Superlattices and Microstructures 77 (2015) 18–24

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

Photoluminescence: A very sensitive tool to detect the presence of anatase in rutile phase electrospun TiO_2 nanofibers

Maryline Nasr [a,b], Adib Abou Chaaya [a], Nadine Abboud [b], Mikhael Bechelany [a,*], Roman Viter [c,d], Cynthia Eid [b], Antonio Khoury [b], Philippe Miele [a]

[a] *Institut Europeen des Membranes, UMR 5635 CNRS Université Montpellier 2, Place Eugene Bataillon, F-34095 Montpellier cedex 5, France*

[b] *Research Platform for Nanosciences and Nanotechnologies, Campus Pierre Gemayel, Fanar, Lebanese University, 90239 Lebanon*

[c] *Faculty of Physics, Experimental Physics Department, Odessa National I.I. Mechnikov University, 42, Pastera 65026, Odessa, Ukraine*

[d] *Institute of Atomic Physics and Spectroscopy, University of Latvia, 19 Raina Blvd., LV 1586 Riga, Latvia*

ARTICLE INFO

Article history:
Received 20 October 2014
Accepted 26 October 2014
Available online 4 November 2014

Keywords:
Titanium oxide
Electrospinning
Nanofibers
Photoluminescence
Anatase
Rutile

ABSTRACT

This paper reports on the synthesis and the characterization of titanium dioxide (TiO_2) nanofibers prepared by electrospinning. The samples were annealed at various temperatures in air for 4 h. The as-spun and annealed TiO_2/PVP composite nanofibers were characterized by scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy analysis (EDX), X-ray diffraction (XRD), Raman spectroscopy and photoluminescence (PL). The results show that the heat treatment has an effect on the crystallization process. Even if the XRD data shows a complete anatase-to-rutile transition in the TiO_2 nanofibers at 900 °C, photoluminescence reveals a small portion of anatase in rutile sample. This observation proved that photoluminescence is a very sensitive tool to detect the presence of anatase in rutile phase TiO_2 nanostructures.

* Corresponding author. Tel.: +33 467149167; fax: +33 467149119.
E-mail address: mikhael.bechelany@univ-montp2.fr (M. Bechelany).

http://dx.doi.org/10.1016/j.spmi.2014.10.034
0749-6036/

1. Introduction

In the last decade, the elaboration of new nanoscale materials such one-dimensional nanostructures have attracted considerable attention [1–6]. Different methods have been used to produce one-dimensional nanomaterials such as thermal evaporation [7], freeze-drying method [8], physical vapor deposition [9], and chemical vapor deposition [10]. Among these methods, the simplest technique to design nanofibers is the electrospinning. This method was first introduced by Anton [11]. It is a versatile and cost-effective technique for the production of multi-functional nanofibers from various polymers, polymer blends, composites, sol–gels, and ceramics [12]. The fibers are rather uniform in diameter ranging from tens of nanometers to several micrometers [13,14]. The basic principle of this technique is based on generating the direct movement of charged molecules by applying a high voltage. The droplets coming from the polymer solution, through the spinneret, would then be ejected in the form of a liquid jet forming the nanofibers on the collector.

Among the different types of oxide semiconductors produced by this method, Titanium oxide (TiO_2) is one of the most extensively studied materials because of its remarkable optical and electronic properties along with its chemical and thermal stability [15]. Due to these outstanding properties, TiO_2 has been used in wide range of applications such as chemical sensors [16,17], catalytic filters [18,19], and solar cells [20,21]. TiO_2 has four crystalline phases: anatase, rutile, and brookite and so-called high-pressure phase of srilankite-like structure. Rutile is a stable phase at high temperature, where anatase and brookite would transform to rutile when treated at high temperatures.

In addition, TiO_2 nanostructures demonstrate room temperature photoluminescence in visible (440–570 nm) and IR (800–860 nm) intervals of the wavelength spectrum, in particular for anatase and rutile phases respectively [22–25]. The emission of anatase nanostructures has usually two bands, related to self-trapped excitons luminescence (440–510 nm) and deep levels formed by oxygen vacancies (515–560 nm) [26–28]. Photoluminescence in rutile phase concerns deep levels, related to Ti^{3+} states [15,25]. It was mentioned that photoluminescence in TiO_2 is sensitive to ambient conditions and thermal treatment [24,25]. PL in TiO_2 nanostructures is ruled by the surface charge and could be changed by the adsorption of gas and biomolecules on TiO_2 surface [29,30], what makes an impact on some applications if the TiO_2 is used in optical sensors or biosensors for instance.

In the present paper we report the fabrication of TiO_2 nanofibers by electrospinning method and detailed optical and structural characterization of the obtained nanostructures. The structural and optical changes induced by high temperature annealing will be discussed. The high sensitivity of the photoluminescence technique for detecting anatase trace in rutile phase will be also highlighted.

2. Materials and methods

2.1. Materials

In this study titanium tetraisopropoxide [Ti(O*i*Pr)4; 97%,], PVP (Mw = 1,300,000), ethanol (98%) and acetic acid (100%) were purchased from Sigma–Aldrich.

2.2. Preparation of TiO_2 nanofibers

Fabrication of the TiO_2 nanofibers was achieved by electrospinning. The TiO_2 sol was prepared by hydrolyzing 3 ml of titanium tetraisopropoxide with a mixture of 2 mL of ethanol and 2 mL of acetic acid. 0.3 g of PVP was separately dissolved in 3 mL of ethanol and then added to the TiO_2 sol solution. The precursor mixture was stirred for 2 h at room temperature to obtain sufficient viscosity required for electrospinning. The electrospinning solution was placed into a 22 ml syringe with a 25 gauge stainless steel needle at the tip. The syringe pump was adjusted to 0.4 ml/h of feeding rate. Then, the electric voltage of 25 kV was applied between the needle and the collector. The distance between the tip of the syringe needle and the collector (Al plate) was fixed to 10 cm. The as-spun nanofibers were left overnight in air to fully hydrolyze. To remove the polymer and achieve crystallinity, the