Study of TiO_2 nanofibers prepared by electro-spinning technique

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Abstract

The nanostructured material properties are different from the bulk materials. Nanofibers are widely studied for many applications like tissue engineering, wound dressings, electronics, storage, catalysts, protective clothing, sensors, and cosmetics. In this study, pure form of one-dimensional TiO_2 nanofibers have been successfully obtained by electrospinning technique and TiO_2 nanopowders are synthesized by a conventional Sol-Gel method followed by high temperature calcinations. The as-obtained products are characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy-Dispersive X-Ray (EDX) spectroscopy. The XRD results reveal the crystallite size of the synthesized material. SEM images depict the formation of nanopowders and nanofibers. EDX studies confirmed the presence of Ti and O in the prepared samples. Copyright © 2019 VBRI Press.

Keywords: Anatase, electrospinning, nanofibers, rutile, TiO_2.

Introduction

Among one-dimensional (1D) nanostructured materials such as nanotubes (NTs) [**1**], nanorods (NRs) [**2**], and nanowires (NWs) [**3**], nanofibers (NFs) has attracted more attention due to their unique physical and chemical characteristics. NFs have been the focus of interest in recent times due to its unique properties like larger specific surface areas, higher aspect ratio, and better pore interconnectivity compared to other nanostructured materials. A nanofiber is a continuous fiber, slender, elongated and thread like object or structure, which has a diameter in the range of billionths of a meter and are difficult to see with the naked eye so they are studied using magnification [**4**]. Until now, numerous methods such as Self-assembly [**5**], Template-assisted synthesis [**6**], Wet chemical synthesis [**7**], Chemical Vapor Deposition (CVD) [**8**], and Electrospinning have been applied to the preparation for nanofibrous materials. Among these, Electrospinning is currently the only versatile method of fabricating continuous uniform fibers which is carried out at room temperature under atmospheric condition [**9-11**]. NFs with many morphological structures such as hollow [**12**], yarn [**13**], core-shell [**14**] and porous [**15**] structures can be obtained by modifying process parameters including feed rate, applied voltage, nozzle design, collector type, tip-to-collector distance, and calcination treatment through electrospinning. The morphology and diameter of the fibers can be adjusted by varying the processing parameters. The interest in this technique is due to its simplicity, process controllability, low production cost and scalability for producing industrial quantities [**16**].

Titanium dioxide or Titania (TiO_2) is one of metal oxide semiconductors that have been considerably investigated and utilized in a wide range of applications such as catalytic devices, solar cells, sensors, and other optoelectronic devices [**17-21**]. It is widely used material in both research and industrial fields due to its inherent chemical stability, transparency, high abundant in nature, slow rate of charge carrier recombination and low cost [**22**]. TiO_2 is an alkaline binary oxide with wide band gap (2.8-3.3eV) that exists in both crystalline and amorphous forms. Till now, 14 structural phases are identified, in which 11 phases are crystalline and 3 are amorphous phases. Out of 11 crystalline phases only three phases are mainly considered [**23**]. They are naturally existing polymorph of TiO_2, namely anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). Of these phases, anatase, and rutile are found to be suitable for photocatalytic applications whereas brookite is the metastable form which is not commonly observed in minerals. It is very difficult to synthesize TiO_2 in pure form [**24**].

Anatase TiO_2 is metastable and exhibits more photoactive phase and high activities for solar cell applications due to its higher band gap (3.2 eV). But, rutile TiO_2 is more thermodynamically stable and owing to it low intrinsic photocatalytic activity with lower band gap (3.0 eV); it can be applied in the tissue engineering and cosmetics [**17**, **25-27**]. The amorphous phases are photocatalytically inactive. Zheng Miao *et al.* [**28**] have synthesized nanowires of diameter 10-

40 nm by cathodically induced sol-gel template method from an aqueous solution containing a Ti precursor. Lakshmi. B.B *et al.* [**29**] have reported via the template method followed by Sol-gel obtained both TiO_2 nanotubes and nanofibers which offered high surface area due to the high porosity of the template membranes and reported increased rate of photodecomposition of salicylic acid. Mingfeng Chi *et al.* [**8**] fabricated (PrB_6) through a catalyst-free chemical vapor deposition (CVD) process and established that the as-synthesized nanowires were polycrystalline with 10-100nm in diameter and 2-10 μm in length. Dan Li and Younan Xia [**30**] had demonstrated the fabrication of titania nanofibers with controllable thinner diameters and porous structures.

Based on all the above insights the present work is an attempt to fabricate TiO_2 nanofibers diameter in average order of 20-50 nm. The prepared nanofibers could exhibit high surface to volume ratio with enhanced physiochemical property and better catalytic activity.

Experimental details

Preparation of TiO_2 nanopowder by Sol-Gel method

2g of poly (vinylpyrrolidone) powder (PVP, Mw = 1 300000) was measured then added 9ml of absolute ethanol and 5ml of acetic acid in a capped bottle. The obtained solution was stirred at room temperature for 1 h to generate a homogeneous polymer solution. Then 2.0g Titanium tetra-isopropoxide was added to the solution. Stirred the mixture continuously for another 1 h and made a precursor solution. Calcined them at 550 °C for 2 h to form anatase TiO_2. The sample was collected and then triturated in an agate mortar to obtain fine nanopowders.

Preparation of TiO_2 nanofiber by electrospinning technique

2g of poly (vinylpyrrolidone) powder (PVP, MW = 1 300 000) was measured and added to a mixture of 9ml of absolute ethanol and 5ml of acetic acid in a capped bottle. The obtained solution was stirred at room temperature for 1 h to obtain a homogeneous polymer solution. To which 2.0g Titanium tetra-isopropoxide was added to the solution. The mixture was stirred continuously for another 1 h to make precursor solution. 3ml of the precursor solution was loaded into a 5ml plastic syringe equipped with a blunt metal needle of 0.8 mm outer diameter and 0.6 mm inner diameter. A stainless-steel plate covered with a sheet of aluminum foil was taken as the collector. The distance between the needle tip and collector to 12 cm and the voltage was set between 9-20 kV [**31**]. When the electric field was applied, the polymer solution was highly charged, under electrostatic interaction the solution bulged and Taylor cone was formed. At a critical voltage, a repulsive force was faced by the solution which overcomes surface tension and jet erupted towards the collector [**32**]. The as-collected nanofibers were calcined at 800°C for 2 h to form rutile TiO_2 nanofibers.

Results and discussion

XRD

The Crystal structure of Titanium dioxide (TiO_2) was investigated by using powder XRD.

Structure and Crystallite size of TiO_2 nanopowder and nanofiber

The phase structure of TiO_2 nanopowders and nanofibers was studied by performing X-ray Diffraction experiments using CuK_α radiation. The XRD patterns obtained for TiO_2 nanopowders as well as nanofibers are shown in **Fig. 1**. The obtained patterns show the crystalline nature of the synthesized samples. Diffraction peaks of nanopowders at 2Θ = 25.47, 37.98, 48.15, 54.19, 55.18, 62.9, 70 and 75.3 corresponding to planes (101), (004), (200), (105), (211), (204), (220) and (215) respectively were observed. The peaks were in good agreement with anatase phase of TiO_2 (JCPDS, PDF card 21-1272) [**33**].

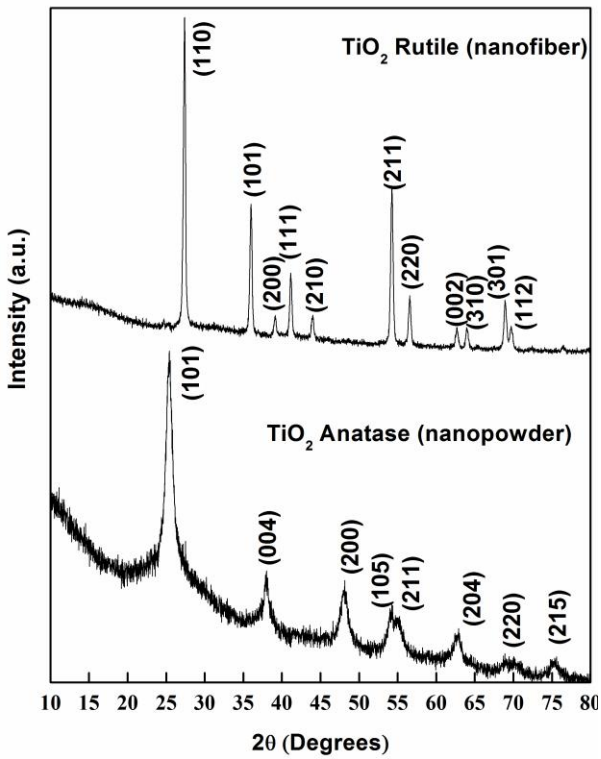

Fig. 1. XRD pattern of synthesized TiO_2 nanopowders and TiO_2 nanofibers.

The peaks of the TiO_2 nanofibers at 2 Θ = 27.37, 36.04, 39.16, 41.06, 44.02, 54.2, 56.51, 62.75, 64, 68.95 and 69.7 which could be perfectly indexed to the planes (110), (101), (200), (111), (210), (211), (220), (002), (310) , (301) and (112) respectively. The obtained data agrees well with rutile phase of TiO_2 (JCPDS, PDF card

21-1276) [**34**]. Both the morphologies adhered well to the tetragonal structure. The lattice parameters of the same were tabulated below.

Table 1. Lattice constants of the synthesized TiO_2 nanopowder and nanofiber.

Sample	Observed		Std JCPDS	
	a(Å)	c(Å)	a(Å)	c(Å)
TiO_2 (nanopowder)	3.759	9.465	3.7842	9.5146
TiO_2 (nanofiber)	4.597	2.9619	4.5933	2.9592

Moreover, the Crystalline size of the nanoparticles was calculated from the XRD spectrum by applying the Scherrer formula,

$$D = K\lambda / (\beta \cos \Theta)$$

where, λ is the wavelength of the X-ray radiation (CuK_α = 1.5406 Å) K is constant taken as 0.9, β is the line width at half maximum height and Θ is the diffracting angle. The average crystallite size of TiO_2 nanopowder was around 8 nm. The average crystallite size of TiO_2 nanofiber was around 26 nm. Furthermore, no peaks corresponding to any other crystalline material were found in the recorded diffractograms.

SEM

Morphological features of TiO_2

SEM is used to investigate the morphological features of TiO_2 nanopowders and nanofibers. **Fig. 2 (a)** and **(b)** shows the SEM image of the TiO_2 nanopowders. The nanopowders were agglomerated spherical particles.

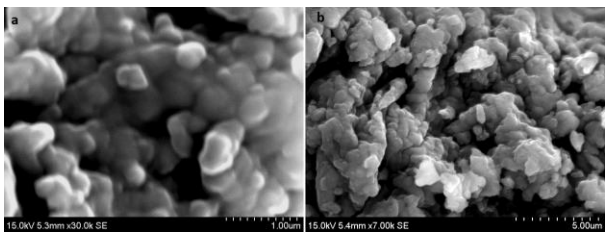

Fig. 2. (a) and (b) SEM image of the TiO_2 nanopowders.

Fig. 3 (a) and (b) shows the SEM image of calcined TiO_2 nanofibers. It could be observed that the pure TiO_2 aligned in random orientation because of the bending instability associated with the spinning jet [**35**]. The surface of TiO_2 was smooth, without any secondary nanostructures.

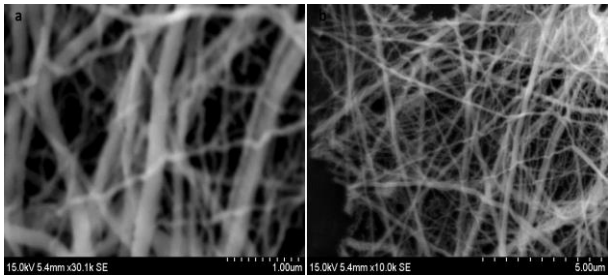

Fig. 3. (a) and (b) SEM image of TiO_2 nanofiber.

The image shows the typical circular fibers were obtained because of the rapid evaporation of the solvent [**36**].

EDX

Fig. 4 and **Fig. 5** shows the Energy Dispersive X-Ray (EDX) spectrum of TiO_2 nanopowders and nanofibers respectively. It indicates that O and Ti elements existed in TiO_2 nanopowders. Ti and O elements were present in electrospun TiO_2 nanofibers [**37**].

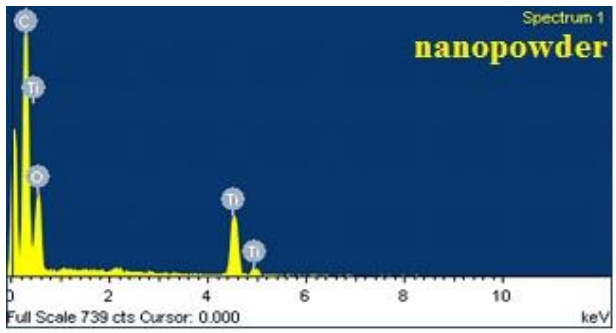

Fig. 4. Energy dispersive X-ray (EDX) spectrum of TiO_2 nanopowders.

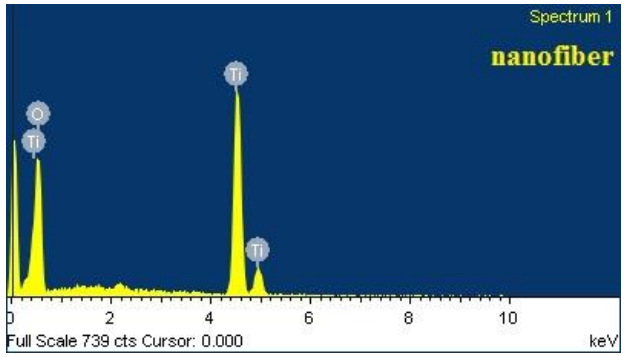

Fig. 5. Energy dispersive X-ray (EDX) spectrum of TiO_2 nanofibers.

Conclusion

Pure Titania nanopowders as well as nanofibers were prepared by conventional Sol-Gel and Electrospinning Technique respectively. Formation of pure phase TiO_2 nanopowders and nanofibers were confirmed by XRD studies. Surface morphology and elemental composition of the materials analysed using SEM and EDX respectively confirmed the formation of TiO_2 nanofibers and nanopowder. Further no other impurities could be detected from EDX Spectra. The doping effects with various metals and transition metals on rutile TiO_2 phase stability of nanofibers and anatase TiO_2 nanopowders are under investigation and will be reported elsewhere in the near future.

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