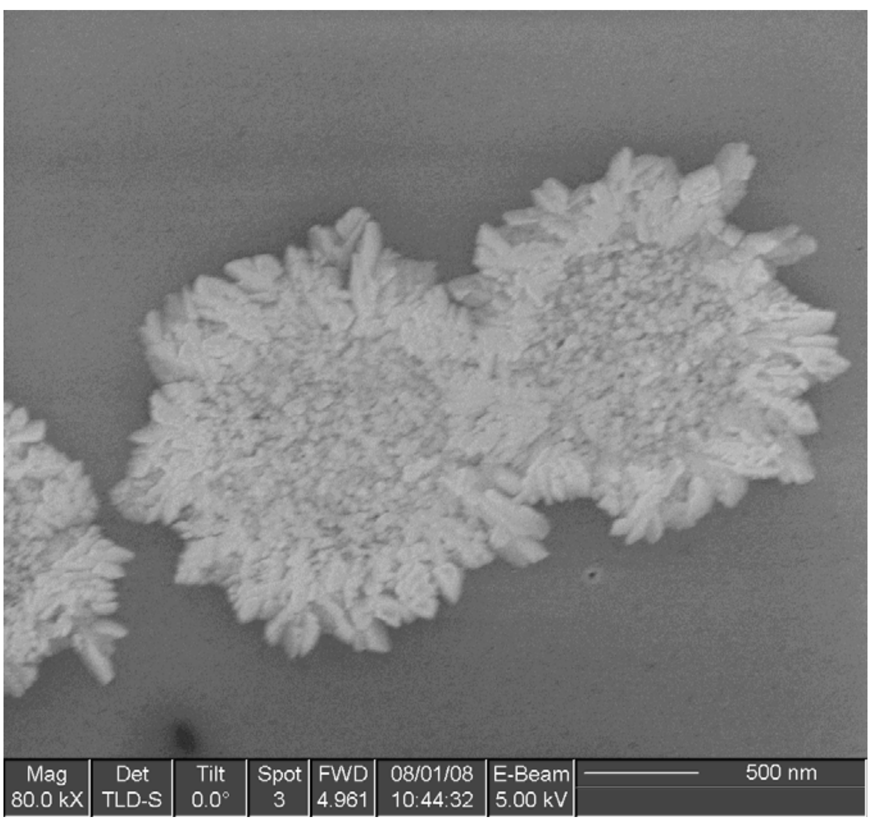

Figure 13

By the look on the fibers, compared to the ones studied by Punniamoorthy Ravirajan, et al, the fibers that were obtained are indeed zinc oxide fibers. In figure 13, the fibers look like crystals; this is the shape of zinc oxide.

Finally, we used the Raman Spectrometer to see the fibers spectrum and to be certain that what we had was indeed zinc oxide (Figure 14).

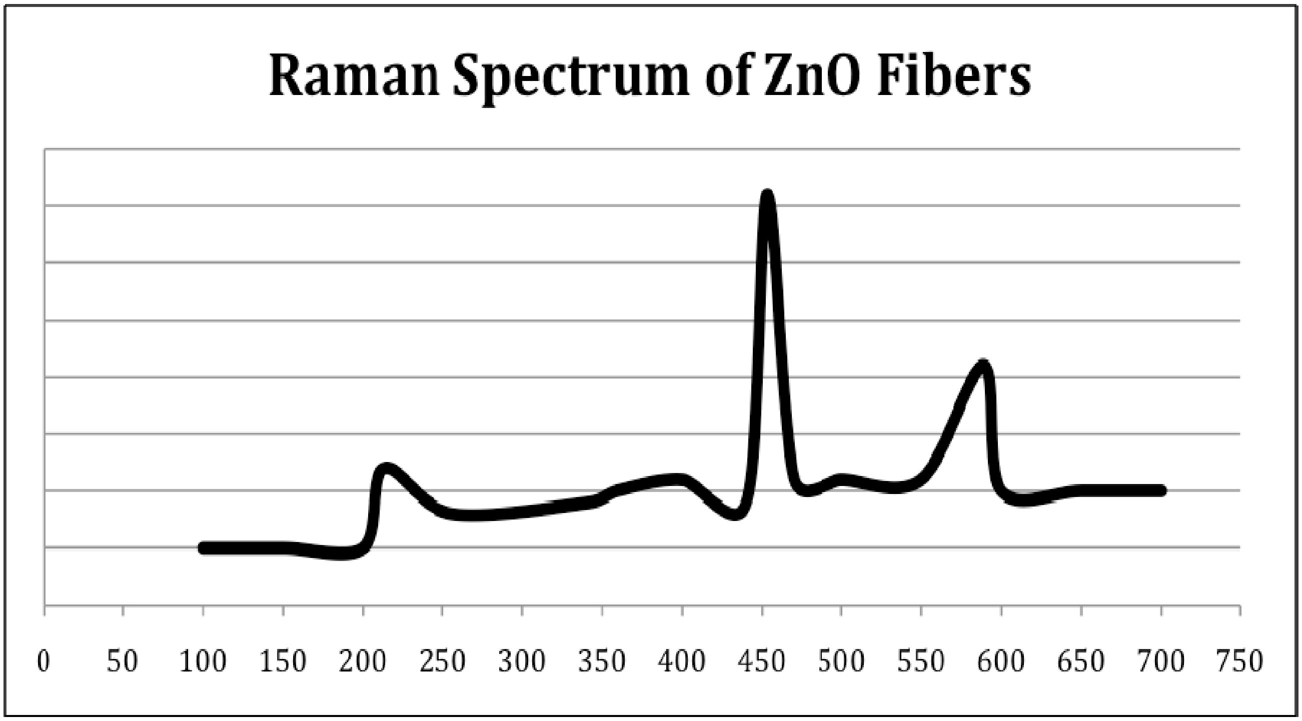

Figure 14

The spectrum tells us that thete are three important signals. The first one is a weak signal at 213 cm^{-1}; the second signal is a strong peak at 453 cm^{-1}; and a thrid one a medium peak at 589 cm^{-1}. Comparing this values with the ones in the study by Periasamy Viswanathamurthi, et al, means that our values are close to the ones in the study. With this in mind we can assume that our fibers are composed by zinc oxide.

5. DISCUSSION AND CONCLUSIONS

The methodology that was developed the first time did not produce any results that could be use for the Dye Sensitized Solar Cells (DSC). By changing the concentration of the mixture, we were able to get better results but still no fibers in the collector. The reason for this is that the solvent used was water. Water has a boiling point at 100^oC, which is high and it doesn't has the time to vaporize before it gets to the collector. This doesn't let the fiber to spin and what you get is a lot of dots in your collector.

By changing the concentration of the solution we didn't had any good results, the only thing that seem to change was when the voltage was changed. This was because higher voltage allows the jet to get charged, but he distance was too short and the jet didn't get completely charged.

After the change of the solution methodology, the electrospinning process was performed. In the electrospinning process fibers were obtain in a silicon collector. It seems that by changing the solvent to a more volatile one fibers can be developed. This is because the solvent evaporates before it gets to the collector and this allows the jet to solidify and finally create a fiber. This was check using the Scanning Electron Microscope. With the microscope pictures of the fibers were taken and the fibers that were obtained were not aligned. By this we can tell that the methodology developed to generate fibers was successful only to generate fibers but not to obtain them aligned.

Following the heating of the fibers, the pictures taken with the optical microscope. With this pictures we can only tell that after the heating there were still fibers, and that the heat does not affect the way that the fibers are arranged when they are collected. After the pictures we analyze the fibers using the Raman Spectrometer. There was a problem because the fibers were deposited on silicon plates and silicon has two signals that overlap the zinc oxide signals. We had to run some background spectrums of silicon in order to subtract them from the fiber's spectrums. With the results we can conclude that the composition of the fibers was indeed zinc oxide.

We can conclude that the first methodology developed for zinc oxide fibers do not work to generate zinc oxide fibers. After the changing of the methodology we can conclude that the methodology works to generate zinc oxide fibers but these fibers are not aligned.

6. Recommendations

This part of the project is just the beginning; there are many things to do with the work that has been done. First, a methodology must be developed in order to get aligned fibers. This methodology must consist in changing the voltage applied to the syringe used for electrospinning and changing the distance between the collector and the syringe.

Another recommendation is that if this project is going to be reproduce, would be better to use a collector with heat capacity different than silicon. Silicon is active in most of the characterization methodologies.

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