Synthesis and Characterization of Titania Nanostructures

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Nanotechnology has entered a revolutionary stage where the structure and properties of materials can be investigated, characterized and controlled at the nanoscale. New physical properties tend to appear at the nanoscale, giving rise to novel material performance characteristics. These unusual properties have attracted enormous interest in their potential for applications in magnetic, optical, electronic and other devices. Current interests in nanostructured materials have stimulated renewed efforts in electrospinning.

Electrospun nanostructures have large surface-to-volume ratios compared to conventional textile fibers. The large surface areas enhance properties such as adsorption of chemicals. Electrospinning was first explored in the 1930s [1] as a simple and versatile method for making fibers from polymer solutions with diameters typically ranging from 10 to 500 nanometers. The length of electrospun nanofibers depends on the time of electrospinning and can be kilometers in a short period of time.

Electrospinning combined with sol gel coating can be used to synthesize titania nanostructures. Recently, electrospinning + sol gel has proven to be a versatile and reliable method of synthesizing nanostructures. Polymer nanofibers can be synthesized using electrospinning of 20 wt% nylon-6 beads and 80 wt% formic acid. A rotating drum apparatus depicted in Fig. 1 was constructed to collect continuous nanofibers. Large sheets of nanofibers as shown in Fig. 1 were collected after 8 hours of spinning time. The apparatus consists of a high voltage power supply, a rotating cylindrical collector, and a syringe pump. Flow rate of the polymer solution can be controlled using the syringe pump. Two syringes containing polymer solution are placed on the syringe pump. In general multiple syringes are used to increase the production rate of nanofibers, since multiple syringes drive more solution than a single syringe. The high voltage power supply has two terminals, the high voltage terminal was connected to the needle containing solution and the grounding terminal was connected to a conducting sheet on which the fibers are collected. The conducting sheet is placed on the surface of the cylinder of the rotating drum. Aluminum foil is generally used as a conducting sheet in our laboratory. A pendant drop is formed at the tip of the pipette, and voltages of around 20 kilovolts are used to create electrical forces at the surface of the drop. The resulting fields overcome surface tension and create an electrically charged jet [2]. Polymer jets run continuously, producing a nanofiber that may be many kilometers in length, which is usually collected as a non-woven sheet.

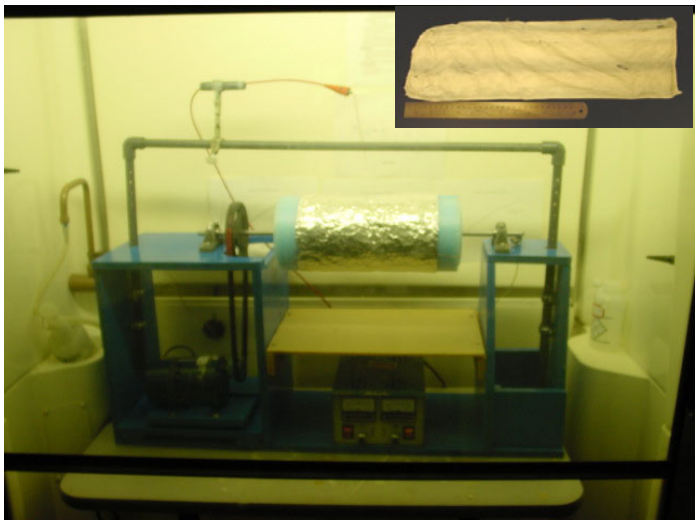

Fig. 1 Rotating drum apparatus along with large sheet of nanofibers electrospun in our laboratory. The scale in the foreground of the inset is a 12 inch (30 cm) ruler.

The electrospun polymer nanofibers are coated using a modification of a published sol-gel recipe [3]. A detailed discussion on sol gel processing was given by M. Gopal et.al.[3], G. Emig et. al. [4], and B.B. Lakshmi et. al. [5]. Sol gel precursor was prepared using pure titanium isopropoxide (Sigma Aldrich), pure isopropanol (Fisher Scientific), 5 M nitric acid (Fisher Scientific) and triply distilled filtered water. The chemicals were used as received without further purification. The concentration of the nitric acid was reduced to 5 M by addition of triply distilled filtered water. 144 ml of distilled water was mixed uniformly with 20 ml of 5 M nitric acid under vigorous stirring. 10 ml of isopropanol was added to the resultant solution drop by drop under stirring. Cloudiness formed instantaneously after adding 2 ml of titanium isopropoxide, and a transparent solution was produced after aquasonicating for 30 minutes. The polymer mats electrospun earlier were soaked in the sol gel solution for hydrolysis and condensation reactions. The whole mixture was kept at 60 ^{o}C for 3 hours in order to obtain rutile coated polymer nanofibers. The same procedure, but at 90 ^{o}C for 1.5 hours was used to create anatase coated titania nanofibers. Milky white precipitate was observed indicating the formation of titania nanoparticles.

Anatase to rutile transformation takes place around 400 ^{o}C [6,7]. The crystalline structure of the titania can be altered by controlling the synthesis temperature and the concentration of the nitric acid in the sol gel recipe. The unique properties of nanocrystalline titania materials can be exploited for various applications. The crystalline state is very crucial for some applications. Amorphous titania is used for optical coatings [8,9] whereas rutile is used for dielectric layers due to higher dielectric constant [10,11]. Uniformly coated polymer nanofibers are heated above the melting temperature of the polymer (275 ^{o}C) in order to degrade polymer template. The sol gel coated nanofibers retain the fibrous morphology even after melting of the polymer nanofibers. Calcination at 300 ^{o}C and 700 ^{o}C produced pure anatase and rutile titania nanofibers, respectively.

Scanning electron microscope (SEM) images of rutile titania coated nanofibers having diameters about 200 nm can be seen in Fig. 2A. Fig. 2B is an image of titania nanofibers after sol-gel processing and slow heating to 275 ^{o}C in an oven for 2 hours. Heating the resultant

nanofibers to 700 ^{o}C pyrolizes the nylon-6 completely, leaving titania nanofibers with 150 nm diameters as seen in Fig. 2C. Shrinkage in the diameter of the nanofibers is observed when the nanofibers are heated, due to the thermal degradation of the polymer.

Scanning Electron Microscopy, Transmission Electron Microscopy, Fourier Transform Infrared Spectroscopy and X-Ray Diffractometer were used to study the diameter, size distribution, phase and crystalline structure of the titania nanostructures.

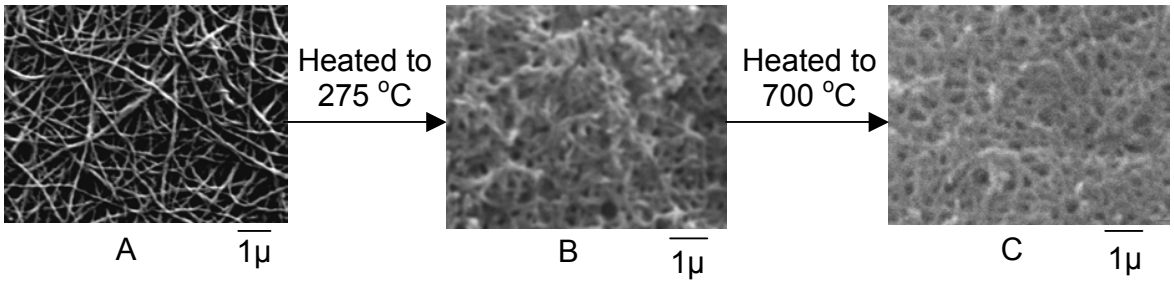

Fig. 2 (A) SEM image of titania coated nylon-6 nanofibers. (B) SEM of titania coated nylon-6 nanofibers heated at 275 ^{o}C for 2 hours. (C) SEM image of titania nanofibers heated at 700 ^{o}C for 2 hours.

Keywords: Nanostructures, electrospinning, sol gel.

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References:

(1) Formhals, A. US Patent No. 1975504, **1934**
(2) Yarin, A. L.; Koombhongse, S.; Reneker, D. H.; (2001) *J. Appl. Phys* **89***,* 3018.
(3) Gopal M.; Moberly Chan W.J.; De Jonghe L.C.; (1997) J. Mater. Sci. **32,** pp.6001
(4) Emig G.; Wirth R.; Zimmermann-Chopin R.; (1994) *J. Mater. Sci.* **29,** pp.4559
(5) Lakshmi B. B.; Dorhout P.K; C.R. Martin; (1997) *Chem. Mater.* **9,** pp. 857
(6) Zhang H.; Banfield J.F.; (1999) *Am. Mineral.* **84**, pp. 528
(7) A. A. Gribb, J. F. Banfield: American Mineralogist **82**, 717-728, 1997.
(8) Harris A. W.; Ludden B.P.; Bailey D.C.; (1992) *Vacuum* **43**, pp. 143
(9) Falaras P.; Xagas A.P; (2002) J. Mater. Sci. **37**, pp. 3855
(10) Kim E.K.; Son M.H.; Min S.K.; Han Y.K.; Yom S.S.; (1997) *J. Cryst. Growth* **170**, pp. 803
(11) Insignia A. S.; Grace J. R.; Bai D.; Zhu J.; (2000) *Powder Technology* **111**, pp.104