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Short communication

Flexible ceramic nanofibermat electrospun from TiO_2–SiO_2 aqueous sol

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Abstract

Flexible ceramic nanofibers have been electrospun from a novel TiO_2–SiO_2 aqueous sol. The nanofibers obtained have an average diameter of around 150 nm and are amorphous even after heat treatment at 600 °C for 3 h in air. Since the material is amorphous it may be considered as electrospun glass nanofiber. Fracture in glass usually initiates from surface defects and in the absence of any preferred plane propagates perpendicular to the surface. The presence of surface defects on the heat treated nanofibers could not be detected on SEM and TEM images. It is hypothesized that the observed flexibility is due to significant reduction in surface defects.

Keywords: A. Sol–gel processes; C. Toughness and toughening; D. SiO_2; D. TiO_2; Fibers

1. Introduction

Synthesis of nanofibers has received considerable attention in recent years due to their potential applications in several areas including but not limited to tissue engineering [1,2], filtration [3] and catalyst support [4,5]. Amongst the various techniques to produce nanofibers, electrospinning is a versatile process which gives ample opportunities to manipulate the fiber diameter and morphology [6]. In this communication we first introduce a novel stable TiO_2–SiO_2 aqueous sol and then present the flexible TiO_2–SiO_2 nanofibermats electrospun from it. There have been numerous publications on electrospun ceramic nanofibers [7–9] but most such research involves polycrystalline ceramics. The fracture toughness of single crystals of ceramics generally ranges from 0.3 to 2.0 MPa $m^{1/2}$ while polycrystalline ceramics have a much higher toughness in the range of 2–4 MPa $m^{1/2}$. In comparison amorphous glass has a much lower toughness of 1 MPa $m^{1/2}$ and lower. However, when coated with polymer to prevent surface defects, near theoretical strains to failure have been observed in glass fibers with fiber diameter of 125 μm [10]. In this paper we attempt to explore the flexibility of nano-scale electrospun amorphous ceramic fibers. Flexibility would improve the applicability of the fibermats in such applications as high efficiency particulate air (HEPA) filters while maintaining much higher mechanical robustness.

2. Experimental procedure

An aqueous TiO_2–SiO_2 sol was prepared by mixing two separate sols (sol A and sol B). 1 mole of H_2O with a pH of 2.3 (pH modified by HNO_3) was added to 0.5 mole of 3-glycidoxypropyltrimethoxysilane (GPTMS) and stirred to produce a homogeneous solution. 0.5 mole of titanium butoxide was added to the solution to produce sol A. In a separate batch 22 mole of H_2O, whose pH has been modified to 2.3 by HNO_3, was homogeneously mixed with 0.5 mole of GPTMS. 0.2 mole of tetraethyl orthosilicate (TEOS) was added to the solution to make sol B. Sol A and sol B were mixed to produce the aqueous TiO_2–SiO_2 sol. In the physics of electrospinning, reduction in surface tension is positively correlated to decrease in average fiber diameter [11]. Thus ethanol (200 proof) was added to the stable aqueous sol in 1:1 proportion by volume to reduce its surface tension [12]. Polyvinylpyrrolidone (PVP) with molecular weight 1.3×10^6 was added to aid the process of electrospinning [13].

Electrospinning is a process in which an electric field is used to draw fibers. Its capacity to lower the fiber diameter far below than that possible with conventional wet spinning comes from the whipping instability resulting from combination of several factors – electric field, surface tension and viscosity [11]. In our

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work, an electric field strength of 1 kV/cm was maintained over a collector distance of 25 cm and flow rate was maintained at 0.6 ml/h. Aluminum foil, wrapped over a heating plate, was used as collector. The newly formed fibers are wet and can fuse before drying entirely. Such fusion inhibits fibers from sliding over each other. To prevent this phenomenon the collector was maintained at 85 °C to ensure rapid drying. The electrospun fibermat was heat treated at 600 °C for 3 h in air.

3. Results and discussion

The heat treated fibermat is flexible as shown in Fig. 1. It can be easily bent to a radius of curvature of 3.4 mm and certain portions of it can be bent to even smaller radius of curvature of 1.3 mm. As observed from the morphology of the fibers in Fig. 2, the mean diameter of obtained fiber is 157 ± 42 nm ($N = 50$) within one standard deviation. Previous research has reported complete selective oxidation of PVP at heat treatment over 500 °C [7]. Further no carbon was detected by energy dispersive spectroscopy (EDS). So the contribution of PVP on the flexibility can be safely excluded.

Selected area diffraction (SAD) of the fibers shows a diffuse pattern, characteristic of amorphous phase. It is hypothesized that formation of Si–O–Ti bonds [14] in the system inhibits the crystallization of TiO_2 even at 600 °C. The nanofibers formed of the resulting amorphous ceramic are mechanically robust. During the process of fracture two new surfaces are created. Due to the lack of any preferred plane, crack propagates perpendicular to the surface in glass [15]. However research has shown that in glass the crack initiates from surface defects and in absence of defects, strength and strain to failure reaches values close to theoretical estimations [10,16,17]. So in the past glass fibers, drawn from melts, have been coated with polymers to inhibit the formation of surface defects [10,17]. Nano-scale ceramic fibers have been produced by numerous research groups in the last decade but such fibers have been polycrystalline. We found only one such group reporting limited flexibility in polycrystalline titania fiber [18–20]. Flexible ceramic fabrics are also commercially available but such materials have a mean fiber diameter several times higher than 1 μm (e.g. zirconia cloth (type ZYK-15 and type ZYW) from Zircar). Fig. 2(B) presents an image of commercially

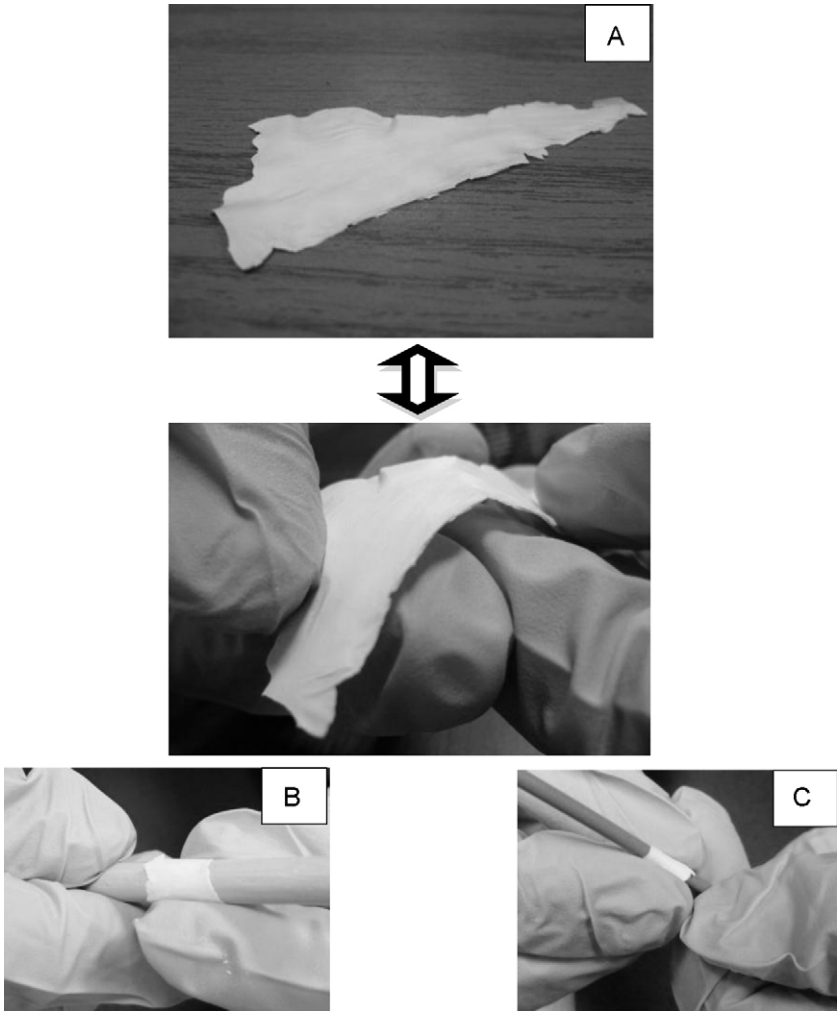

Fig. 1. (A) Heat treated electrospun fibermats are flexible and can be bent. (B and C) Heat treated fibermats curved to 3.4 mm and 1.3 mm radius of curvature (i.e. 6.8 mm and 2.6 mm diameter), respectively.

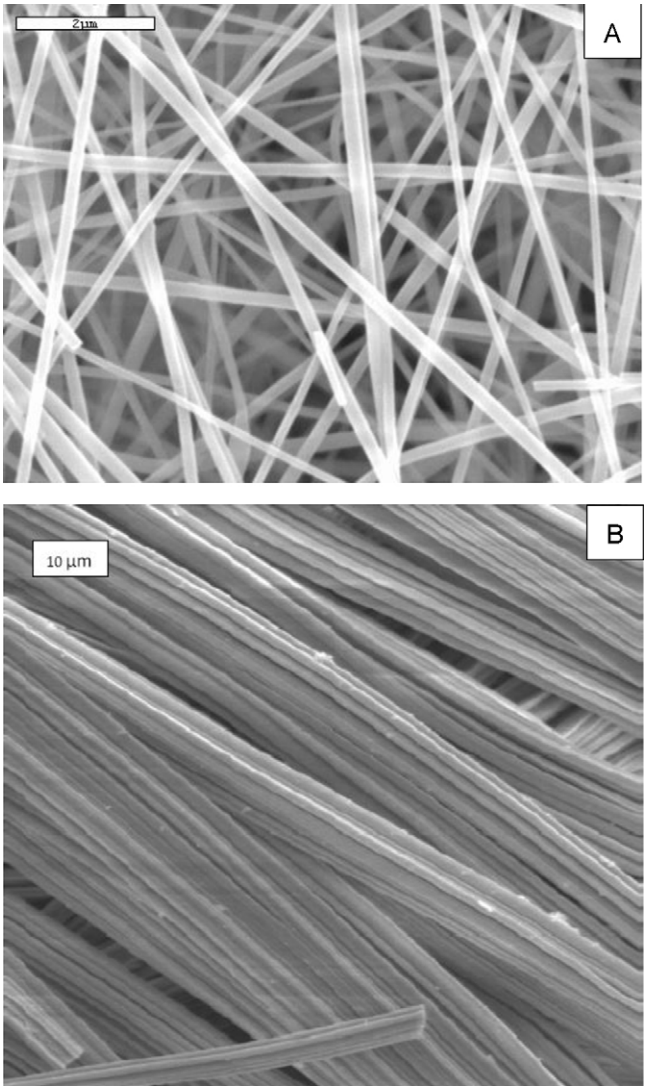

Fig. 2. (A) Fiber morphology of TiO_2–SiO_2 nanofibers electrospun from aqueous sol containing 2.0% w/v PVP (M_W 1.3×10^6). Ethanol was used to reduce surface tension and decrease average fiber diameter. The scalebar represents 2 μm. (B) SEM image of commercially available ZYK-15 flexible zirconia fibermat. Fibers are serrated and each several micron in diameter. Image obtained from product specifications from Zircar Zirconia, Inc.

available flexible zirconia cloth for comparison. After thorough review of available literature, it is to the best of our knowledge that this is the first time glass nanofibermat with excellent flexibility have been prepared by electrospinning without the need to coat individual fibers with polymers. No surface defect was observed under SEM and TEM, which may explain the observed flexibility (large SEM and TEM images available in the supporting information). Another significant observation was made by ultrasonicating the fibermat. Even after continuous vigorous ultrasonication in deionized water for 20 min, the fibers maintained their general fibrous morphology; although they broke into shorter length of several tens of μm. A similar observation was made for 500 nm amorphous SiO_2 nanofibers in the past [21]. These shorter fibers have the potential to be used as reinforcements for polymer and dental composites.

4. Conclusion

An aqueous sol of TiO_2–SiO_2 was prepared and electrospun. The mats of electrospun nanofibers were heat treated at 600 °C. No phase was crystallized during the heat treatment. No surface defect was observed in SEM and TEM images. It is likely that with the reduction in surface defects, the number of crack initiation sites on the surface also decreases, explaining the improved flexibility. Ceramic nanofibers have a unique advantage over polymeric nanofibers in terms of mechanical strength but their brittleness has been the Achilles' heel. Our endeavor to improve flexibility is expected to make it a much more compelling choice in the field of high efficiency air filtration. The fibermat synthesized, with average fiber diameter of around 150 nm, is an excellent candidate for HEPA filters. The small fiber diameter ensures large specific surface area, making it a potential choice as catalyst. The fibers break into shorter filaments after ultrasonication, but maintain the general fibrous morphology. These filaments have potential to be used as reinforcements in composites.

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