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Fabrication and microwave-transparent property of fluffy SiBNO ultrafine fibers by electrospinning

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ABSTRACT

SiBNO ceramic fibers are promising materials in radar-wave-transparent applications due to their excellent dielectric property and high mechanical strength. In this paper, three-dimensional (3D) fluffy SiBNO ultrafine fibers were fabricated by electrospinning of polyborosiloxane (PBSO) sol and pyrolysis up to 1000 °C under NH_3. The construction of fluffy structure was well manipulated through adjusting the environmental humidity during the electrospinning process. The obtained SiBNO fibers with typical amorphous structure display a uniform distribution with an average diameter of 1.5 μm. Moreover, the SiBNO fibers exhibit excellent dielectric property with the average dielectric constant and loss tangent of 4.44 and 0.0029 at 2–18 GHz, respectively. These fluffy architectures demonstrate great potentials in nano-composite materials, which can promote precursor impregnation into three dimensions.

1. Introduction

SiBNO with excellent dielectric property and high mechanical strength are promising to be used as spacecraft materials [1]. Recently, SiBNO ultrafine fibers have received increasing attention due to its large surface to volume ratios, which have great potential applications in catalyst supports and fiber reinforcements for wave-transparent composites.

Electrospinning is an effective way of generating ultrafine fibers with controllable diameters [2–4]. However, most of the reported electrospun fibers are in flat topography with small thickness and compact packing. It is difficult for the dense fibers mat to impregnating solution [5]. When used as reinforcing fibers, precursor infiltration is prevented to penetrate inside the fiber mat, limiting their use in composite materials. The preparation of three-dimensional (3D)/fluffy fibers by electrospinning without auxiliary devices is still a challenge [6]. So far, three-dimensional melt electrospinning, near-field electrospinning and modifying collectors have been developed to fabricate 3D electrospun fibers [5]. Besides, 3D structures of electrospun fibers can be obtained through careful selection of the solution components and properties [7]. For example, Li et al. have reported an extraordinary self-assembled 3D fibrous stackings fabricated by electrospinning [8]. It was found that the relative humidity during the electrospinning process plays a key role in determining the 3D structures. The enhanced surface charge density of the fibers from increasing humidity can increase repulsions to fabricate self-supported 3D nanofiber mats [7].

In this paper, 3D fluffy SiBNO fibers were fabricated by electrospinning of PBSO sol and followed pyrolysis at 1000 °C under NH_3 atmosphere. By careful conditioning of moisture, the fluffy structure of the fiber was obtained. Moreover, SiBNO fibers with the average dielectric constant and loss tangent about 4.44 and 0.0029 at 2–18 GHz, respectively.

2. Experimental

Methyltriethoxysilane (MTES), tetraethoxysilane (TEOS), boric acid ($B(OH)_3$), alcohol (EtOH), nitrate acid (HNO_3, 1 mol L^{-1}) and polyethylene oxide (PEO, M_w = 1,000,000) were used to prepare the spinning solutions. MTES, TEOS, $B(OH)_3$, EtOH, HNO_3 and PEO were mixed together with a mass ratio of 0.8:0.9:0.11:2:1:0.01. Thereafter, electrospinning was performed on a single-needle electrospinning setup (Fig. S1, Supporting Information) with a voltage of 15 kV and a distance of 15 cm between needle and aluminum foil collector. The flow rate was kept at 0.5 mL h^{-1}. The temperature and relative humidity within the sealed chamber were monitored and adjusted using a humidity control system consisted of an air compression pump, a heating lamp, and a humidifier. The humidity has a ±2% RH fluctuation during the experiment and all

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the humidity values mentioned in the manuscript are the average values. The as-spun fibers were pyrolyzed to SiBNO fibers in a tubular furnace at 1000 °C for 2 h under ammonia atmosphere.

The morphologies and the chemical composition were characterized by a field emission scanning electronic microscopy (FESEM, S-4800, Hitachi) equipped with an energy-dispersive X-ray spectroscope (EDS). X-ray diffraction (XRD) patterns were collected in a Bruker Advanced D8 diffractometer. Fourier transform infrared (FTIR) spectra were recorded by a Nicolet-360 spectrometer. X-ray photoelectron spectroscopy (XPS) measurement was performed with a Thermo Scientific Escalab 250Xi machine using Al Kα. Elemental analysis of carbon was performed using Leco equipment (CS-444 furnace) calibrated with CO_2 gases. The dielectric constant and loss tangent were measured by test equipment (Model E8363C, Agilient Technologies, USA).

3. Results and discussion

Previous report has shown that the concentration of dissociated ions in the fibers can be regulated by changing the humidity of the electrospinning conditions, which can adjust the like-charge repulsions among fibers finally [7]. The humidity was controlled to manipulate the formation of 3D structures of the electrospun fibers in this study, as shown in Fig. 1. It can be seen that the fibers spread evenly over the collector plate at the low relative humidity of 30% RH (Fig. 1a). With the increase of humidity to 40% RH (Fig. 1b), the fluffy structure was formed in the central region of the collector. When increasing the humidity to 50% RH, cotton-like fibers can be observed in Fig. 1c. The resulting 3D structure is too fluffy to keep on the collector and has a tendency to fall down due to its gravity. The fibers preferred to stretching out from plate and being parallel to the electric field when further increasing the humidity to 60% RH (Fig. 1d). We believe that the colloid electric double layer structure in silica sol can dissociate into negatively charged ions, contributing mostly to like-charge coulombic repulsions. As a result, the as-spun fibers repelled each other and formed a fluffy 3D structure. A cone-like fibers cluster with the height of 10 cm is shown in the inset of Fig. 1b. Interestingly, the cone structure kept stable after removing the electric field. The average fiber diameter of the as-spun PBSO fibers was about 2 μm (Fig. S2, Supporting Information).

The fibers after pyrolysis at 1000 °C under ammonia atmosphere still kept fluffy structure (Fig. 2a). This cotton-shaped SiBNO fibers cluster may promote the infiltration of precursor in making composites. SEM image in Fig. 2b shows the uniform distribution of SiBNO fibers with an average diameter of 1.5 μm. Preliminarily, EDS results display that SiBNO fibers were composed of silicon, oxygen and nitrogen (Fig. S3, Supporting Information). The boron signal was not observed due to its small amount.

The FT-IR spectra of PBSO and SiBNO are shown in Fig. 2c. In comparison to the spectrum of PBSO, the O-H peak (3424 cm^{-1}) become weaker in that of SiBNO sample. The Si-CH_3 and C-H bonds at 778, 1276 and 2976 cm^{-1}, respectively, disappeared in the spectrum of the SiBNO sample, which can be explained by the reactions between Si-CH_3 units and NH_3 [9]. Furthermore, the absorption peak of Si-O-Si bands at 1371 cm^{-1} turns broad and shifts to lower wave numbers at 1275 cm^{-1}, implying the formation of Si-N-Si bonds [10].A broad peak can be observed at about $2\theta = 22°$ in the XRD pattern (Fig. 2d), attributing to the amorphous nature of silica. The SiBNO fibers are expected to possess high-temperature resistance due to the amorphous structure up to 1000 °C.

In order to investigate the composition of the fibers, XPS survey spectrum and curve-fitting for Si_{2p}, B_{1s}, N_{1s} and O_{1s} were performed. The Si, B, N and O elements were detected from the survey spectrum (Fig. S4, Supporting Information). As shown in Fig. 3a, the Si_{2p} XPS spectrum can be fitted into two peaks at binding energies of 102.7 and 103.6 eV, corresponding to Si (N, O) and Si-O, respectively [11]. The B_{1s} peak can be separated into three peaks at 190.6, 191.7 and 193.3 eV, corresponding to B-N, B (N, O) and B-O bonds (Fig. 3b), respectively [12]. The N_{1s} peak shows only two components at 398 and 398.5 eV for N-B and N-Si bonds (Fig. 3c), respectively [13]. Furthermore, O-B and O-Si bonds can also be detected

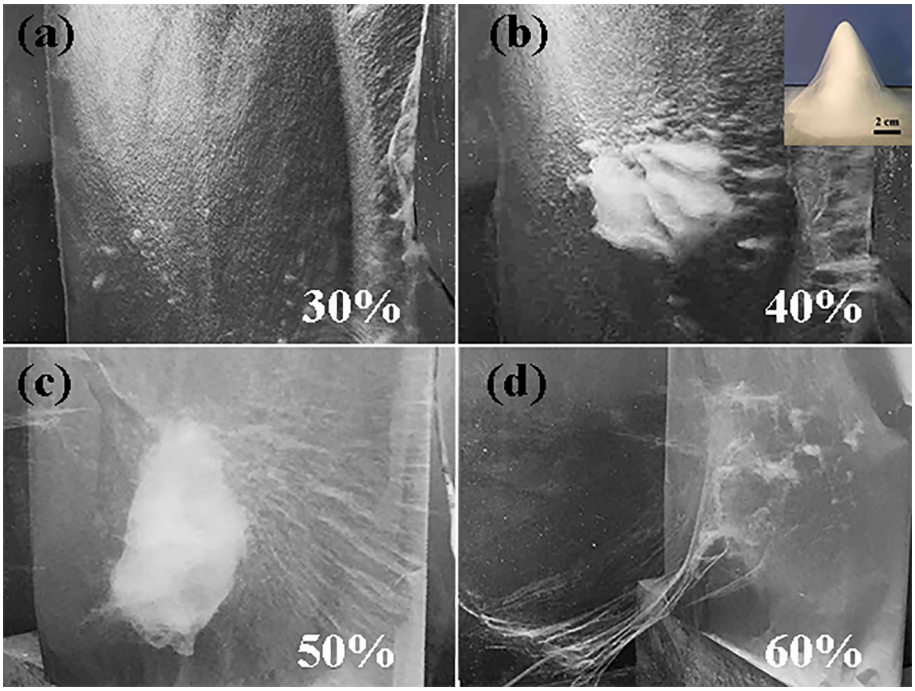

Fig. 1. Photographs images of electrospun mat structures prepared at different relative humidity conditions by electrospinning of PBSO sol. (a) 30% RH; (b) 40% RH; (c) 50% RH; (d) 60% RH. Insets: Photographs of the cone-like PBSO fibers obtained by prolonging spinning time to 2 h at the relative humidity of 40% RH.