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High-temperature fiber matrices: Electrospinning and rare-earth modification

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We demonstrate the production of nonwoven mats of high-temperature organic and inorganic fibers by electrospinning. Specifically, glass/ceramic (tetraethylorthosilicate–SiO) and fire-blanket (polydiphenoxyphosphazene–PDPP) precursors are electrospun, and the resulting fibers are characterized by scanning electron microscopy, thermogravimetric analysis, and infrared (IR) spectroscopy. We find that the SiO fibers are smaller in diameter and more uniform than the PDPP fibers, and stable to higher temperatures. We also coat these fiber systems with several rare-earth nitrates, and find that these coatings can be used to selectively modify the near-IR spectra of the fibers. This work extends the use of electrospinning into two new classes of materials, and demonstrates that we can subsequently modify the optical properties of the electrospun fibers. © 2003 American Vacuum Society. [DOI: 10.1116/1.1575219]

I. INTRODUCTION

The development of new tools and techniques for understanding nanoscience leads us to consider their potential applications in nanotechnology. While there has been a rapid increase in the types of structures and materials that can be produced at the nanoscale, nanotechnology will not flourish until industrially relevant processes for synthesizing these structures on a large scale are developed. One such process that has already been scaled up for manufacturing purposes is the electrospinning of polymer nanofibers. A wide variety of electrospun polymeric materials and shapes have been reported,^{1–7} including those exhibiting specific surface chemical properties.⁸ Electrospun nanofibers have been used as biomaterials, filtration media, and as mechanical supports for other materials.

In conjunction with experimental efforts, models of the electrospinning process can be used to develop it into a manufacturing tool. Efforts to develop theoretical frameworks and predictive models of the electrospinning process are under way.^{5,6,9} Recent modeling efforts can predict the trajectories of fiber segments by taking into account the net local electric field on different regions of the charged jet. These efforts promise to provide deeper insight into the dynamics of electrospinning.⁵ The experimental findings re-

ported here extend electrospinning into two novel materials systems for high-temperature ($T > 300^\circ\text{C}$) applications. In doing so, we provide additional material-specific information for the models and further demonstrate the versatility and viability of the electrospinning process for materials development.

A schematic of a typical electrospinning apparatus is shown in Fig. 1. In general, a polymer precursor solution is held in a pipette above a collector with a large voltage applied between the two. The pendant drop at the tip of the pipette becomes a cone, and a charged jet of the precursor solution is ejected from the tip of the cone when the forces due to the applied electric field overcome the surface tension of the pendant drop. The jet exhibits a spiraling path whose onset is best described as an electrically driven bending instability. High-speed stroboscopic photography is used to observe the paths as they evolve, to help elucidate the important parameters. The properties of the nanofibers produced depend on many process variables including the nanofiber material, the solvent, the magnitude of the applied voltage, and the distance and geometrical relationship between the pipette and the collector.

Electrospun nanofibers can be coated after spinning using either sol-gel techniques or thermally activated vapor phase processes.^{10–12} Plasma-enhanced processes can also be used but the fibers must be stable with respect to ion bombardment from the plasma. Continuous thin-film coatings around

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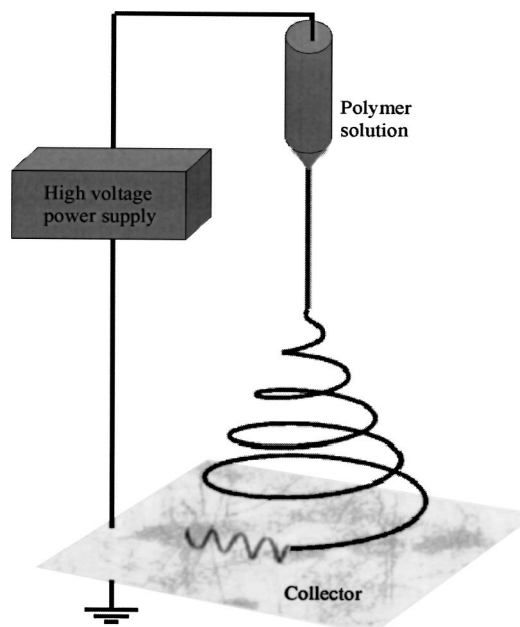


FIG. 1. Schematic illustration of a typical electrospinning apparatus. The polymer solution is held in a pipette above a collector in the presence of an electric field of magnitude greater than 1 kV/cm. The pendant drop at the tip of the pipette becomes a cone, and a charged jet of solution exits the apex of the cone when the forces due to the electric field overcome surface tension. The jet then undergoes an electrically driven bending instability and exhibits a spiraling path.

the entire fiber circumference can be produced in a single deposition step, but these are generally not of uniform thickness. Normally the quality of thin-film materials depends on the substrate temperature during deposition, and the highest quality films are deposited at temperatures in excess of one third of the melting temperature of the film. Thus many semiconducting materials, for example, are deposited at substrate temperatures in excess of 300 °C. There is a need, therefore, to investigate the synthesis of high-temperature fiber materials for use as potential substrates for high-quality semiconducting and/or ceramic thin films.

As part of our efforts to expand the range of potential applications involving electrospun nanofibers, we present results involving two classes of high-temperature materials not previously produced in nanofiber form: glass and/or ceramic materials (SiO) and fire-blanket materials (polydiphenoxyphosphazene–PDPP). We demonstrate the ability to form nonwoven fabrics from these materials, and investigate their temperature stability as well as their structural and infrared optical properties. The goal of this work is to extend electrospinning to higher temperature materials systems in order to enable advances in technologies such as gas filtration, waste-heat management and optoelectronics. Each of these economically important technologies requires materials that can withstand high temperatures while providing high surface area per unit volume. As an example of one approach at enabling new technology, we coat these fiber systems with rare-earth based materials to demonstrate that we can selectively modify their optical properties.

II. EXPERIMENT

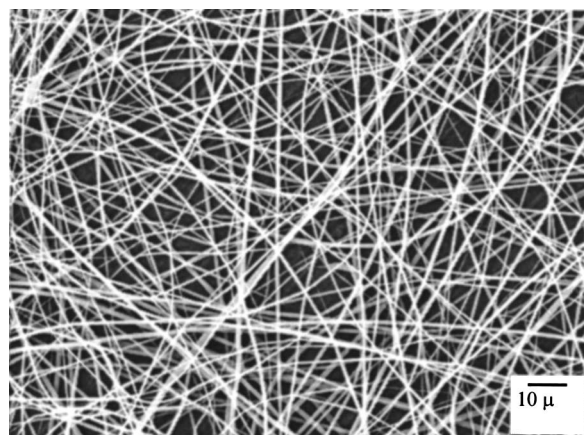
The precursor solution for the SiO fibers is prepared from tetraethylorthosilicate (TEOS, Acros Organics, Inc.) dissolved in ethyl alcohol and hydrochloric acid. A mixture of TEOS 1M:H₂O 2M:HCl 0.01M in alcohol is prepared in a vial and kept in an oven at 60 °C for polymerization and solvent evaporation. The viscosity of the mixture increases with time, and the resulting sol-gel solution is ready for electrospinning when the viscosity reaches that of a 5% polyethyleneoxide (MW 400 000), a solution with which we have significant experience. Although we do not measure the viscosity of our electrospinning solutions in every case, a viscosity on the order of 50–100 cP works well. The sol-gel solution is placed in a pipette having a tip opening approximately 0.5 mm in diameter. The pipette is suspended 20 cm above a carbon sheet which serves as the collector in the case of SiO. An electric field of about 1 kV/cm is maintained using a potential difference of 20 kV (Gamma High Voltage Research D-ES30) between the pipette and the carbon sheet.

The PDPP fibers are produced from a precursor solution of polydiphenoxyphosphazene (Scientific Polymer Products, Inc., MW 379 000). The spinning solution is formed from 0.5 g of the polymer dissolved in 4 g of tetrahydrofuran at room temperature. The solution is then loaded into a pipette similar to the one described above and electrospun with an electric field of roughly 1.7 kV/cm (21.5 kV applied with a pipette to collector distance of 13 cm). The PDPP fibers are spun onto and collected from the surface of distilled water with stainless-steel flat washers (13.5 mm inner diameter and 31 mm outer diameter), followed by drying in an oven at 60 °C for several hours.

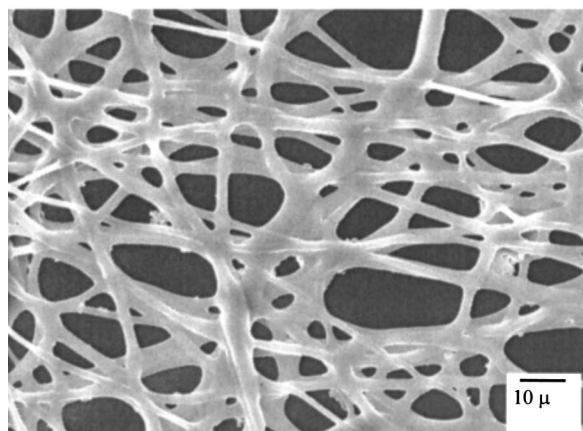
The nanofibers are coated with rare-earth materials using a nitrate solution. For example, erbium (III) nitrate (Strem Chemicals, Inc.) is prepared in ethyl alcohol in a range of concentrations from 15 to 45 wt%. The nanofibers are coated by immersion in the rare-earth solution followed by drying in an oven. The similar chemistry of the rare earths allows us to follow the same procedure for holmium and ytterbium nitrates. The structural properties of the fibers are characterized by scanning electron microscopy (SEM, JEOL JEM-5310) operating at 20 kV and 60 μ A. Thermogravimetric analysis (TGA, TA Instruments 2950) is used to determine the relative thermal stability of the fibers using a temperature ramp of 10 °C/min. Optical absorption spectra of nonwoven mats are obtained using a Fourier transform infrared (Nicolet Nexus 670) bench. Absorbance spectra are obtained in both the mid- and near-IR regions with 4 cm⁻¹ resolution after averaging 400 scans.

III. RESULTS AND DISCUSSION

In this work we prepare both inorganic and organic high-temperature fibers from new materials systems. As expected, the inorganic fibers are more stable to higher temperatures than the organic fibers. SiO and PDPP fiber matrices produced by the electrospinning technique are shown in the scanning electron microscopy micrographs of Fig. 2. In both cases, the fibers form a nonwoven mat. The average fiber



(A)



(B)

FIG. 2. Scanning electron microscope images of electrospun (A) SiO and (B) PDPP fibers. In both cases, the fibers form a nonwoven mat. The SiO fibers are more cylindrical in shape and have smaller average diameters than the PDPP fibers.

diameter is observed to be on the order of $1\ \mu\text{m}$ for SiO, with smooth cylindrical fiber shapes [Fig. 2(A)]. The PDPP fibers [Fig. 2(B)] are on average larger and exhibit more irregular shapes than the SiO fibers. PDPP has a relatively low glass transition temperature (much less than room temperature), and the irregular shapes of the electrospun fibers may result from flow of the polymer at room temperature. Although the average size of these fibers is larger than the anticipated nanometer range, many of the fibers, especially in the SiO case, are submicron in diameter. The fiber diameter is controlled by the concentration of the precursor, solvent evaporation, and the electric fields present during electrospinning. Determining which set of parameters optimizes the production of smaller-diameter fibers for these new material systems is a major component of our ongoing experimental and modeling efforts.

One of the most important physical processes determining the final size distribution of the fibers is solvent evaporation. A typical segment of the jet moves both sideways and in the direction of the applied electric field between the spinner tip and the collector. The fiber stretches as a result of the electrostatic repulsion between similarly charged regions of its

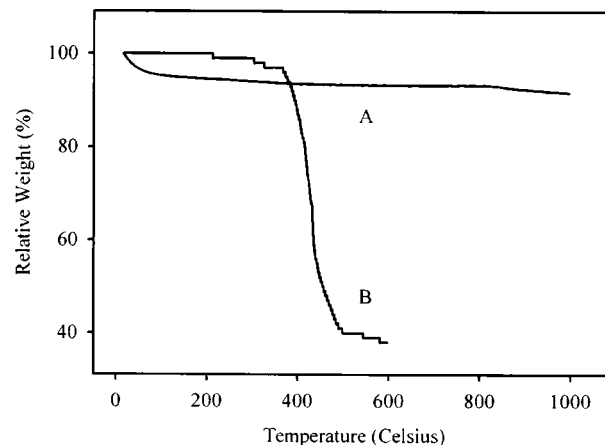


FIG. 3. Thermogravimetric analysis of nonwoven mats of electrospun (A) SiO and (B) PDPP fibers. The thermal stability of the PDPP fibers is better than for many other organic systems, but the inorganic SiO material is stable to much higher temperatures.

own surface. At the same time, solvent evaporation accelerates due to the increasing surface to volume ratio. As the fiber material becomes more viscous it is less likely to stretch and bend. Thus a complicated time-dependent coupling exists between the forces present on the fiber during its motion. If the solvent evaporates too quickly, the fibers solidify before their diameters have been reduced significantly. On the other hand, if solvent evaporation is too slow a spray of droplets rather than continuous fibers results. In the interest of forming fibers from new materials and studying their behavior, we initially accept a larger average diameter than is our ultimate goal ($< 100\ \text{nm}$). This gives us a starting point from which to fine tune the solvent mixture and concentration along with the other processing parameters such as geometry and voltage. We refer the interested reader to Ref. 6 for details of how evaporation is accounted for in models of the electrospinning process.

It is important to verify that these materials maintain their thermal integrity in fiber form for possible high-temperature filtering, waste-heat management, or optoelectronic material synthesis. The thermal stability of the fibers is assessed using TGA as shown in Fig. 3. The SiO fibers are stable to temperatures in excess of $800\ ^\circ\text{C}$ (trace A), whereas the PDPP fibers begin to degrade at temperatures above $300\ ^\circ\text{C}$ (trace B). Hot-stage microscopy and infrared spectroscopy (not shown) after annealing indicate that these fiber systems are thermally stable below the degradation temperatures found in TGA.

Sol-gel coating after electrospinning is one means of tailoring the fiber properties for a wide variety of potential applications. Caruso, Schattka, and Greiner have used a similar approach to coat electrospun nanofibers with titanium dioxide.¹⁰ To demonstrate this for another class of materials, we coat both the SiO and PDPP fibers with rare-earth nitrates to modify their properties. In the near IR, these coatings significantly alter the optical properties of the fibers. Figure 4(A) is a spectrum of SiO fibers coated with a 30 wt% solution of holmium nitrate. Whereas the near-IR spectrum of

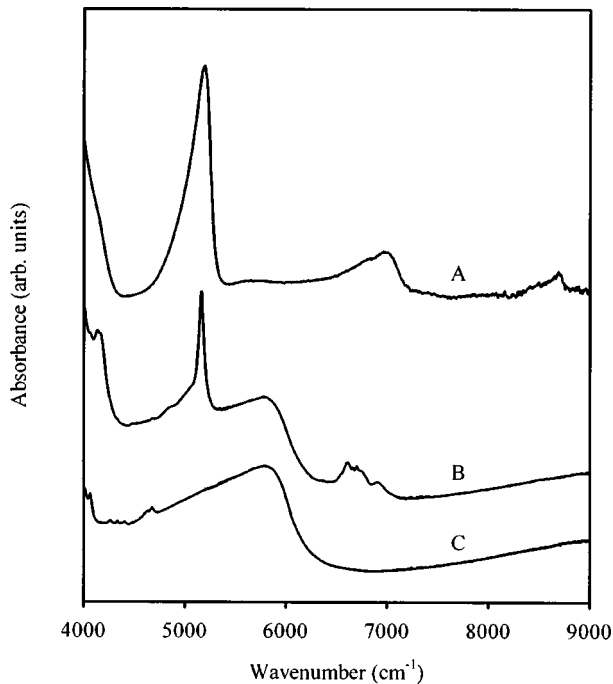


FIG. 4. Near-IR spectra of (A) SiO fibers coated with holmium nitrate, (B) PDPP fibers coated with erbium nitrate, and (C) as-spun PDPP fibers. In (A), structure near 5100 and 8600 cm^{-1} is attributed to holmium, whereas in (B) the erbium signature is near 6600 cm^{-1} . Features near 5200 and 6800 cm^{-1} are related to the hydrated-nitrate coatings which encapsulate the rare-earth species.

SiO is essentially featureless in this spectral range (not shown), the coated fibers exhibit strong absorption bands near 5200 cm^{-1} , with smaller features near 6800 and 8600 cm^{-1} . Holmium transitions are expected at roughly 5100 and 8600 cm^{-1} , which can therefore account for two of the observed absorption bands.

Figure 4(B) is a spectrum of PDPP fibers coated with a 30 wt% solution of erbium nitrate. Comparing this with Fig. 4(A), we see a sharp 5200 cm^{-1} peak and 6600 cm^{-1} structure. Transitions of Er^{+3} species lie near 6600 cm^{-1} , thus accounting for this band, but not explaining the sharp 5200 cm^{-1} absorbance. Having ruled out cross contamination of the Er and Ho species (note that spectrum B has no feature near 8600 cm^{-1} and A has no 6600 cm^{-1} structure), we propose that the nitrate-hydrate structure is responsible for the nonrare-earth bands seen at 5200 and 6800 cm^{-1} . Figure 4(C) shows the spectrum of uncoated PDPP fibers for reference, making it clear that the coatings significantly alter the near-IR spectra of the nonwoven mats.

In the mid IR we see in Fig. 5(A) that SiO fibers coated with a 30 wt% solution of ytterbium nitrate yield a spectrum assignable to SiO, with some hydroxyl signature above 3000 cm^{-1} . Thus the coating has essentially no effect on the fibers or their mid-IR spectra. This is also seen in the case of PDPP fibers, where for comparison we show a spectrum of as-spun fibers [Fig. 5(C)] and one obtained after coating with a 30 wt% solution of erbium nitrate [Fig. 5(B)]. Again, the fiber spectra look essentially identical with or without coatings, except for the hydroxyl contribution.

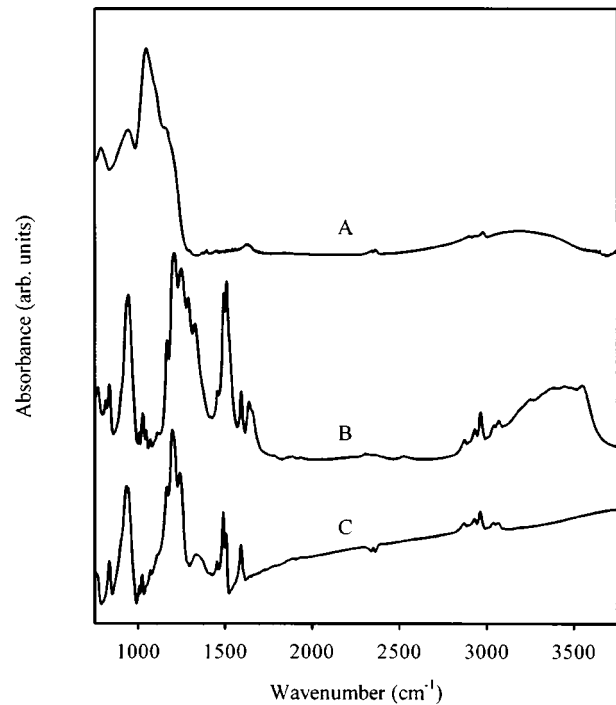


FIG. 5. Mid-IR spectra of (A) SiO fibers coated with ytterbium nitrate, (B) PDPP fibers coated with erbium nitrate, and (C) as-spun PDPP fibers. The rare-earth coatings do not significantly modify the mid-IR spectra of the fibers, except for hydroxyl contributions from the hydrated-nitrate structure.

Thus we find that although our coatings do not significantly change the mid-IR spectral properties of either SiO or PDPP fibers, the near-IR regions are modified substantially. There are spectral differences depending on the identity of the rare-earth species, in our case erbium, holmium and ytterbium, and there are near-IR contributions that seem to originate from the presence of the hydrated nitrate structure. We have not pursued detailed band assignments for these features, as they presently only serve to demonstrate the concept that electrospun fibers in general and high-temperature fibers in particular can be modified with coatings to selectively alter their optical properties.

Submicron and nanometer-diameter fibers can serve as high-surface-area supports or substrates for a variety of materials. Thin-film materials can be deposited onto the high-temperature fibers by sol-gel or vacuum techniques. The temperature stability of the fibers can be used to adjust and/or control the properties of the coated fiber. Our group has recently reported the use of electrospun fibers as substrates for metallic, oxide, and nitride thin films deposited by physical and chemical vapor deposition techniques.¹³ The fiber temperature can be used to control the crystal structure of the deposited film. For example, at low fiber temperatures we observe columnar nanocrystalline deposits on the nanofibers. At temperatures above 400 °C, where the SiO fibers would still be stable, we expect to be able to deposit high-quality semiconducting thin-film coatings. This is part of our ongoing effort as we develop nanofiber electrospinning for new technologies.

The results presented here demonstrate that we cannot

only produce fibers from high-temperature materials with electrospinning, but also modify them with a simple coating procedure after production. These results have implications for technologies that benefit from high surface area per unit volume materials. The high-temperature fibers produced as part of this effort extend electrospinning to materials that are synthesized or used over a wide range of temperatures. The work reported here paves the way toward many useful applications for electrospun nanofibers.

IV. SUMMARY

Nanofibers stable at high temperatures promise to be useful in many different applications. Electrospinning, which has been used previously to produce nanofibers from many different materials, is used here to produce high-temperature fibers from two new classes of materials. These electrospun fibers are suitable substrates for films deposited by sol-gel and vapor phase techniques, as demonstrated with a series of rare-earth nitrates. Electrospinning is a suitable process for manufacturing the next generation of nanoscale materials for a variety of applications.

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