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Centrifugal Jet Spinning for Highly Efficient and Large-scale Fabrication of Barium Titanate Nanofibers

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Abstract

The centrifugal jet spinning (CJS) method has been developed to enable large-scale synthesis of barium titanate nanofibers. Barium titanate nanofibers with fiber diameters down to 50 nm and grain sizes around 25 nm were prepared with CJS by spinning a sol-gel solution of barium titanate and poly(vinylpyrrolidone) with subsequent heat treatment at 850 °C. XRD and FTIR analysis demonstrated high purity and tetragonal perovskite structured barium titanate nanofibers. SEM and TEM images confirm the continuous high aspect ratio structure of barium titanate nanofibers after heat treatment. It is demonstrated that the CJS technique offers a highly efficient method for large-scale fabrication of ceramic nanofibers at production rates of up to 0.3 gram/minute.

1. Introduction

One dimensional ceramic nanomaterials including nanorods, nanoplates and nanofibers are widely used as building blocks in nanotechnology due to their unique structure and properties such as high aspect ratio, large specific surface area and chemical/mechanical stabilities [1-4]. One dimensional ceramic nanostructures have been synthesized by various processes, including, hydrothermal [1,5,6], laser ablation [7,8], chemical vapor deposition (CVD) [9-11] and electro-spinning [12-14]. The shared disadvantages of current fabrication methods for one dimensional nanomaterials include, complex processing parameters (e.g. reaction temperature, pressure), low yield, low efficiency, long duration, and costly equipment (e.g. reaction chamber, autoclave) and processes [7,11,14]. For example, the yield of ceramic nanofiber with traditional electro-spinning method is about 1 mg per hour [15-17]. The low yield and efficiency of electrospinning would raise the fabrication cost of ceramic nanofiber as advanced functional materials in devices. Thus, methods capable of increasing yield and efficiency for generating one dimensional nanomaterials are of great interest for promoting their further application in various engineering fields.

Ferroelectric materials like barium titanate exhibit spontaneous polarization without an externally applied field that can be reversed and reoriented with the direction of an externally applied field [18-20]. Barium titanate has been extensively studied as it displays strong microwave absorption properties, a potential to increase ferroelectric non-volatile memory density, and high-performance capacitors [16-21]. High aspect ratio BaTiO₃

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nanostructures (nanorods, nanowires, nanotube and nanofiber) have been studied and synthesized because of their potential to increase ferroelectric non-volatile memory density by orders of magnitude [23-25]. The unique properties of high aspect ratio BaTiO₃ nanostructures are critical to study nanoscale material ferroelectricity and are also important in light of miniaturizing piezoelectric transducers and actuators [21,22], ultrasonic devices [26], switchable aircraft antenna systems and medical imaging detectors [27].

In this letter, we use a novel, facile, efficient and low cost fabrication technique, termed centrifugal jet spinning, to make barium titanate ceramic nanofibers. The centrifugal jet spinning (CJS) technique utilizes the centrifugal force of a DC motor and viscous characteristic of liquids to generate continuous fiber structures. The CJS system consists of a DC motor powered hollow chamber with two orifices passing through the chamber wall and a set of product collecting rods. Comparing to electro-spinning method, CVD/PVD method and hydrothermal method, the cost of CJS spinning system is as low as \$10 while usually a single reaction chamber/autoclave required for CVD/PVD method/hydrothermal method could cost up to thousand dollars. It is also found that the production rate of nanofiber with CJS technique is up to 1 gram per minute in our previous study [28]. In this report, we aim to fabricate barium titanate ceramic nanofibers by heat treating fibers obtained by spinning a sol-gel solution using the CJS technique. The sol-gel is created by mixing precursors of barium titanate with a polymer solution (10 wt% polyvinylpyrrolidone in ethanol). Synthesis of BaTiO₃ ceramic nanofiber can be an example for large-scale and highly efficient fabrication of other ceramic nanofibers with the CJS technique.

The configuration of the system is shown schematically in Figure 1. Spinning solutions are continuously fed into the chamber at a certain flow rate. As the motor spins, the centrifugal force exceeds the capillary force of the spinning solution in the orifice, resulting in jets of spinning solution being ejected from the rotating chamber. The ejected solution jet gets thinner and elongated due to shear forces generated by a combination of centrifugal forces, resistance with air, and evaporation of solvent. The inherent viscosity of the solution jet maintains its continuous structure. The extent to which the jet thins determines the final diameter of the fiber, and one of the factors influencing this is the angular speed of the spinning chamber. The higher the angular speed of the spinning chamber the larger the centrifugal force experienced by the solution jet. The angular speed can be translated into the chamber rotational speed in this case. As the spinning process proceeds, the evaporation of solvent makes the solution jet thinner until the liquid jet solidified into fibers. The collection posts were positioned radially in the system to collect solidified fibers in between the rods. A flexible air tape was attached on the spinning chamber and an aluminum sheet encircles the periphery of the system beyond the collecting rods in order to manipulate the air and to create couette air flow in the spinning system. The formation of couette air flow in the system facilitates the collection of fibers during the spinning process. In the previous study [28], we characterized the influence of spinning solution viscosity, solution jet surface tension, chamber rotational speeds (i.e. centrifugal force), solvent volatility, chamber wall thickness, orifice sizes and ambient parameters (humidity, type of atmosphere and pressure) on the morphology of the obtained fibers. The fabrication process of barium titanate nanofiber is optimized according to the phase diagram of spinning solution viscosity and spinning chamber rotational speeds provided in the previous study [28].

2. Experimental method

2.1 Materials fabrication

2.1.1 Synthesis of spinning solution—To prepare the sol-gel precursor of barium titanate, barium acetate and titanium isopropoxide were used as starting materials with 1:1 molar ratio to achieve stoichiometric BaTiO₃. First, 1.275 g of Ba(CH₃COO)₂ was dissolved

in 6 ml of acetic acid and stirred for 10 minutes. Then 1.475 ml of $[(\text{CH}_3)_2\text{CHO}]_4\text{Ti}$ was added drop by drop under continuous stirring. PVP ($M_w = 1,300,000$ Da; $\text{PDI} = 2.5$) and ethanol (200 proof) were used without further purification. PVP was dissolved in ethanol and sonicated for 5 minutes to prepare 10 wt% uniform polymer solutions. The resulting PVP-ethanol solution was added into the barium titanate sol-gel continuously with vigorous stirring followed by vortexing. All chemicals were purchased from Sigma-Aldrich and used without further purification.

2.1.2 Centrifugal jet spinning (CJS) for generating barium acetate nanofibers

—A hobby motor (9-18 volts, Radio Shack®) was used to power the CJS system. The rotating hollow chamber was machined from Teflon tubes, and has a outer diameter of 15 cm and an inner diameter 10 cm. The side orifices through the chamber are 400 μm in diameter. The rotational speed control is realized by changing the voltage supplied to the motor. A home-made brass coupling was used to connect the motor shaft with the rotating chamber. Spinning solutions were spun under 7000 rpm and 9000 rpm respectively. All spinning experiments were performed in ambient at room temperature. The feed rate of the spinning solution was held constant at 1 ml/min. The distance between the center of the chamber and the product collecting rods is 15 cm in this study. After spinning the PVP-BaTiO₃ composite fiber, the composite fibers were calcinated in the furnace at 850 °C for 6 hours to obtain BaTiO₃ nanofiber.

2.2 Materials characterization methods

2.2.1 Scanning electron microscopy (SEM)—All samples were sputter coated before observation with SEM (Supra 55 Carl Zeiss, Germany). SEM images were taken at three different locations for each sample with different magnifications. The fiber diameter distributions were analyzed with the help of ImageJ software.

2.2.2 X-ray diffraction (XRD)—The XRD patterns were recorded on a Panalytical X'Pert diffractometer (Westborough, MA) using Cu K α radiation with a nickel filter. BaTiO₃ nanofibers were grounded and placed in a zero background silicon holder for XRD pattern scanning.

2.2.3 Fourier transform infrared spectroscopy (FTIR)—FTIR spectra of silica nanoparticle and silica nanofibers were obtained using a Perkin Elmer Spectrum One FTIR spectrometer (Waltham, MA). Potassium bromide (KBr) powder was first dried at 300 °C for 2 hours, and then was blended with barium titanate nanofibers before tests. The resulting mixture was pressed into pellets for analysis. Thirty-two scans were averaged to obtain the final signal. Baseline correction was made based on the background spectrum collected before the test.

3. Results and discussions

The polymer feed rate of precursor solution into the chamber was 1 gram per minute, which because of the high rotational speed was ejected soon after it entered the chamber. Measurements of weights of fibers before and after calcination resulted in an estimated production rate of barium titanate ceramic fibers at 0.3 gram per minute. The SEM images of electrospun barium titanate fibers and the fiber diameter distributions are shown in Figure 2. Diameters of 50 fibers were measured with Image_J to obtain the fiber diameter distributions. Figure 2(a) and Figure 2(e) show PVP-BaTiO₃ composite fibers spun at 7000 rpm and 9000 rpm respectively. It is demonstrated in Figures 2(c) and 2(g) that the average composite fiber diameter decreased from 1.497 μm to 788 nm with increasing spinning speed. The morphology of BaTiO₃ nanofibers after calcination are shown in Figures 2(b)

and 2(f), respectively. The decomposition of PVP reduced the average diameter of BaTiO₃ nanofibers to 208 nm and 99 nm as analyzed in Figure 2(g) and 2(h). The fiber diameter of BaTiO₃ nanofiber is tuned by varying the rotational speed of the spinning chamber. Increasing of rotational speed reduces the fiber diameter of PVP-BaTiO₃ fiber and annealed BaTiO₃ nanofiber. The fiber diameter distribution is narrower for both as-spun composite fiber and annealed nanofiber synthesized at 9000 rpm than 7000 rpm. After thermal treatment, the smooth surface of the composite fibers was transformed into granulated polycrystalline surface with BaTiO₃ grains. The grain size was measured with Image J, which gives an average grain size of 26 nm. The continuous microstructure of the composite fiber was maintained after decomposition of PVP. Figure 3 shows the TEM images of BaTiO₃ nanofiber collected after thermal annealing. The bright field TEM image shows that the fiber consists of grains with size around 25 nm which is consistent with the grain size measurement from SEM images. The SAED pattern of the individual grain from BaTiO₃ nanofibers in the inset of Figure 3 (b) is found to be along the [001] zone axis. The diffraction spots of (010) and (100) planes are characteristics of crystalline BaTiO₃. SEM images and TEM images confirm the formation of BaTiO₃ nanofiber with diameter down to 50 nm with grain sizes around 25 nm.

The structural characteristics and phase purity of the synthesized PVP-BaTiO₃ composite fibers and BaTiO₃ nanofibers were investigated using an X-ray diffractometer. X-ray diffraction (XRD) patterns of as-synthesized composite fibers and annealed barium titanate nanofibers are shown in Figure 4. XRD patterns of the composite fibers in Figure 4 (a) do not exhibit a sharp Bragg peak, which indicates an amorphous structure of the PVP-BaTiO₃ fibers. After heat treatment at 850 °C, the XRD pattern (b) in Figure 4 confirmed the well-defined tetragonal structures with the *P4mm* Space group (JCPDS card No. 05-0626) [29-31]. Other peaks did not appear in the diffractogram, which indicated that decomposition of PVP upon heat treatment did not leave any residue. The crystallographic analysis of obtained BaTiO₃ nanofiber from both the SAED and XRD confirms the tetragonal perovskite crystal structure of BaTiO₃ nanofiber. Ferroelectricity induced nonvolatile electric polarization is one of the important properties of the perovskite crystal structured BaTiO₃ which received considerable attention because of their potential utilization in nonvolatile memory devices [32-35].

FTIR spectra of as-synthesized fibers and annealed barium titanate nanofibers are collected and presented in Figure 4. In the PVP-BaTiO₃ composite fiber spectra, the absorption peaks at 2956 cm⁻¹, 1660 cm⁻¹ and 1280 cm⁻¹ represent the C-H, C=O and C-N stretching vibration respectively in PVP [36-38]. In the FTIR spectra of BaTiO₃ nanofiber, the characteristic peaks for PVP are absent indicating the complete removal of PVP. The prominent absorption band at 615 cm⁻¹ suggested the stretching of Ti-O stretching vibrations and the occurrence of the octahedral TiO₆ connected with each other [31]. The peak at 560 cm⁻¹ comes from the stretching vibration of TiO₆-Ba bond [39,40]. FTIR also validates the XRD data analysis in demonstrating the formation of high purity BaTiO₃ nanofiber after heat treatment of PVP-BaTiO₃ fibers. Thus, it is demonstrated that the CJS technique is capable of synthesizing high purity tetragonal structured BaTiO₃ ceramic nanofibers with subsequent heat treatment.

4. Conclusion

In this paper, sol-gel precursors of barium titanate and polymer solution were utilized to spin composite nanofibers using the CJS technique. Subsequent heat treatment resulted in barium titanate fibers with an estimated production rate as high as 0.3 gram/minute. The diameter of barium titanate nanofibers is tunable by changing the rotational speeds of the spinning chamber with finest nanofiber diameter down to 50 nm. The formation of

tetragonal structured perovskite barium titanate nanofibers was characterized with XRD and FTIR to confirm the high purity and crystal structure of the resulting barium titanate nanofiber. The morphological and structural analysis demonstrated that the CJS technique can offer a highly efficient, simple and versatile method for synthesizing barium titanate ceramics nanofibers with thermal treatment. The CJS technique could be potentially used to large-scale fabrication of other ceramic nanofibers.

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Highlights

- We introduce a simple and highly efficient fabrication method of ceramic nanofiber
- BaTiO₃ nanofiber assembly was fabricated from Centrifugal jet spinning(CJS)
- CJS production rate is 500 times higher production rate compared to electrospinning
- The morphology of BaTiO₃ ceramic nanofiber can be easily controlled

Figure 1. Schematic drawing of the CJS system

Figure 2.

SEM and fiber diameter distribution before and after calcination obtained by spinning at two different speeds, 7000 rpm and 9000 rpm, are shown in (a-d) and (f-h) respectively. (a) PVP-BaTiO₃ fiber spun at 7000 rpm; (b) BaTiO₃ nanofiber annealed at 850 °C from composite fiber spun at 7000 rpm; (c) diameter distribution of PVP-BaTiO₃ fiber spun at 7000 rpm; (d) diameter distribution of BaTiO₃ fiber annealed at 850 °C from composite fiber spun at 7000 rpm; (e) PVP-BaTiO₃ fiber spun at 9000 rpm; (f) BaTiO₃ nanofiber annealed at 850 °C from composite fiber spun at 9000 rpm; (g) diameter distribution of PVP- BaTiO₃ fiber spun at 9000 rpm; (h) diameter distribution of BaTiO₃ fiber annealed at 850 °C from composite fiber spun at 9000 rpm.

Figure 3.
(a) BaTiO₃ nanofiber annealed at 850 °C from composite fiber spun at 7000 rpm; (b) BaTiO₃ nanofiber annealed at 850 °C from composite fiber spun at 9000 rpm. (Scale bar: 50 nm) with inset of selected area diffraction pattern of BaTiO₃ nanofiber.

Figure 4. XRD pattern of PVP-BaTiO₃ composite fiber as spun (a) and BaTiO₃ nanofiber annealed at 850 °C (b).

Figure 5. FTIR spectra of PVP-BaTiO₃ composite fiber as spun and BaTiO₃ nanofiber annealed at 850 °C.