Fabrication and Characterization of TiO_2 /ZnO Nanofibers from PVAc Electrospun Microfiber for Renewable Energy Application

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ABSTRACT

We report the study of titanium dioxide/zinc oxide nanofibers obtained from the calcination of precursor poly (vinyl acetate) fibers with titanium isopropoxide and zinc nanopowder, which were prepared by the electrospinning technique. The structure and morphology of nanofibers and precursor fibers were studied by Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and FESEM-EDS. The FTIR and XRD analyzes confirmed the formation of crystalline structures of titanium (anatase) and zinc oxides (hexagonal wurzite), after the calcination of the nanofibers at 500 °C. SEM micrographs show that both precursor fibers and nanofibers form random porous membranes, that TiO_2/ZnO nanofibers and precursor microfibers have average diameters in the range of 200 to 225 nm. The TiO_2/ZnO nanofibers are electrically conductive. These characteristics suggest that titanium dioxide/zinc oxide nanofibers would have potential application for the manufacture of solar cells.

Keywords: electrospinning, TiO_2/ZnO nanofibers, poly(vinyl acetate) precursor, titanium isopropoxide, zinc oxide

1 INTRODUCTION

The use of nanofibers with metal oxides in solar cells allows continuous and rapid electron transport, allowing better efficiency of the solar cell due to improved surface activity. With the coaxial stretching [1] electrospinning technique of a viscoelastic solution, porous membranes made of continuous fibers can be obtained.

The nanofibers are notable because they have characteristics as a very large surface area in relation to the volume [2], surface flexibility, porosity high [3], interconnected pores [4] and superior mechanical performance compared to other known forms of the material, which gives them properties for applications in the field of energy utilization [5,6].

By means of this technique micro and nanofibers are produced from a polymer, which may be in solution or as a melt, which is contained in a syringe having a very thin diameter needle. Due to the application of a high voltage applied between the needle and a metal manifold, a jet of liquid is formed and transformed into solid fibers upon reaching the manifold.

2 MATERIALS AND METHODS

Polyvinyl acetate (PVAc) of MW 100,000 g/mol, titanium isopropoxide (IsoPTi) 97%, nanopowder of zinc particles less than 50 nm and 99% purity, 99.5% N, N dimethylformamide (DMF), and 99.7% acetic acid, all of Sigma Aldrich (México).

2.1 Characterization

The qualitative analysis of the organic functional groups of the polymer solution was performed by FTIR using a Nicolet 6700 (Thermo Scientific) spectrometer in transmission mode.

The morphology of the nanofibers was studied by scanning electron microscopy, under a microscope SEM, JEOL JSM 7600F, equipped with EDS-FESEM to reveal the presence of Ti, Zn and O elements in TiO_2 / ZnO nanofibers.

The crystallinity and phases were analyzed using a Siemens D500 powder X-ray diffractometer, with CuKα1 lamp (λ = 0.15406 nm) of radiation, in a range of 2θ from 20 to 50 ° C at room temperature. The viscosity of the polymer solution was analyzed in the Brookfield digital viscometer DV2T .

4g of PVAc was mixed with MDF (49% w/w) at room temperature with vigorous stirring for 6 hours, was added a solution of IsoPTi dissolved in acetic acid in a proportion of 0.25% w/w. To the resulting solution was added 0.1 g of nanopowder of Zn. The resulting colloidal solution was stirred for 10 minutes before being electrospinning.

2.2 Preparation of TiO_2 / ZnO nanofibers by electrospinning

Once the polymer solution was prepared, the different parameters of the electrospinning process were standardized. The homogeneous colloidal solution was charged into a 5 ml plastic syringe with metal gauge needle (0.7*30 mm, 22G x 1 ¼"), which was placed in the piston of the injection pump of the equipment NE-4000 (New Era Pump Systems, Inc.).

The needle was connected to a high voltage source (Glassman High Voltage Inc.), to apply a potential difference of 15 kV.

The final conditions used to produce electrospun nanofibers were the result of a systematic process of experimentation of all process parameters. The final parameters with which the best nanofiber formation characteristics defined were: flow rate of 0.5 ml/h, needle-collector distance of 16 cm, applied voltage of 15 kV and the size of the aluminum foil was (15 x 15) cm^2.

The electrospinning membranes were removed from the aluminum and subjected to calcination in an electric muffle to a heating ramp of 5 °C/min until reached 500°C, This temperature was maintained for 2 hrs, with a decrease of 5 °C/min up to a temperature of 25 °C. The calcination temperature was modified taking the conditions presented in a previous work [7].

The calcination of the nanofibers of (PVAc/IsoPTi/Zn) was performed at 500 ° C Because Zn has a melting point of 419.5°C.

3 RESULTS AND DISCUSSION

3.1 Infrared Spectroscopy

Figure 1 shows the FTIR spectra of the polymer solution of PVAc y PVAc/IsoPTi/Zn in the range of 500 to 4000 cm^{-1}. The absorption bands of the group CH_3 appear to 1366 and 1432 cm^{-1} for the PVAC and to 1391 cm^{-1} for the PVAc/IsoPTi/Zn. Two representative peaks C=O y C-O in 1724 and 1225 to 1014 cm^{-1} respectively, are clearly observed in both formulations. The signals that appear at 655 cm^{-1} and 597 cm^{-1} correspond to the vibration of the stretching bond Ti-O and flexion bond O-Ti-O respectively. These peaks of the IsoPTi can be assigned as bonds O–Ti–O–Ti [8].

These results confirm the formation of TiO_2 in the nanofibres. The presence of Zn could not be analyzed because it is a metallic element.

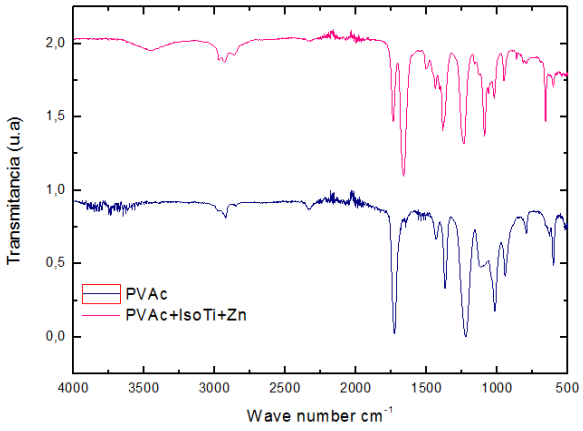


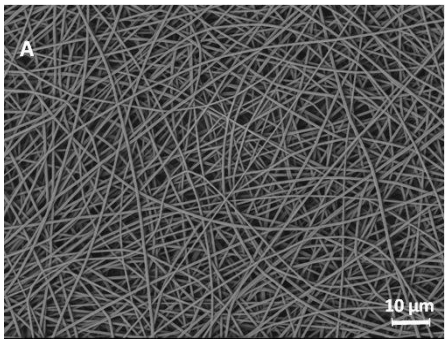
Figure 1: Spectrum FTIR of PVAc and PVAc/TiO_2/ZnO

3.2 Characterization

The IsoPTi tends to hydrolyze and polycondensate in the polymer solution [9]. According to the proposed condensation reaction diisopropyl ether was obtained. The latter is a hydrocarbon liquid with lower boiling point (69 °C) compared to the solvent used (DMF, 153 °C), so it can be stated that it evaporated during the electro-spinning process. At the moment of being electroed from the polymer solution, an increase in viscosity was detected with the aid of the viscometer DV2T.

The increase in viscosity was possibly due to the addition of the metal precursor IsoPTi, since it is considered a metal alkoxide compound. This could be explained by the condensation reaction [9] between titanium isopropoxide and PVAc through the functional C=O within the structure of the polymer. To control the chemical crosslinking of the PVAc, the IsoPTi was dissolved in acetic acid (CH_3COOH), which facilitated the electrospinning of the polymer solution by improving the viscosity. For this reason, the viscosity of the pristine PVAc solution was 5.604 Pa.S while the viscosity of the colloidal solution PVAc / IsoPTi / Zn decreased to 0.4818 Pa.S with the addition of acetic acid, which improved the cross-linking of the PVAc chains, by the effect of the titanium isopropoxide when mixed with the PVAc.

In Figure 2A the membranes are shown with pristine PVAc nanofibers at 1000 X and the figure 2B to 5000 X. It can be seen that nanofibers are obtained with average diameters of 426 +/- 60 nm without superficial defects with homogeneity in the size and texture of the fibers. As observed in the nanofibres obtained, the average diameter is a function of the electrospinning parameters.



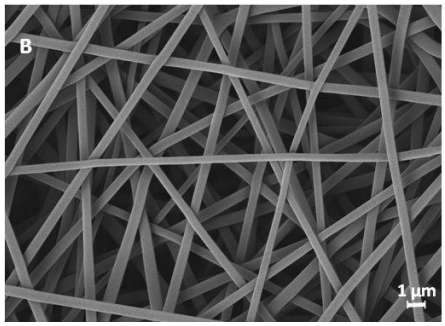
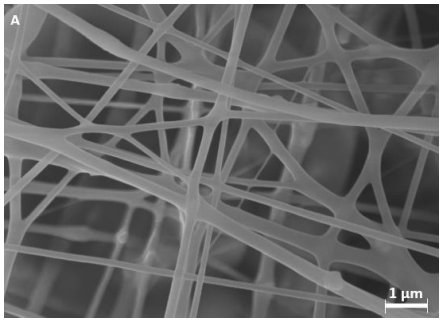


Figure 2: SEM images of pristine PVAc nanofibers obtained from the Materials Research Institute IIM- UNAM. A) 1000X B) 5000X

The nanofibers of (PVAc / IsoPTi / Zn), before being calcined, have good morphology with few defects (Figure 3A and 3B). The average diameter of the fibers was 227 +/- 20 nm.



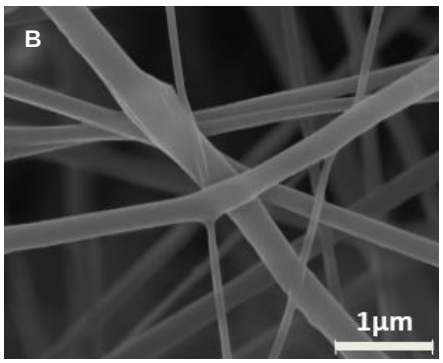


Figure 3: SEM image of nanofibers of PVAc/IsoPTi/Zn A) 10000X B) 25000X

Once the PVAc / IsoPTi / Zn composite fibers were obtained, they were calcined at 500 °C under the conditions indicated above in order to remove the PVAc and to transform the IsoPTi and the Zn into TiO_2 y ZnO.

In the micrography of figure 4A at 10000X, TiO_2 nanofibers are observed after the calcination of PVAC/IsoPTi precursor nanofibers at 500 °C. It can be seen that the fiber morphology did not change significantly, but compared to nanofibers PVAc/IsoPTi/Zn without calcining (Figure 2), the fibers exhibit crosslinking and the surface of the TiO_2 fibers appears more rough. This can be attributed to the organic phase (PVAc) being lost during calcination, causing the change from a soft surface to a more rigid one.
It's this as in figure 4A shows that the TiO_2 continuous nanofibers had a diameter of 284 +/- 60 nm, since by the heat treatment at 500 °C of the nanofibers, the Ti was transformed to TiO_2 in the crystalline anatase phase as evidenced in the XRD study.

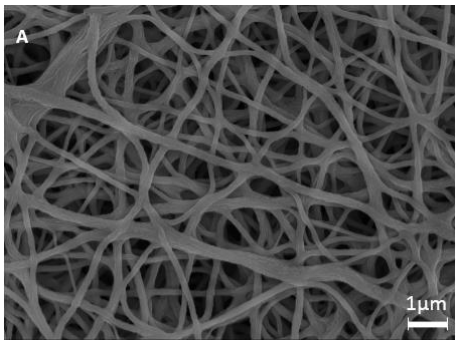


Figure 4: SEM image of calcined TiO_2 nanofibers A) 10000X

The nanometric order of the fiber diameters and the homogeneity of the morphology are indicating that the electro-silvery metal nanofibers have potential properties to generate clean energies.

The FESEM-EDS analysis was performed to show that Zn does not vaporize at this temperature and coexists with TiO_2 (Figure 5). The signals indicating the presence of Zn and TiO_2 in the obtained nanofibers are evident, which corroborates the results obtained from XDR analysis. The calcination of the microfibers also generated the complete decomposition of the PVAc by oxidation of the carbon in CO_2 and H_2O. These nanofibers presented homogeneity and regular shape after the calcination. These results are complemented by XRD analysis.

Figure 5. FESEM-EDS images of TiO_2 / ZnO calcined nanofibers. A) 10000X, B) 50000X and C) FESEM EDS results of calcined nanofibers. The elemental composition of nanofibers in atomic percentage is: O = 74.81, Ti = 21.82 y Zn = 3.37. These nanofibers, due to their high surface roughness and high surface area, can improve reagent adsorption.

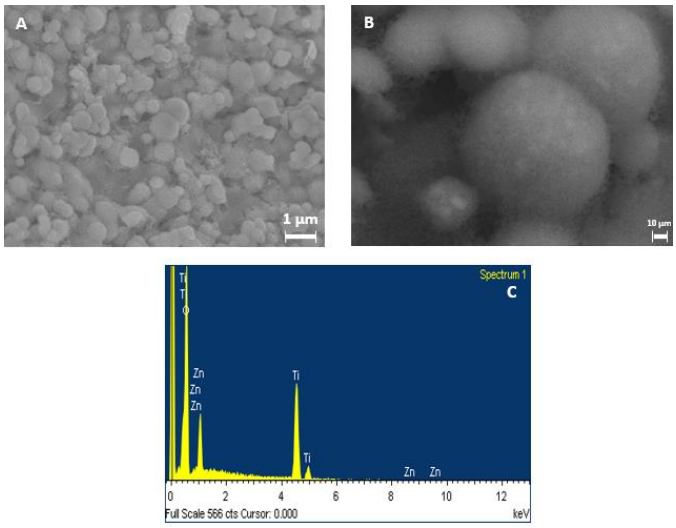


Figure 5: FESEM EDS images of calcined nanofibers of PVAc/IsoTi/Zn. A) 10000X B) 50000X C) FESEM EDS results of calcined nanofibers

3.3 X-Ray Diffraction

The XRD diffractogram of the calcined nanofibers is shown in Figure 6. This diffractogram corresponds to the calcined TiO_2 nanofibers, the Bragg angles (2θ) which appear at values of 25.2°, 36.9°, 37.8°, 38.8° y 48° correspond to the crystalline planes (101), (004) y (200), (JCPDS card No 21-1272), confirming the presence of the anatase phase of TiO_2.

The figure 6 shows the crystalline phase of ZnO hexagonal wurzite. The angles 2θ presented at values of 31.9°, 34.5°, 36.2° y 47.5° correspond to the crystalline planes (100), (002), (101) y (102) (JCPDS card No 01-089-0510). The results of FESEM-EDS and XRD confirm the oxidation of Zn by the effect of calcination. These results were compared with other reported studies [10,11] which show similar results. The characteristic peaks clearly show that the PVAc decomposed and that the nanofibers are composed of TiO_2 / ZnO which could serve as photoelectrode in energy storage devices.

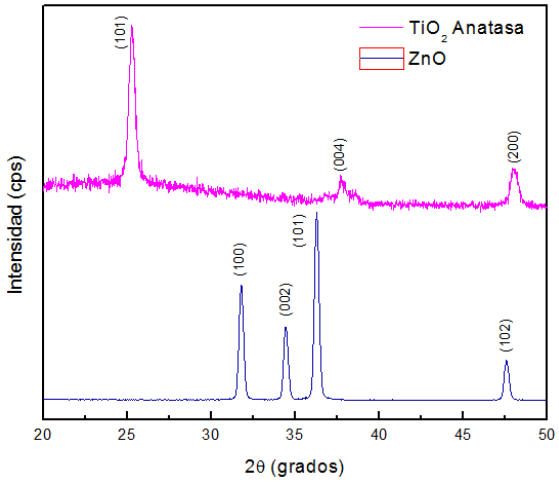


Figure 6: XRD diffractogram of calcined nanofibers of TiO_2ZnO

CONCLUSIONS

The appropriate conditions were established for the preparation of the precursor fibers: 15 kV of applied electric potential, 16 cm of needle-to-plate distance and a flow rate of 0.5 ml / hr. By means of the calcination of the precursor fibers, TiO_2 / ZnO nanofibers were obtained with excellent surface morphology and with an average diameter of 200 +/- 40 nm from precursor microfibers of PVAc, titanium isopropoxide and zinc nanopowder, which is an experimental evidence of the potential of these materials in technological applications to show suitable characteristics in nanometric scale.

The characterization by SEM, XDR, FESEM-EDS and FTIR confirmed that the calcined TiO_2 / ZnO nanofibers are composed of crystalline phases of TiO_2 (anatase) and ZnO (hexagonal wurzite).

ACKNOWLEDGMENTS

This project was developed with the financial support of the Project PAPIIT- UNAM IN108116.

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