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Preparation and characterization of Samaria nanofibers by electrospinning

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Abstract

Samaria nanofibers were prepared by electrospinning homogeneous viscous solutions of samarium citrate in polyvinyl alcohol (PVA) and calcining the nanofibers at 1000 °C for 2 h. PVA solutions of varied concentrations e.g. 19%, 23% and 25% (by weight) were used as polymer precursors. Electrospinning was carried out at 9 kV DC by maintaining tip to collector distance (TCD) of 7 cm. Thermogravimetric analysis (TGA) of nanofibers room temperature (RT) to 800 °C indicates the complete decomposition of organics below 750 °C with a weight loss of 55%. The morphology of nanofibers was observed under scanning electron microscope (SEM). The nanofibers are found cylindrical with fiber diameter in the range of 200–500 nm and aspect ratio > 1000. The average diameter of the fibers increases with the increase in PVA concentration. The diameter of calcined Samaria nanofibers reduced by 43% due to loss of organics and shrinkage.

Keywords: Samaria; Samarium oxide; Electrospinning; Nanofibers

1. Introduction

Samarium oxide (Sm_2O_3) also known as Samaria or samarium Sesquioxide is a rare earth refractory oxide with a melting point of 2335 °C. It belongs to cubic crystal structure, appears yellowish-white and its density is 7.6 gm/cc [1]. Samarium oxide is used for different applications: as an optical film, as an insulator in metal-oxide-metal (MOM) structure, in optical glass to absorb infrared light, as thin films capable of protecting metallic substrates from corrosion attack, as a dopant in glass fibers and doped samarium oxides as electrolyte [2]. Samarium oxide doped with ceria possesses high ionic conductivity, therefore, used in Solid oxide fuel cell (SOFCs). It forms permanent magnets along with cobalt. It is also used as a catalyst for dehydration of alcohols and for oxidative coupling of methane. Samarium oxide is generally prepared by the decomposition of its nitrates, oxalates, acetates etc. Large surface area is highly desirable for catalyst applications. Nanofibers are known for their large surface areas to volume ratio, therefore, are ideal for the above applications.

Among different methods to produce nanofibers, electrospinning is a bottom-up approach gaining attention in recent years for the fabrication of polymer and ceramic nanofibers [3]. It is a very simple and versatile technique for synthesizing nanofibers or fiber mats from wide range of organic polymers or a combination of polymer/metal oxide precursors for various applications [4–19].

In electrospinning process, a strong electrostatic field is applied to the tip of a metallic needle of a syringe containing viscous organic solution. The electrostatic field once surpasses a threshold value corresponding to the repulsive forces generated due to similar charge concentration higher than the surface tension and viscous drag forces. The jet moves toward a ground plate acts as counter electrode. The jet subdivides into large number of nanofibers, therefore, the solvent dries very fast. On continuation of the deposition process, the nanofibers deposit randomly oriented in the form of thin sheet above the counter electrode.

There is hardly any literature available on electrospinning of Samaria nanofibers. Frontera et. al prepared Samaria

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nanofibers using nitrate precursors [2]. However, the main drawback of the process is poor quality of fibers generally produced from nitrates, chlorides, bromides etc. Therefore, in the present study, efforts are made to prepare samarium oxide nanofibers using citrate precursor with different percentages of solid loading to study the changes in the morphology of green and heat treated nanofibers.

2. Experimental

Samarium carbonate, (Indian Rare Earths, 99.9%), citric acid, (SD fine, 99.5%), polyvinyl alcohol (PVA) (Mw= 1,25,000, SD fine) and distilled water were used as the starting chemicals. Nearly 2 g of citric acid was completely dissolved in 3 ml of distilled water. 1 g of samarium carbonate was added to the above solution and was slightly heated for completion of the reaction. The solution then cooled in an ice cooled water bath to obtain a clear tinge yellow solution. 5 cc of 12.5% PVA solution was mixed with the samarium citrate solution (19% by weight PVA in the whole solution) and the whole content was constantly stirred for homogenization. Similarly, the other two solutions of samarium citrate+PVA was prepared using 6.25 cc (23% by weight) and 7 cc (25% by weight) of 12.5% PVA solution. The viscous solution was then subjected to electrospinning by taking a small quantity (3 ml) of the solution in a syringe with metallic needle to which the positive terminal of the high voltage source was connected. A grounded flat metallic stand covered with aluminum foil served as counter electrode. The experiments were carried out by maintaining a distance of 7 cm between the tip of the syringe and the collector. A schematic drawing of the electrospinning set up is presented in Fig. 1. The solution flow rate was maintained at 1.5 ml/hr and the humidity of the chamber was maintained in the range of 50–60%. The voltage was gradually increased till the liquid came out through the needle and split into web of fibers collected on the aluminum foil. The solution preparation methodology and electrospinning conditions are summarized in Table 1. The composite nanofibers were calcined at 1000 °C for 2 h using heating and cooling rates of 3 °C/min. The morphology of as-spun nanofibers was observed under a scanning electron microscope (Carl Zeiss Supra 40 VP, Germany) after vacuum coated with a thin layer of gold. About 20 randomly selected fibers taken from SEM micrographs were used for the determination of average fiber diameter and their distribution.

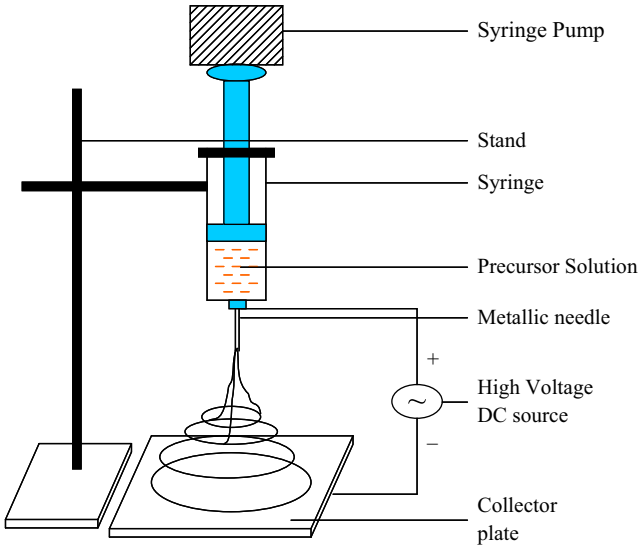

Fig. 1. Schematic drawing of the electrospinning set up.

3. Results and discussions

3.1. Thermogravimetric analysis of samarium citrate+PVA composites

Nearly 2 mg of dried electrospun samarium citrate+PVA nanofibers taken in a platinum crucible was subjected to

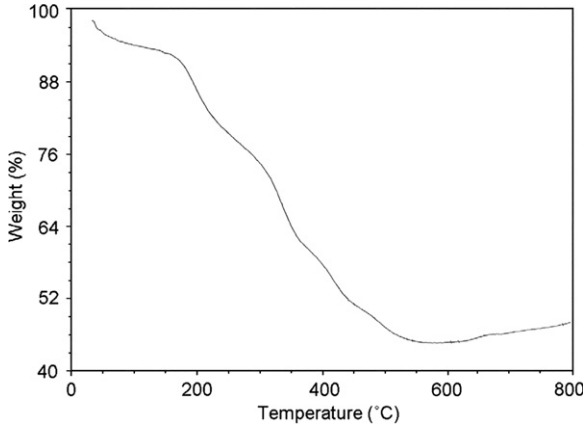

Fig. 2. Thermogravimetric analysis of samarium citrate + PVA nanofibers.

Table 1
Preparation of samarium citrate + PVA solution and electrospinning conditions.

Chemical precursors	Preparation of solution	Electrospinning conditions
(I) Samarium carbonate (II) Polyvinyl alcohol (PVA) (Mw, ~1,25,000) (III) Citric acid, (IV) Distilled water	(i) Samarium carbonate was dissolved in citric acid, solution (ii) 19%, 23% and 25% PVA solutions prepared with distilled water at room temperature with constant stirring for 2 h. (iii) PVA solutions were mixed with samarium citrate solution and stirred continuously for homogenization.	(i) Nozzle dia. (internal): 0.5 mm, (ii) Tip to collector distance (TCD): 60–70 mm, (iii) Voltage: 9 kV, (iv) Humidity: 50–60% (v) Flow rate: 1.5 ml/h

thermal analysis with a heating rate of 10 °C min^{-1}. The resulting TG curve is shown in Fig. 2. The mirror weight loss below 100 °C is due to the removal of traces of adsorbed water molecules/moisture. The weight loss between 100 and 350 °C is due to the dehydration of lattice water of citrate ion ($C_6H_5O_7^{3-}$) as well as from excess citric acid. The weight loss between 350 and 450 °C is due to the decomposition of PVA as well as samarium citrate molecules to samarium carbonate. In last stage the weight loss up to 700 °C is could be due to decomposition of samarium carbonate to samarium oxide. The above weight loss is in fully agreement with the studied carried out by Wu et.al [19] in their paper on thermal behavior of rare earth citrate hydrates and by Budrugeac [20] on kinetics of the complex process of thermo-oxidative degradation of polyvinyl alcohol. The total weight loss was complete below 750 °C and was about 55%. Therefore, the calcination temperature was selected at much higher temperature (1000 °C) to make sure all the organics

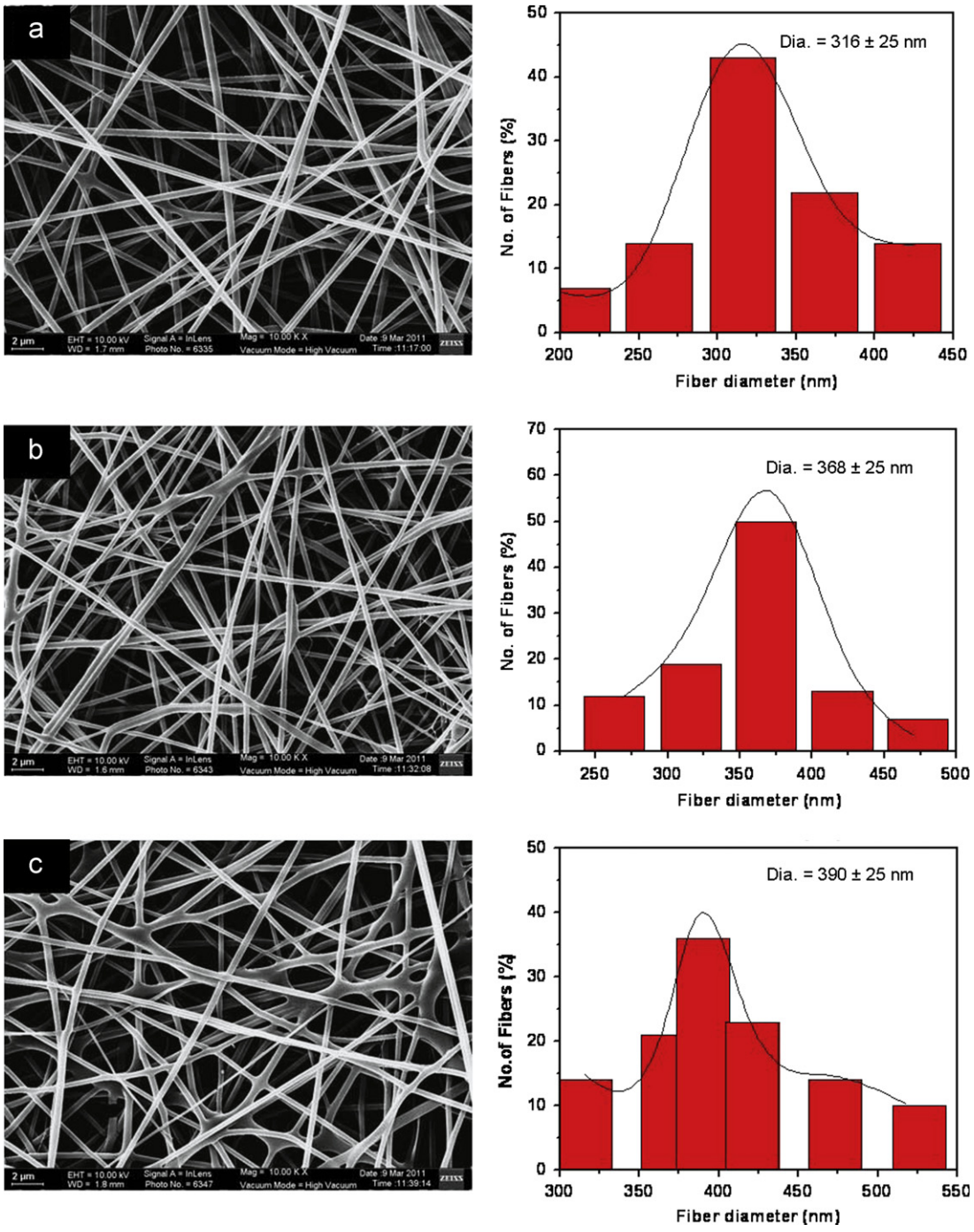

Fig. 3. SEM micrographs of samarium citrate + PVA nanofibers having: (a) 19%, (b) 23% and (c) 25% PVA content and their corresponding diameter distributions.

are expelled and also fibers are partially sintered for their easy handling.

3.2. SEM characterization of the samarium citrate+PVA composite nanofibers

The morphology of the as-spun samarium citrate nanofibers and their distribution of diameter with variation in PVA concentration are shown in Fig. 3(a–c). It can be seen that the prepared fibers have a cylindrical structure with smooth surface due to amorphous nature. The histogram of average diameter of the fibers for different PVA concentrations (19–25%) shows the increase of fiber diameters with increase in PVA concentration. For example, the fiber diameter was 316 ± 25 nm for 18% PVA concentration increased to 390 ± 25 nm for 25% PVA concentration. This is probably due to higher viscosity of the solutions with increasing PVA concentration resulted in larger fiber diameters. In general, the morphology of fibers and smoothness are better for higher percentage of PVA solutions due to higher content of organics. The average fiber diameter vs. concentration of PVA solutions is presented in Fig. 4. It is observed that the fiber diameter linearly increases with increase in PVA concentration. This is in similar line of observation made by He et al. [21]. SEM photograph of the Sm_2O_3 nanofiber sintered at 1000 °C for 1 h is presented in Fig. 5 and its diameter distribution in the form of histogram is presented in Fig. 6. It is observed that the fibers retained their fibrous nature but with a rough surface due to loss of organics such as citrates and PVA molecules leaving only Sm_2O_3 grains. From Fig. 6, the diameter of the nanofibers was found reduced to 180 ± 20 nm after heat treatment, which is nearly 43% reduction in diameter compared to it green counterpart. This is due to loss of organics and the shrinkage associated with heat treatment.

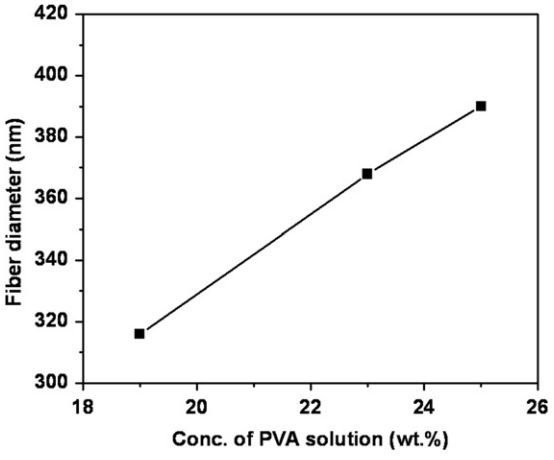

Fig. 4. Fiber diameter Vs. concentration of PVA solution.

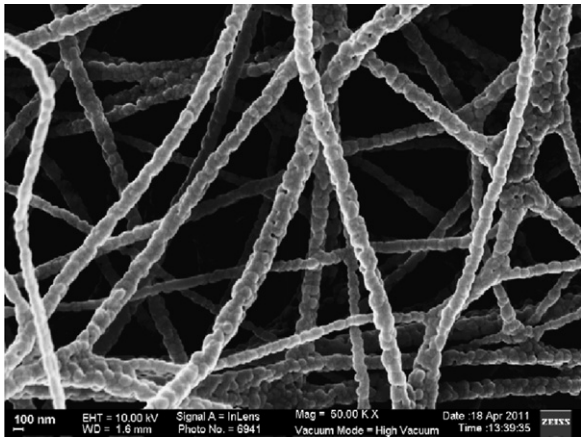

Fig. 5. SEM micrograph of samarium oxide nanofibers having 19% PVA heat treated at 1000 °C/2 h.

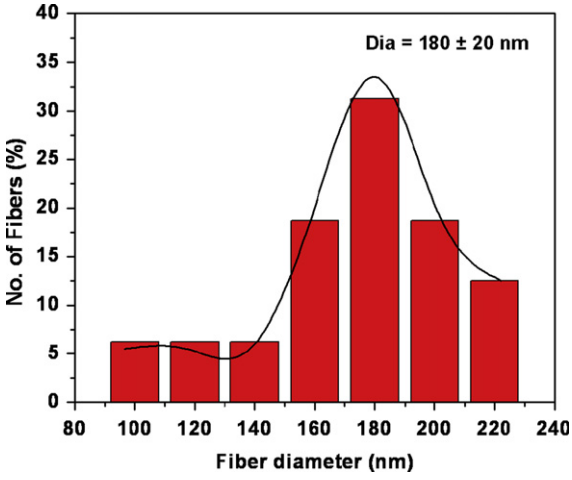

Fig. 6. Diameter distribution of heat treated samarium oxide nanofibers having 19% PVA.

4. Conclusions

Samarium citrate+PVA composite nanofibers were successfully prepared by electrospinning technique and pure Samaria (Sm_2O_3) fibers were produced after calcination at 1000 °C. The fibers are cylindrical with smooth surface and aspect ratio > 1000. The average fiber diameter was found increased linearly with increase in PVA concentration. The surface becomes rough after heat treatment and the diameters of the fibers reduced by 43%. Thermogravimetric analysis of Sm_2O_3+PVA composite nanofibers shows the weight loss of about 55%.

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