Electrospun TiO_2 Fibers as a Material for Dye Sensitizied Solar Cells

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ABSTRACT

Electrospinning is a method for producing polymeric fabric with fibers ranging from 50 to 500 nm in diameter. It has been demonstrated that fibrous structure is preserved even after annealing when precursor of inorganic compound is introduced into polymer solution. Using the Nanospider^{TM}technology TiO_2 anatase with a fibrous morphology can be produced in industrial scale. Our product was characterized by SEM, XRD and nitrogen adsorption measurements. The results evidence that a completely new class of material has been developed. The product morphology and particle size together with its phase purity and surface area predestine nanofiberous TiO_2 to be advantageously employed in various applications as are dye-sensitized solar cells, adsorbents or photocatalysis.

Keywords: electrospinning, titanium oxide, dye sensitized solar cell

1 INTRODUCTION

Electrospinning is in last decades established as a simple and versatile technique for fabrication of endless polymer nanofibers with uniform diameter and diversified composition [1]. The method was recently extended to preparing ceramic nanofibers. This is achieved by spinning of mixture of ceramic precursor and polymer solution and consequential calcining in order to remove polymer template [2], [3].

Among others ceramics emphasised interest lay on titanium dioxide due to its extraordinary electrical, electrochemical and catalytic properties. In dye-sensitized solar cell n-type semiconductive TiO_2 transfers photoelectron from the dye to the collector electrode whereas holes are transferred vie the electrolyte to the counter electrode [4]. Employment of fibrous morphology in the dye sensitized solar cell could reduce electron recombination rate within its transfer through the TiO_2. Furthermore this morphology improves accessibility of the surface, especially in cells with polymer electrolytes [5], [6].

2 EXPERIMENTAL

The TiO_2 fibers were electrospun directly onto a FTO conductive glass from typical spinning solution. This was prepared by mixing of 16.5 g titanium tetraisopropoxide with 33 ml of acetic acid and 33 ml of ethanol. The solution was stirred for 10 min before being added into 82.5 ml of 6 % ethanolic solution of polyvinylpyrrolidone (PVP, M_w= 1300000g/mol). The solution was subsequently electrospun using the Nanospider^{TM} technology. The conductive glass with nanofiberous layer was than calcined at 500°C for 2 h on the air.

Morphology and size of as-prepared titania fibers were observed by scanning electron microscope (SEM). The specific surface area was determined from nitrogen adsorption/desorption isotherms at liquid nitrogen temperature. The B.E.T method was used for surface area calculation. Crystalline phase of the fibers was identified by X-ray diffraction. The surface composition of titania fibers was analyzed by means of XPS technique.

In order to prepare dye sensitized solar cell device, the calcined TiO_2 on the FTO glass was immersed overnight in ethanolic solution of ruthenium dye N945. In order to increase effective surface area of TiO_2 nanofibers the mesoporous particles high specific surface area were created in gaps between nanofibers. The obtained mixture was sensitized by the dye N495 using the same procedure. The assembled devices were than irradiated by solar spectrum simulator in order to obtain photovoltaic characteristics.

3 RESULTS AND DISCUSSION

3.1 Morphology

The fibrous morphology was analyzed before and after calcining. The SEM pictures are shown in Figure 1. The fibrous morphology structure is not affected during heat treatment though macroscopically fibrous layer incline to the strong surface contraction. Using higher resolution SEM analyses the polycrystalline structure was observed with crystalline size in range form 10 to 50 nm 2 and well-defined anatase phase as shown in Figure 3.

There was not observed any adsorption of the dye on the TiO_2 fibers even after 44 hours dipping time in alco-

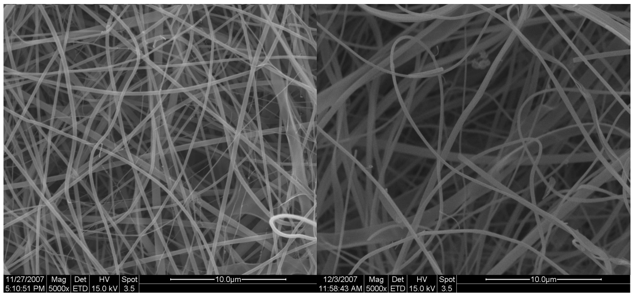

Figure 1: SEM picture of electrospun titania precursor (left) and calcined TiO_2 nanofibers (right)

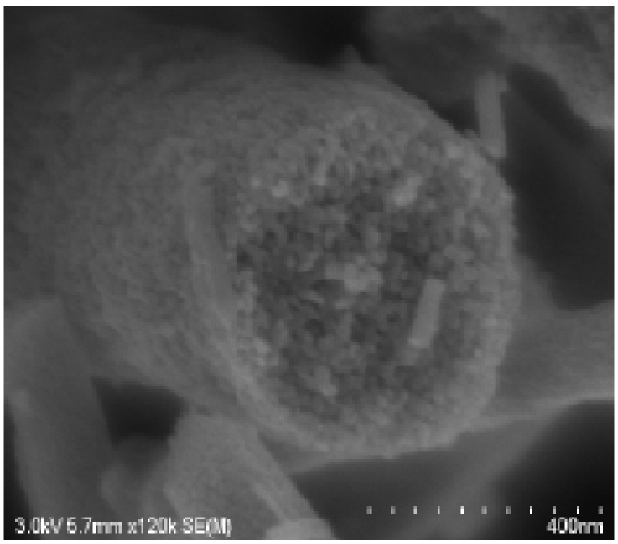

Figure 2: SEM picture of fiber cross section demonstrating polycrystalline fibre character

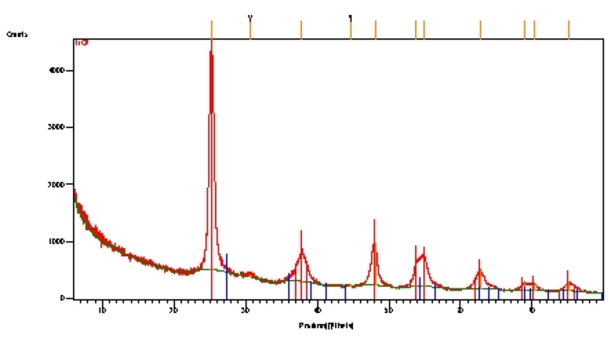

Figure 3: XRD patterns of electrospun TiO_2 fibers after calcination process

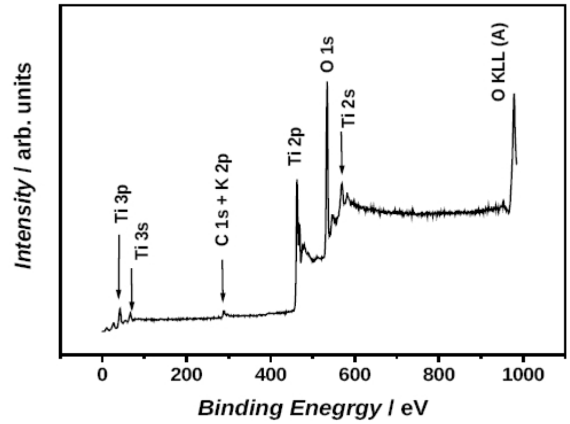

Figure 4: Survey (1000 eV) XP spectrum of TiO_2 fibers

hol solution. The ex-exposed layer was dead white and its surface seemed to be hydrophobic, the dye solution-repellent. Considering the possible inhibition of the adsorption by ex-polymer residue which may remain on the surface after annealing, the surface analysis by ESCA was carried out. The x-ray photoelectron spectrum of the TiO_2 is depicted in Figure 4 The specific surface area of calcined sample was examined using nitrogen sorption/desorption isotherm and the value calculated via B. E. T. model was found to be 60 g/m^2.

The surface composition was calculated from the integral intensity of the characteristic core-level spectra corrected for the Scofield photoionization cross-section (also considering its asymmetry), electron inelastic mean free paths and spectrometer transmission function [7]. The quantitative analysis gave the following atomic ratio: $Ti_{1.00}O_{2.26}C_{0.25}K_{0.02}$. As can be seen the carbon and potassium contaminate the TiO_2 sample. The slightly higher content of oxygen in TiO_2 is caused by the presence of different CO groups as well as by the presence of oxides and hydroxides on the upper TiO2 surface (oxygen component O 1s (II), see Table 1) with the structure different from that in the deeper surface and in the bulk material (the information depth of XPS was about 5-7 nm).

3.2 Photovoltaic characterisation

The J-V characteristics of solar cell device were measured under simulated solar spectrum light source. The short-circuit current density J_{SC}, the open-circuit voltage V_{OC} and overall conversion efficiency η normalized to the intensity of the incident light. The system with pure TiO_2 fibers yields V_{OC}= 811 mV, J_{SC}=2.77 mA/cm^2 and η=1.51 %. The second system were TiO_2 of both fibers and mesoporous particles were used exhibits V_{OC}= 723 mV, J_{SC}=7.93 mA/cm^2 and η=3.96 %.

4 CONCLUSIONS

In present contribution the ability of the Nanospider^{TM} technology to produce fibrous TiO_2 and its applicability in the dye sensitized solar cell was demonstrated. Although the almost no dye adsorption on the fibre surface where observed the assembled solar cell exhibited an solar conversion activity. In experiment where combination of fibrous TiO_2 with mesoporous TiO_2 was was used for setup of solar cell device the solar conversion efficiency TiO_2 was significantly increased. It is the first step towards advanced hierarchical structure engineering benefiting from the fast electron transport through fibrous TiO_2 and the high surface area of mesoporous TiO_2.

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