Electrospun Titania Nanofibers from a Benign and Inexpensive Precursor

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Abstract: *Titanium dioxide or titania (TiO_2) has well-known photoactive antimicrobial attributes. It also readily forms on titanium implants. Recently conducted in vitro studies have demonstrated increased osteoblast functions of nanostructured TiO_2 necessary to promote the efficacy of orthopedic implants. Titania-based ceramics (bulk material, thin films, nanoscale powders, etc.) are generally synthesized by using either a highly corrosive and toxic titanium tetrachloride ($TiCl_4$) and titanium oxychloride ($TiOCl_2$) or rather expensive and moisture sensitive titanium isopropoxide $[Ti(C_3H_7O)_4]$ as the starting chemicals. In this paper, the technique of electrospinning has been used to fabricate non-woven breathable titania nanomats employing titanyl nitrate as a benign and inexpensive precursor.*

Keywords: *Titanium dioxide; Electrospinning; Ceramic processing; X-ray diffraction; Electron microscopy*

1. INTRODUCTION

Titanium dioxide (titania, TiO_2) in pure or doped form has been extensively used in a number of applications, ranging from food coloring, paints, cosmetics, catalysts, antibiofouling, photovoltaic solar cells, sunscreens to gas sensors. In addition, due to its suitable energy band gap ($\approx$ 3.2 -3.5 eV), titania has also gained interest in photonic band gap crystals for the visible spectrum of light due to its high refractive index (nrutile $\approx$ 2.9) and low absorption [1]. Recently, self-cleaning wool-polyamide, polyester and cotton textiles coated with TiO_2 have been also reported [2-7]. One of the unique physical properties of titania is its photocatalysis–a photo-activated antimicrobial/ disinfective activity-where free radicals generated from TiO_2, oxidize organic matter upon activation by light.This property makes the material a candidate for numerous medical applications where infection control is needed. By interposing an effective procedure based on nanotechnology, the bone healing can be made safer and to take place at an accelerated pace, eliminating or mitigating simultaneously the probability of wound infection.

However, the unique photocatalytic property of nanostructured titania as a wound and bone fracture disinfectant has not been exploited hitherto. Constructing non-woven TiO_2 nanothreads and nanomats possessing three-dimensional scaffold structure and

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optimal porosity in conjunction with photo-activated antimicrobial activity could provide a significant improvement in the management of segmental bone defects particularly in the presence of infection. A photoactive TiO_2 nanomat either in pristine form or impregnated with antibacterial agents can be used as an effective ultralight disinfectant gauze for wound healing upon brief activation by light.

Considering that the natural scaffold (extracellular matrix, ECM) consists of a multilayered fibrous and porous architecture, the possibility of utilizing electrospinning as a novel nanomanufacturing technique applicable to tissue engineering has emerged. Several researchers have explored the feasibility of fabricating biothreads containing live cells in benign polymeric matrices that could be used for a number of applications including wound healing and tissue growth. Electrospun fibers are found to possess features that bear morphologic similarity to ECM of natural tissue such as high porosity and effective mechanical properties. They, therefore, meet the essential design criteria of an ideally engineered scaffold [8-9]. We have recently carried out preliminary experiments successfully to attach cells to the electrospun polymeric (poly vinyl pyrrolidone, PVP) as well as ceramic (alumina) nanofibers [10].

With the goal of using nanomats to combat wound infection due to its photoactive attributes, this paper describes the fabrication and characterization of non-woven titania nanofibers, using a simpler and more benign precursor than that has been usually used in the case of titania synthesis. In this case, an aqueous titanyl nitrate $(TiO(NO_3)_2)$ was synthesized from water soluble titanium fluoride (see next section). First, an appropriate ceramic-polymer (cermer) composite of titania electrospun as a continuous non-woven nanofibrillar mat from an optimized mixture of suitable inorganic and polymeric precursor blend. The cermer composite was then processed carefully and the transformation of cermer to high purity, crystallized and morphologically optimized titania was followed by a well-conceived heat-treatment and the systematic phase evolution. The structural and morphological features of the products subsequent to each of such heat-treatments were verified by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) coupled with energy dispersive spectroscopy and selected area electron diffraction (EDS–SAED) techniques. The photoactive efficacy of these electrospun titania nanofibers is currently under investigation and will be reported separately.

EXPERIMENTAL PROCEDURE

Granular polyvinyl pyrrolidone (PVP, average molecular weight ~1.3 × 10⁶, Alfa-Aesar) was used as the polymeric component of the inorganic-organic composite. 15 wt.% PVP solution was made by dissolving PVP powder in reagent grade ethanol (Fisher Chemicals, PA, USA) under constant and vigorous stirring. Due to the pronounced volatility of ethanol during and after the preparation, and the tendency of the solution to dry out and leave a stiff gel in the container upon prolonged storage, the PVP solution was prepared in small batches and only when electrospinning was to be carried out. The inorganic precursor used for electrospinning the cermer composite of titania was made from titanium (IV) fluoride (Alfa-Aesar, MA, USA; purity 98%). In a typical batch

preparation, 1.3254 g of titanium tetrafluoride was dissolved by adding to 50 ml of DI water in small increments over a period of 90 minutes under constant stirring and gentle heating until it dissolved completely giving a clear transparent solution of 0.214 M strength. The resulting solution was diluted with 230 ml of DI water, to which 20 ml of 7.4 N NH_4OH was added slowly under constant stirring. A white precipitate of $Ti(OH)_4$ was formed which was allowed to settle for 2h. The supernatant liquid was tested by adding a few drops of ammonium hydroxide. Absence of formation of fresh precipitate indicated that the reaction was complete.

The $Ti(OH)_4$ suspension was allowed to settle overnight, and tested again for additional precipitation the next day. The supernatant liquid was decanted, the precipitate washed with DI water and centrifuged several times until the decanted liquid acquired a near neutral pH (~8). 15 ml of conc. HNO_3 was added to the hydrated solid $Ti(OH)_4$ [$TiO_2.xH_2O$] under constant stirring, until the precipitate began to dissolve. 10 ml of HNO_3 was added again after 30 minutes and the precipitate started dissolving promptly. After that, every 25 minutes, additional amount of HNO_3 in decreasing volume was added: 5 ml, 3 ml, then finally 2 ml, bringing the total amount of concentrated nitric acid to 40 ml, to completely dissolve the hydrated titanium hydroxide and form titanyl nitrate, $TiO(NO_3)_2$ (TN) - a clear solution with a distinctive luster. It is worth pointing out that titanyl nitrate solution is relatively unstable over long periods and tends to cloud forming hydrated titania again. Therefore, the precursor was synthesized only when needed and was used up quickly over as short period of time.

In order to optimize the electrospinning conditions, the precursor solutions (TN and PVP) were mixed in different volume/volume ratios and stirred into homogeneous viscous solutions. Each of these mixtures (1:1, 1:2 and 2:3 v/v) was drawn into a 10 ml capacity Benton-Dickenson clinical syringe (VWR International, IL, USA). A precision-tip 25 gauge stainless steel needle (EFD Inc., RI, USA) was attached to the syringe, which was mounted on a programmable syringe pump (KDS-100). The preferred orientation of the syringe pump in this work was horizontal. A custom-made dc power supply with the high voltage system (30 kV maximum) from UltraVolt (FL, USA) using modified version of a circuit design developed at NASA Glenn Research Center [11] was used for electrospinning. One terminal of the power supply was connected to the needle, while the other was connected to a grounded stainless steel collector plate.

However, for the ease of sample handling and subsequent thermal processing, ceramic plates instead of metal were used as collector. In order to enhance the fiber collection area, a modified collection set-up was devised. Two (4.5-in. × 4.5-in.) dense alumina plates (0.0625 in. thick, from McMaster-Carr, OH, USA) were employed. The plates were kept ½ -in. apart and connected together to a common junction by attaching short lengths of electrical wires to the center of each plate through blocks of 1-in.² aluminum foil stuck to the back of the plates with double-side tape. This allowed the fibers to spread and collect across the plates including the empty space between them. Other details of this set-up are described elsewhere [12-13].

Using the high-voltage power supply, electrical impulse was applied between the needle and the collectors in order to initiate the e-spinning. After the voltage was turned

on, the syringe pump was started. The voltage was tweaked precisely until the fibers began to form steadily and collect on the plate placed 3-in. away from the tip of the needle; the optimized voltage in this case was found to be 16 kV. A flow rate of 0.02 ml/h was chosen and the *cermer* fibers were spun continuously with short intermittent interruptions of the run for periodic cleaning of the clogged needle-tip from time to time.

After spinning was complete, small amounts of the as-spun composite fibers were used for characterization by scanning electron microscopy. This exercise allowed ascertaining which mixture of the two precursors was the most optimal in terms of the quality of the fibers (free from intertwining, twisting, branching and, liquid globule entrapment, etc.).

The remaining fibers collected on the ceramic plates were fired at 700°C for 1h in static air as per the following heating rate-temperature-soak time profile: 22 (room temperature) to 500°C at a rate of ½° /min. with a hold at 500°C for 1h; 500 to 700°C at a rate of ½° /min. with a hold at 700°C for 1h, followed by cooling from 700 to the room temperature at a rate of 1°/min. The rather small heating and cooling rates were chosen so as to ensure the removal of organic components without destroying the nanofibrillar morphological features in the end product and also to avoid the disintegration of the titania nanofibers into powdery grains. Subsequent to cooling, the samples were collected for characterization by a host of analytical techniques, such as, X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM/TEM), energy dispersive spectroscopy (EDS) and selected area electron diffraction (SAED). The results of photoactivity evaluation and biocidal efficacy of the electrospun titania nanofibers will be reported subsequently.

RESULTS AND DISCUSSION

Caruso *et al.* [14] have prepared hollow titania fibers by soaking the electrospun poly (lactic acid) in a 1:19 (v/v) solution of titanium (IV) isopropoxide and isopropanol, followed by hydrolysis, vacuum drying and calcination at 450°C for 10 h at a ramp rate of 15°/min., 3 h of which were in a nitrogen atmosphere, and 7 h in an oxygen atmosphere. The amorphous titania fibers so obtained were shown to be porous and 500 nm across. As is evident, the technique involves several time-consuming processes: electrospinning of the polymeric skeleton first; preparing of inorganic sol, followed by gel formation and its hydrolysis onto the electrospun polymeric fibers, before the organics are removed to yield the desired ceramic nanofibers. Moreover, the authors claim that the surface of the fiber is not flat but contains small oval indentations, which are due to rapid phase separation during the electrospinning process, where the solventrich regions result in pore formation. This statement equivalent to the postulation of the existence of a 'concentration gradient' region in the dynamic process of fiber formation, is rather speculative and unsubstantiated; this is particularly so, in the light of the absence of any visible 'thinning' along the fiber length. It this were true, one should certainly observe some collapsing and narrowing of the uniform tubes to form 'sheets', in the high magnification micrographs shown by them.

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A similar procedure has also been adopted by Drew et al. [15] to synthesize metal (tin and titanium) oxide coated polymer nanofibers with diameter of the order of 100 nm and coating thickness ranging from 20 to 80 nm. The preparatory technique used here also is quite elaborate and involved, uses complex salts (such as ammonium hexafluorotitanate and ammonium hexafluorostannate) as the precursors and requires a halide scavenger in the form of boric acid. Furthermore, as seen from the SEM images, the metal oxide coating is uneven and non uniform and the TEM images confirm this. Choi et al. [16] have used a sol of titanium and silicon to electrospin silica-doped titania nanofibers onto a rotating drum. They obtained the ceramic fibers by firing them for 2h in the temperature range 500-1000°C. However, while the SEM images of the as-spun fibers and those dried (wrongly called 'calcined' in the paper) at 100°C for 2h alone are shown; no micrographs of the fired samples were included. Hence, the morphological features of the samples calcined in the range 500-1000°C is unknown.

Li and Xia [17] have reported the fabrication of anatase titania porous nanofibers of controlled diameter using an ethanol solution containing both poly(vinyl pyrrolidone) (PVP) and titanium (IV) isopropoxide, via electrospinning followed by calcination in air at 500°C. They shows that the average fiber diameter ranged between 20 to 200 nm depending upon a number of parameters such as the strength and ratio of PVP and titanium (IV) isopropoxide solutions, the strength of the applied electric field, and the flow rate of the precursor solution.

As can be clearly seen from above, the synthesis of pure and/or doped titania nanofibers via electrospinning: (a) involves elaborate routes, or (b) uses either a complex (ammonium fluorotitanate, for example) in combination with a halide scavenger, or a relatively expensive and moisture-sensitive titanium (IV) isopropoxide, as a precursor. Moreover, those cases a technique of coating an electrospun polymeric skeleton with titania precursor followed by calcination, do not produce the as-desired uniform and homogeneous ceramic fibers. In contrast to that, the present work describes the procedure of synthesizing a simple titanium precursor (viz., titanyl nitrate) from a less reactive and benign source (TiF_4) and employs it in the fabrication of high quality titania nanofibers.

As stated above, in order to ascertain an optimized composition that is conducive to yield uniform cermer nanofibers, the aqueous solution containing titanyl nitrate and the PVP solution in ethanol were mixed in three different v/v ratios: 1:1, 1:2 and 2:3, keeping other experimental variables (applied electric field strength, flow rate, the distance between the needle and the collector plates, etc.) constant. The SEM images (Philips XL30 FEG SEM) of the as-spun nanofibers from each batch are shown in Figure 1.

As seen from Fig. 1 (a-b), the fiber spun from a 1:1 (v/v) mixture of the inorganic and organic components are characterized by the present of a large fraction of nearly spherical liquid globules connecting various segments of the fibers. Thus, it appears that this mixture is subject to the combined phenomena of electrospraying (spherilization of the charged droplet upon discharging) and electrospinning. Large population of globules rather than linear fibers, suggest that mixture might not have attained the optimal viscosity in order to satisfy the conditions of forming perfect non-woven fibers. For this purpose, the polymeric content of the solution was increased in the ratio TN: PVP = 1:2. The

SEM images displayed in Fig. 1 (c-d) above indicate that this strategy helped, as the density of liquid blobs greatly diminished, though was not eliminated totally. Some evidence of fiber bending can also be seen, which indicates that the ratio of the two components in the spinning mixture still needs to be optimized. The 2:3 (v/v) mixture of TN: PVP appeared to form the most desired microstructure when electrospun, as could be seen from the nonwoven fibers of uniform thickness in Fig. 1 (e-f). The subsequent discussion pertains to the fibers which were electrospun from a homogeneous solution containing the inorganic and organic precursors in the volumetric ratio of 2:3.

The morphological features of the fired nanofibers of electrospun titania are shown in Fig. 2a. The intact nature of the fibers in the layered mats of titania that were present in the as-spun material, can be discerned in the calcined sample as well. This is by virtue of the judicious firing scheme adopted in this work; even a slightly higher ramp rate has
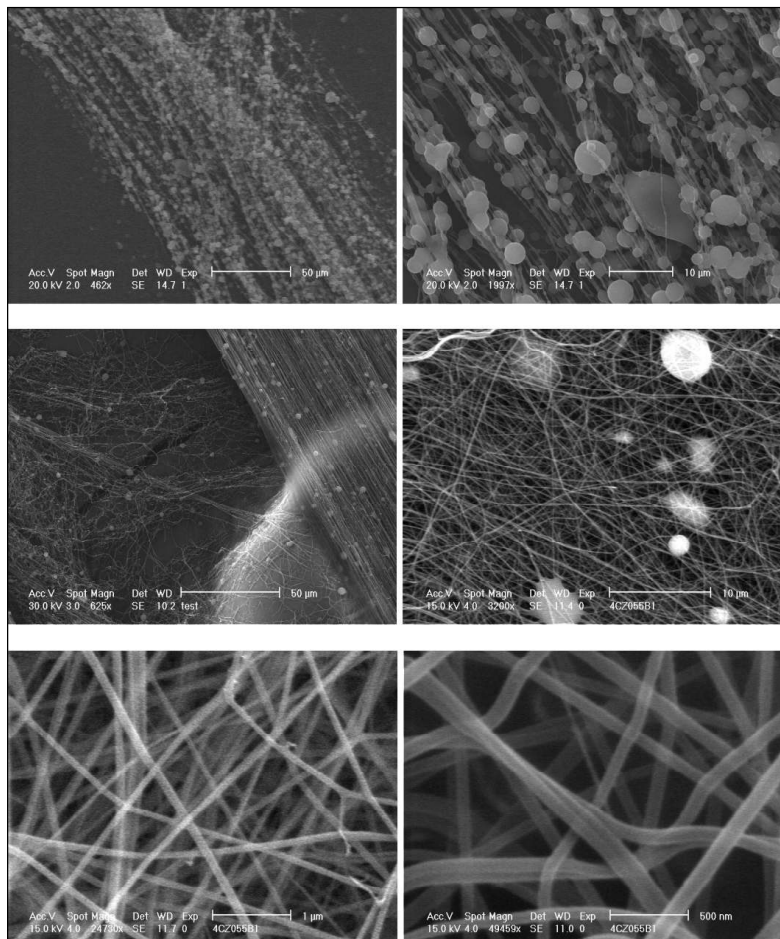

Figure 1: SEM Images of the Cermer Nanofibers Spun from a Solution Containing TN and PVP in Volumetric Ratio of 1:1 (a-b); 1:2 (c-d) and 2:3 (e-f).

been found to cause severe fiber rupturing, rendering them into powdery mass, due to faster combustion of the polymer with a concomitant and sudden release of copious amount of gaseous products. The energy dispersive spectrum (EDS) of the same is shown in Fig. 2b, where the signals due to oxygen and titanium alone are seen; no peak belonging to carbon are present, meaning that the heating profile selected in this work was able to get rid of polymeric components quantitatively.

The TEM images of the nanofibers fired at 700°C as per the schedule described in the previous section are shown in Fig. 3.

It is evident that the heat treatment used in the present work has preserved the fibrous artifact in the processed material. Moreover, the titania fibers are porous and ¡Ü 100 nm across, comprising of interconnected monosized grains, making the structure quite breathable and therefore, amenable for the intended medical application. Using the wavelength of the electron beam (0.0335.) and the length of the SAED pattern on the film, the interplanar distances (d-spacings) for successive diffractions were calculated. They correspond to the ICCD card # 84-1286 for the anatase phase of titania. This is corroborated by the X-ray diffraction pattern (collected on a Philips PW 3050/60 X'pert Pro) of the powdered nanofibers, as shown in Fig. 4; the selected area electron diffraction signature of the calcined fibers is also shown as an inset.
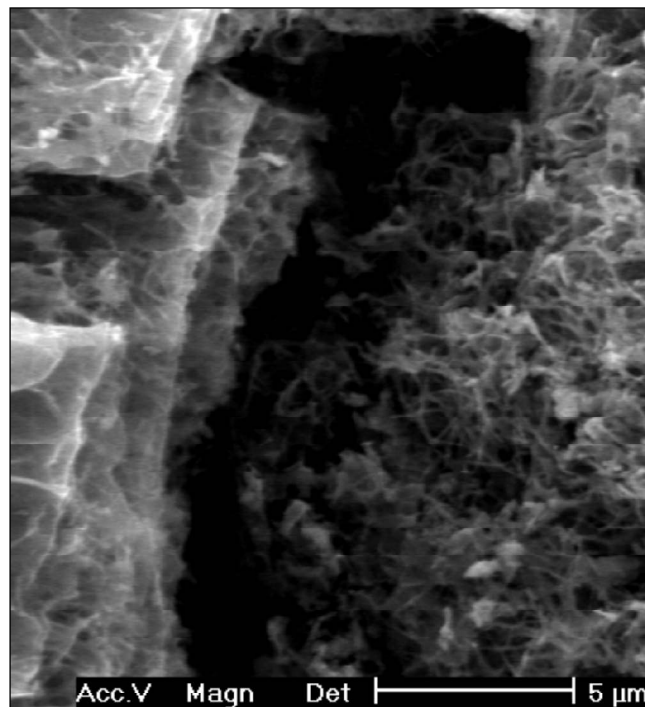

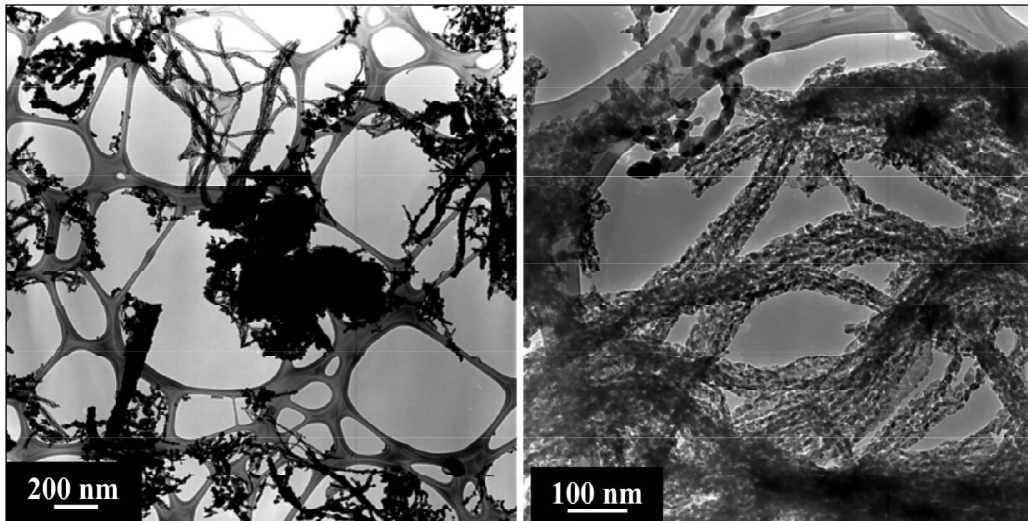Figure 2: (a) SEM Image and (b) EDS Signature in the Cermer Composite Fired at 700°C/1h.

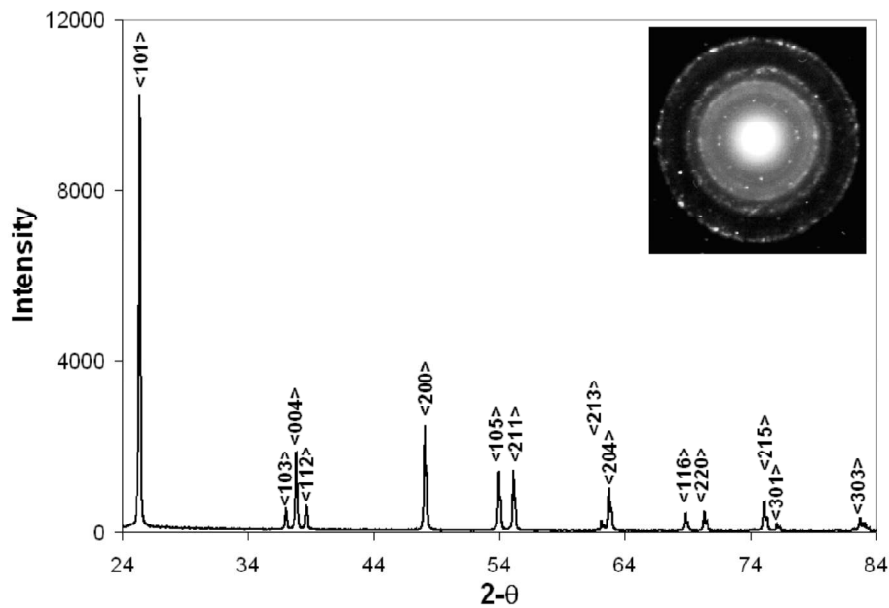Figure 3: TEM Images Cermer Nanofibers Fired at 700°C/1h.

Figure 4: XRD Signature of the Nanofibers Calcined at 700°C/1h (inset: SAED pattern).

CONCLUSION

Titanium dioxide nanofibers were successfully electrospun as a polymeric composite from a benign and inexpensive titanium precursor, viz., titanyl nitrate and polyvinyl pyrrolidone. The as-spun cermer fibers possessing uniform thickness upon firing resulted into breathable titanium dioxide nanomats of anatase modification upon a single-stage firing in air at 700°C for 1 h.

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