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Preparation and characterization of barium titanate nanofibers by electrospinning

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Abstract

PVP–$BaTiO_3$ composite nanofibers were successfully prepared by electrospinning and pure $BaTiO_3$ fibers were produced after calcination at 1000 °C. A homogeneous viscous solution of barium acetate + titanium acetate/titanium isopropoxide in poly vinyl pyrrolidone (PVP) was prepared by varying PVP concentration in the range of 8–12%. The above sols were electrospun at 9 kV DC by maintaining tip to collector distance (TCD) of 7 cm. The electrospun fibers were calcined at 1000 °C for 2 h. Thermo gravimetric analysis (TGA) of the fibers indicates the complete decomposition of organics below 700 °C with 45% weight loss. Scanning electron microscopy (SEM) study shows the fibers cylindrical, smooth with diameters in the range of 50–400 nm and the aspect ratio >1000. The average diameter of the fibers increases with the increase in PVP concentration. The calcined $BaTiO_3$ nanofibers were found to be coarse, brittle and diameter reduced by 12%. FT-IR study confirms the formation of metal oxide bond at higher temperature.

Keywords: Electrospinning; Barium titanate; Poly vinyl pyrolidone

1. Introduction

Barium titanate ($BaTiO_3$) is one of the most extensively studied ferroelectric material with wide range of applications as dielectric capacitors, in non-volatile ferroelectric random access memories, as transducers, as sensors and actuators, in solid oxide fuel cells etc. [1,2]. The ferroelectric properties of $BaTiO_3$ are expected to improve further if prepared in nanofiber form due to their high surface area to volume ratio. Also, ultra thin sheets of nanofibers are handy for miniaturization, therefore, would find applications in nanoscale capacitors, high density dynamic random access memory, ferroelectric random access memory etc. [3].

Electrospinning is a very simple and straight forward technique for the preparation of polymer and oxide nanofibers [4–6]. The process involves the application of a strong electrostatic field to a polymer solution or a homogeneous polymer and oxide precursor sol placed in a container with a metal capillary such as a syringe with metallic needle. The positive terminal of a high DC source is connected to the needle while the negative terminal is connected to the counter electrode, in the form of a metal plate or aluminum foil placed at a distance of about 10 cm. Under the influence of the electrostatic field, the solution experiences repulsive force. As the voltage surpasses a threshold value, electrostatic forces overcome the surface tension, and a fine charged jet is ejected. The jet moves toward the counter electrode, subdivides into large numbers due to high repulsive force, finally deposits in the form of nanofibers on the counter electrode. Initially, this technique was used for the preparation of polymer nanofibers [7]. In recent years; this technique has been used for the preparation of metal oxide/ceramic nanofibers such as alumina, silica, zirconia, titania, nickel oxide, tin oxide, lead zirconate titanate and other oxide materials [8–17].

Although, barium titanate nanofibers were prepared by earlier researcher [18–20] using high molecular weight PVP, a detailed study on variation of PVP/$BaTiO_3$ on fiber morphology is missing. In this paper, an attempt has been made to prepare $BaTiO_3$ nanofibers with different solid loadings and their effect on fiber morphology was studied.

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2. Experimental

2.1. Materials

Barium carbonate ($BaCO_3$) powder (99.0% purity, analytical reagent grade), ethyl alcohol (99.5%) and glacial acetic acid were purchased from M/s. S D Fine Chemicals, Mumbai, India. Titanium-isopropoxide purchased from M/s. Himedia and poly vinyl pyrrolidone (PVP), Mw = 40,000 was procured from M/s. Loba chemie. The above materials were used as starting materials without any further purification.

2.2. Preparation of the composite precursor solution

0.985 g of barium carbonate was dissolved in 3 cc of acetic acid with constant stirring for 1 h to obtain a clear solution of barium acetate. To this solution, 1.475 cc of titanium-isopropoxide was slowly added under continuous stirring to get a clear solution. An 8% PVP solution was prepared in ethyl alcohol. 3 cc of PVP solution was mixed with already prepared barium titanate solution and was continuously stirred for 2 h to obtain a viscous sol suitable for electrospinning. Similarly, 10% and 12% PVP–barium titanate solutions were prepared. A flow sheet of solution preparation methodology is given in Fig. 1.

2.3. Electrospinning of PVP–$BaTiO_3$ composite nanofibers

About 3 cc of the PVP–$BaTiO_3$ composite solution was taken in a syringe with fine capillary metallic needle. The electrospinning was carried out by maintaining tip to collector (TCD) distance of 7 cm and at a DC voltage of 9 kV. The flow rate of the solution was maintained at 1 mL h^{-1}. A schematic drawing of the electrospinning setup is presented in Fig. 2. The positive terminal of a high voltage source was applied to the needle of the syringe while the negative terminal was connected to the aluminum foil collector. The composite fibers of PVP–barium titanium acetate were prepared by subjecting the solution to a high electrical potential (9 kV) for 2 h. The same procedure was followed for the electrospinning of other two solutions. The details of the solution preparation methodology and electrospinning conditions are summarized in Table 1.

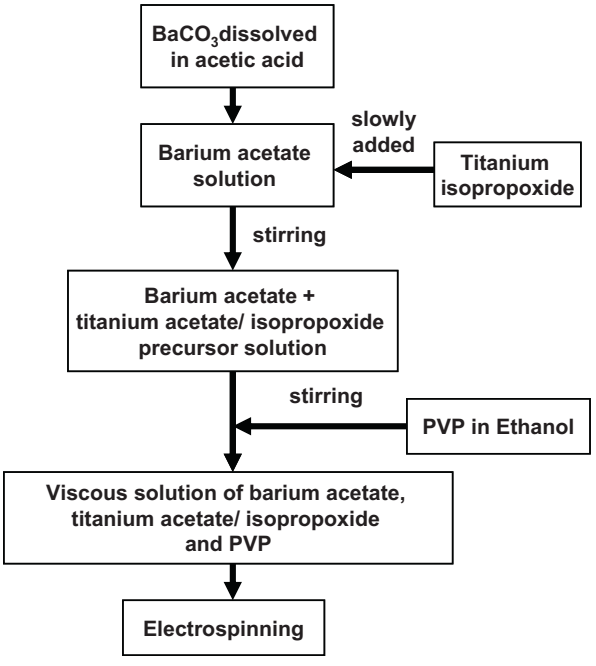

Fig. 1. Flow sheet of barium titanate precursor solution preparation.

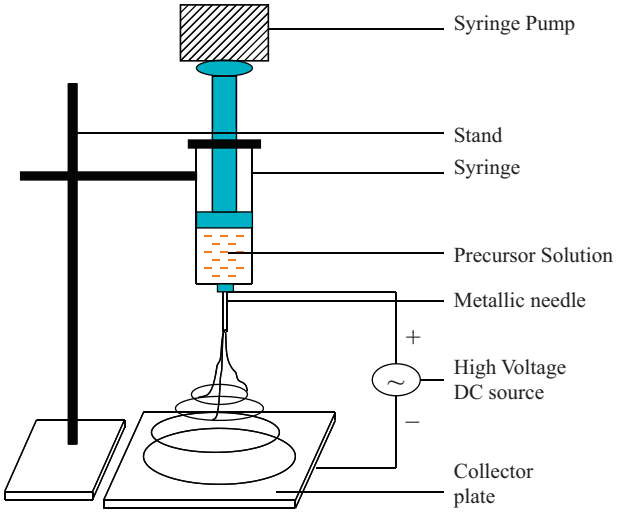

Fig. 2. Schematic drawing of the electrospinning setup.

3. Characterization

The PVP–$BaTiO_3$ composite nanofibers were subjected to thermogravimetric analysis (TGA) using Universal V2.6D, TA instrument. The sample holder was heated in air at a rate of 10 °C min^{-1}, in the temperature range from 50 to 800 °C. The resulting TG curve is shown in Fig. 3. The composite nanofibers were calcined at 600 °C to study the oxide fibers after the removal of organics and also at 1000 °C for 1 h to study the sintering behavior of fibers. The as-spun and calcined nanofibers were characterized by FT-IR spectrometer (FT-IR spectrometer, VECTOR-22 model, Bruker, Germany) in the scanning range of 500–4000 cm^{-1} and were presented in Fig. 4. The morphology of the fibers was ascertained using a scanning electron microscope (Carl Zeiss Supra 40 VP, Germany). The average fiber diameter and the distribution of fibers were determined using ~20 randomly selected fibers taken from SEM micrograph. The morphology of green fibers and their diameter distributions with change in PVP concentration are shown in Fig. 5a–c. SEM photograph of sintered $BaTiO_3$ nanofiber and its diameter distribution is presented in Fig. 6.

4. Results and discussion

4.1. Thermo gravimetric analysis of PVP–$BaTiO_3$ composites

From Fig. 3, it is observed that the minor weight loss below 100 °C is due to the removal of traces of solvents/moisture. The weight loss between 250 and 400 °C is due to decomposition of

Table 1
Solution preparation and electrospinning conditions.

Chemical precursors	Solution preparation methodology	Electrospinning conditions
(i) Barium carbonate, (ii) titanium iso-propoxide, (iii) acetic acid, (iv) ethanol, and (v) poly vinyl pyrrolidone (PVP) (Mw, ~40,000).	(i) Barium carbonate and titanium isopropoxide dissolved in acetic acid, (ii) 8%, 10% and 12% PVP solutions in ethanol prepared at room temperature, and (iii) prepared PVP solutions were mixed with barium titanate solution and stirred continuously for homogenization.	(i) Nozzle dia. (internal): 0.5 mm, (ii) tip to collector distance (TCD): 7 cm, (iii) voltage: 9 kV, (iv) humidity: 50–60%, and (v) solution flow rate: 1 mL h^{-1}.

PVP and acetate molecules [21]. Similarly, the weight loss during 575–625 °C is considered due to the decomposition of organic groups from the organometallic precursor (titanium isopropoxide) and its intermediate phases (titanium isopropoxide acetate) [22]. The weight loss was complete below 700 °C and was about 45% of the total weight. Therefore, the calcination temperature was selected at much higher temperature (1000 °C) to make sure all the organics are expelled and also fibers are partially sintered for their easy handling.

The reaction of titanium isopropoxide in acetic acid proceeds in two ways i.e. (i) either two isopropoxide groups or (ii) all the isopropoxide groups are replaced by acetate groups. Accordingly, the two equations can be written as:

$$Ti[(CH_3)_2CHO]_4 + 2CH_3COOH \leftrightarrow Ti(CH_3COO)_2[(CH_3)_2CHO]_2 + 2(CH_3)_2CHOH \quad (1)$$

$$Ti[(CH_3)_2CHO]_4 + 4CH_3COOH \leftrightarrow Ti(CH_3COO)_4 + 4(CH_3)_2CHOH \quad (2)$$

The reaction of barium carbonate with acetic acid is as per the equation:

$$BaCO_3 + 2CH_3COOH \leftrightarrow Ba(CH_3COO)_2 + H_2O + CO_2 \quad (3)$$

The theoretical weight loss after heat treatment of the above nanofibers as per calculation is 53% for partial replacement of isopropoxide molecules and 40% for complete replacement by acetate ions including the loss from barium acetate and PVP. The actual weight loss as per TGA graph is ~45% which indicates the existence of both partially replaced as well as completely replaced isopropoxide molecules by acetate ions in the precursor solution.

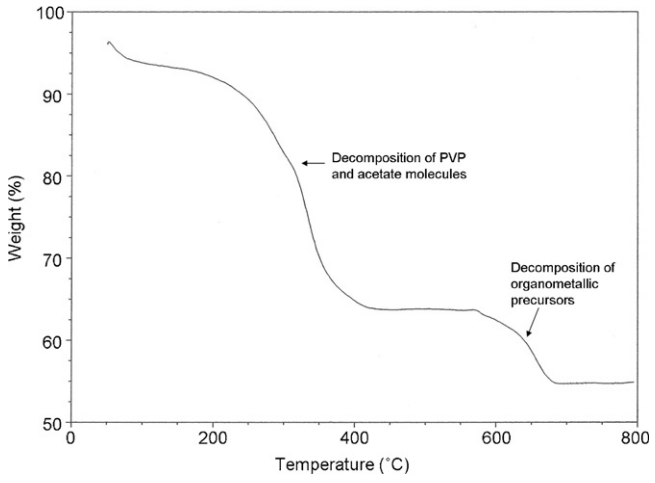

Fig. 3. Thermogravimetric analysis of PVP–$BaTiO_3$ nanofibers.

4.2. FT-IR analysis

The spectrum of nanofibers (Fig. 4) shows a very broad band around 3600–3200 cm^{-1} corresponding to hydrogen bonded O–H stretching vibration due to presence of moisture in the sample. The triplet peaks present at 2965–2854 cm^{-1} correspond to the asymmetric and symmetric C–H stretching vibrations of methyl groups (from acetate and isopropoxide molecule) [23,24]. The peaks at 1744 and 1652 cm^{-1} correspond to stretching vibrations of C=O bonds present in acetate and PVP molecules. The more intense peak around 1300–700 cm^{-1} corresponds to the skeletal C–C, C–O and C–N vibrations of PVP polymer [24]. The intensities of these vibration bands are reduced at higher temperatures. The presence of a peak at 570 cm^{-1} corresponding to Ti–O vibration of fibers calcined at 600 °C confirms the formation of $BaTiO_3$. This peak becomes sharper and narrower at higher temperature (at 1000 °C) due to the formation of metal oxide bonds.

4.3. Morphology of PVP–$BaTiO_3$ composite nanofibers

From the SEM photographs (Fig. 5a–c), it is observed that the fibers are cylindrical and the average fiber diameter increases with PVP concentration. For example, the fiber diameter increases from 150 ± 25 nm for 8% PVP to 250 ± 25 nm for 12% PVP concentration. This is due to high viscosity of the solution at higher PVP concentration. In general, the fibers are smooth and straight at higher concentration due to higher content of the organics. SEM photograph of the calcined $BaTiO_3$ nanofibers (Fig. 6), shows the fiber surface is uneven due to loss of organics. The diameter of the sintered fibers is reduced to 220 ± 25 nm, about 12% less compared to its green counterpart.

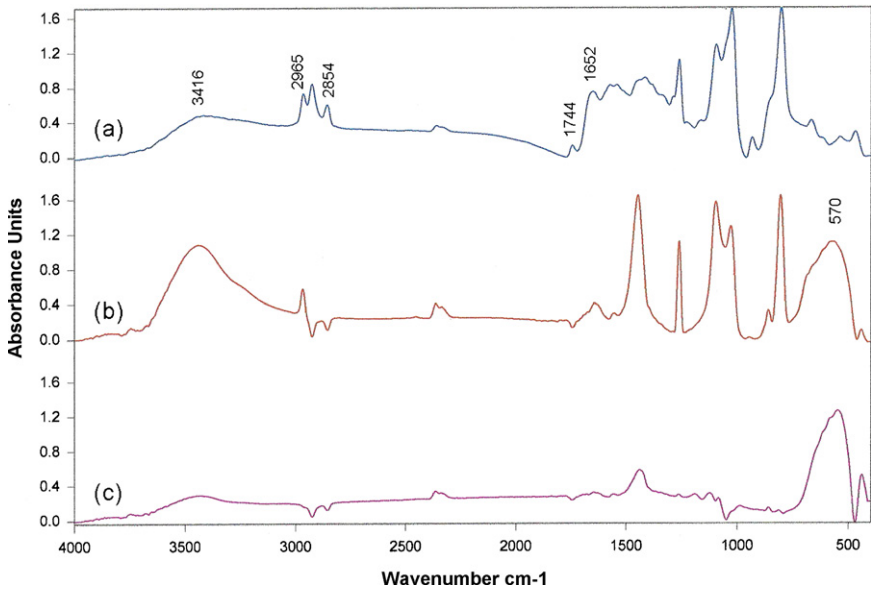

Fig. 4. FT-IR analysis of PVP–$BaTiO_3$ nanofibers (a) as spun, (b) calcined at 600 °C and (c) calcined at 1000 °C.

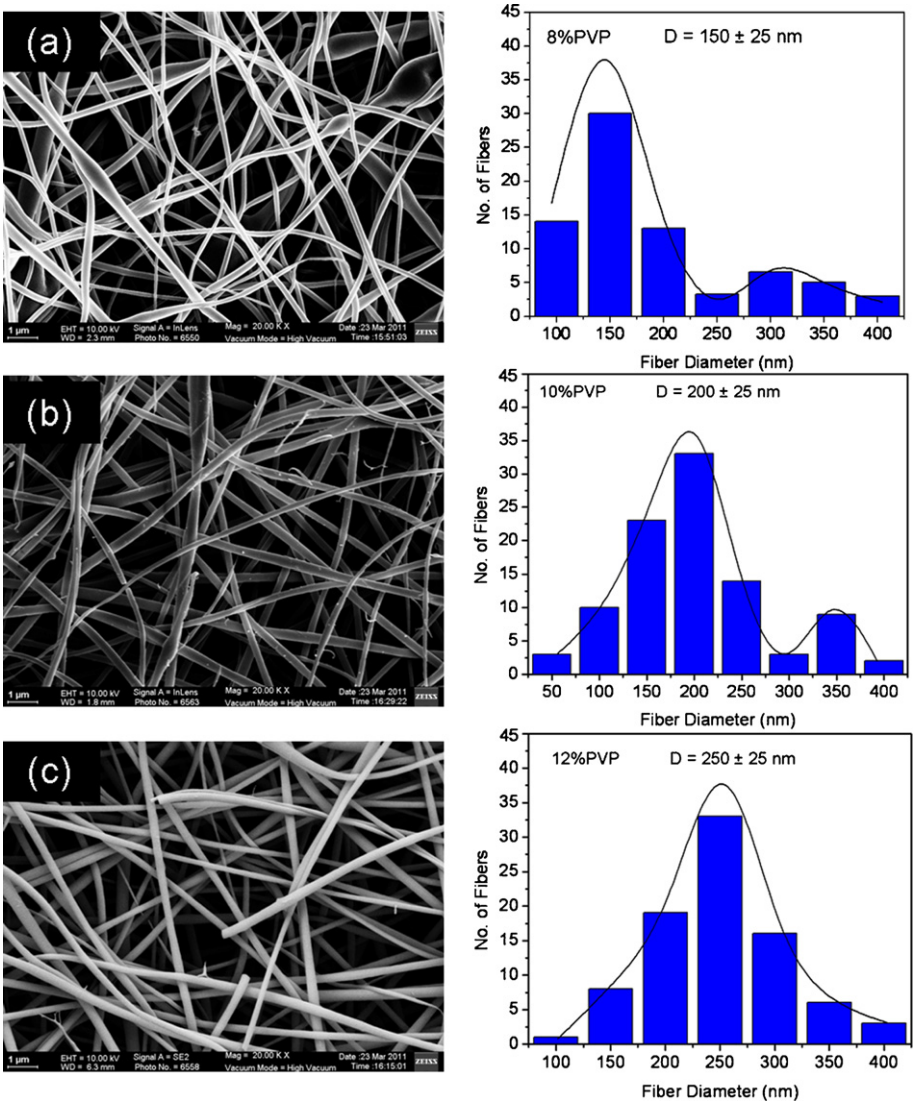

Fig. 5. SEM micrographs of PVP–$BaTiO_3$ nanofibers with (a) 8%, (b) 10% and (c) 12% PVP concentration and their corresponding diameter distributions.

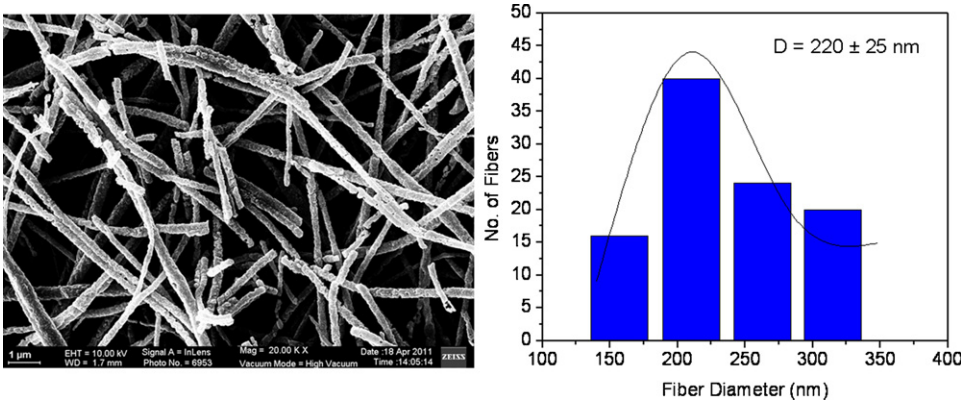

Fig. 6. SEM micrograph of $BaTiO_3$ nanofibers (12% PVP) heat treated at 1000 °C/2 h.

5. Conclusions

PVP–$BaTiO_3$ composite nanofibers were successfully prepared by electrospinning technique and pure $BaTiO_3$ fibers were produced after calcination at 1000 °C. The fiber diameter was found more for higher PVP concentration. The as spun fibers are smooth and cylindrical. TGA of PVP–$BaTiO_3$ composite nanofibers indicate the presence of a mixture of partially replaced titanium isopropoxide and fully converted titanium acetates. FT-IR study confirms the formation of metal oxide bond at higher temperature.

Acknowledgments

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