Short communication

Processing and characterization of electrospun Y$_2$O$_3$-stabilized ZrO$_2$ (YSZ) and Gd$_2$O$_3$-doped CeO$_2$ (GDC) nanofibers

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Abstract

The technique of electrospinning was employed to fabricate uniform one-dimensional (1-D) inorganic–organic composite nanofibers from alcoholic solutions containing polyvinyl pyrrolidone (PVP) and suitable aqueous precursors of yttrium and zirconium ions in one case and gadolinium and cerium ions in the other. Upon firing and sintering under carefully pre-selected time-temperature profiles (heating rate, temperature and soak time), ceramic nanofibers retaining the original morphological features observed in the as-spun composition were obtained. Analytical tools, such as simultaneous TG–DSC, Raman spectroscopy and SEM were employed to elucidate the pathway of ceramic phase formation and the systematic evolution of morphological features in the spun and the processed fibers. X-ray diffraction was used to identify the crystalline fate of the final products. It was found that several millimeter long, uniform YSZ and GDC nanofibers of high phase purity could be fabricated.

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1. Introduction

One aspect of current interest and great relevance to the fundamental understanding of the behavior of materials is the role of dimensionality and size on their optical, chemical and mechanical properties for application in a wide range of devices [1]. In this regard, one-dimensional (1-D) systems with nanoscale attributes are being synthesized and studied in great details. Owing to the nanoscalar features and peculiar shapes, one-dimensional systems exhibit novel physical and chemical properties that can be exploited in optics, catalysis and data-storage devices. Thus, they become model systems to study and correlate the theoretical explanations that are still in progress. Such behavior is almost non-existent in the bulk material, where the particle size is in the micron level. There is growing interest in introducing such attributes in nanosized inorganic materials as well. The most obvious advantage of doing so is the possibility of their application as quantum dots in a host of devices, such as MEMs, lab-on-a-chip sensors/detectors, structural elements in artificial organs and arteries, reinforced composites, micro solar cell electrodes, micro fuel cells and photocatalysts (splitting of water and in the deactivation of chemical and biological weapons), to name a few. For instance, polymer nanofibers are used as selective gas separation membranes, filters, biomedical materials (drug carriers and as scaffolds for tissue engineering), protective clothing, space mirrors and precursor platforms or scaffolds for the nanotube/nanowire synthesis.

A novel technique for fabricating 1-D structures is electrospinning. The technique of electrospinning uses external electrical forces to produce novel polymeric fibers of diameters in the range of 3–1000 nm, depending upon the strength of the applied voltage between a drop of the precursor solution (or melt) and the collecting surface. Electrospinning occurs when the electrical forces at the surface of the drop overcome the surface tension. When this happens, the solution or melt is ejected as an electrically charged jet and shoots towards the oppositely charged electrode. Upon reaching the collector surface, it gets neutralized and collects as dry nanofibers. Electrospinning is a rather old, relatively unknown but simple, convenient and inexpensive method. The first patent was issued more than 70 years ago [2]. During the past few years, however, it has seen a revival. Several
papers have been published and over 30 US patents have since been issued [3–13].

The possibility of extending the concept to ceramic systems has opened a new era in nanoscale research during the past couple of years. It is possible to synthesize these one-dimensional nanofibers in pure form or as suitable ceramic–polymer composites. It is also envisaged that by controlling the jet orifice, one can control and the internal diameter of the resulting nanofibular structures.

In this communication, we report the fabrication of two key ceramic components of great relevance in fuel cells and catalysis, namely 8 mol% yttria-stabilized zirconia (8YSZ) and 10 mol% gadolinia-doped ceria (10GDC) in nanofibrillar structures. The target compositions were first electrospun in the form of polymer–ceramic (‘polycer’) composite fibers, which were subsequently processed to yield ceramics of the desired composition. The transformation of polycer to ceramic was followed by TG–DSC and the final product was verified by Raman spectroscopy, X-ray diffraction and SEM–EDS techniques.

2. Experimental procedure

2.1. Preparation of the ceramic precursor solutions

High-purity zirconyl chloride, ZrOCl₂ (99.99%) was procured from Millennium Chemicals, Australia. Yttrium nitrate, Y(NO₃)₃ · 6H₂O (99.995%), gadolinium nitrate, Gd(NO₃)₃ (99.99%) and ammonium cerium(IV) nitrate, (NH₄)₂ Ce(NO₃)₆ (99.99%), all from Alfa-Aesar, MA, USA, were used as the precursors for the synthesis of YSZ and GDC fibers. The choice of the inorganic precursors was based on their appreciable and ready solubility in water. In the case of YSZ, adequate amount of zirconyl chloride and yttrium nitrate powders were accurately weighed and separately dissolved in minimum volume of de-ionized water by gentle stirring until clear. Subsequently, the two solutions were mixed together and stirred for additional 2 h for effective ionic level mixing and homogenization. In the case of GDC, accurate amounts of ammonium cerium nitrate and gadolinium nitrate powders were first individually dissolved in de-ionized waters under constant and gentle stirring. The two aqueous solutions of gadolinium nitrate and ammonium cerium nitrate were then mixed under constant stirring, which was also continued for additional 2 h. The weight calculations were made so as to give 50 ml of a 0.01 M stock solution containing Y³⁺ and Zr⁴⁺ ions in one case and, Gd³⁺ and Ce⁴⁺ ions in the other, corresponding to 8 mol% yttria-stabilized zirconia (8YSZ) and 10 mol% gadolinia-doped ceria (10GDC) solid solution, respectively.

2.2. Preparation of the polymeric precursor solutions

Granular polyvinyl pyrrolidone (PVP, average molecular weight ~1.3 × 10⁶, Alfa-Aesar, MA, USA) was used as the polymeric component of all the composites fabricated in this study. The polymeric solution was made by dissolving the PVP granular powder in reagent grade ethanol (Fisher Chemicals, PA, USA) under constant and vigorous stirring to give 15 wt% PVP solution. This concentration was arrived at and selected after several preliminary iterations with respect to the desired viscosity of the inorganic–organic composite solutions were carried out. Due to pronounced volatility of ethanol during and after the preparation, the PVP solution was prepared only when electrospinning was to be carried out; PVP solutions tended to dry out and leave a stiff gel in the container upon prolonged storage.

2.3. Spinning of the fibers

For the electrospinning experiments, equal volumes of the precursor solutions (YSZ or GDC and PVP) were added to a
beaker and thoroughly mixed with the aid of a magnetic stirrer to form a homogeneous viscous solution. After mixing, this solution was drawn into a 5 ml capacity Benton-Dickenson clinical syringe (VWR International, IL, USA). Precision-tip 1 or 1.5 in. long stainless steel needles from EFD Inc., RI, USA (23 or 25 gauge) were attached to the syringe, which was mounted on a programmable syringe pump (KDS-100). The syringe and needle make and type, flow rate and amount to dispense were entered in the syringe pump memory through the front panel.

The pump could be operated either in horizontal or vertical configuration and no difference was noted in the quality of the fibers thus produced. The preferred orientation of the syringe pump in this work was horizontal. A custom-made dc power supply (30 kV maximum) with the high voltage system from Ultra Volt (FL, USA) and a circuit design originally developed at NASA Glenn Research Center [14] was used for the electrospinning of fibers. One terminal of the power supply was connected to the needle, while the other was connected to the collector plate. The collector plate was grounded.

Several different types of collector plates were used. A simple collector plate was made by layering several thicknesses of aluminum foil into approximately, a 4 in. × 4 in. square. For the ease of sample handling and subsequently processing, ceramic dishes/plates were used to collect the fibers. In the case of ceramic dishes, a small 1 in. × 1 in. of aluminum foil was attached to the back of the dish with double-side tape and the electrode was hooked to the foil. This allowed the fibers to be collected directly onto the ceramic plate. Using the high-voltage power supply, 12–15 kV was applied between the needle and the collector plate in order to initiate the electrospinning. After the voltage was turned on, the syringe pump was started. The voltage was tweaked precisely until the fibers began to form steadily and collect on the collector plate facing the syringe, placed about 3 in. away from the tip of the needle. Typically, 1 ml of the solution was spun at a time, with a flow rate between 0.03 and 0.12 ml/h. Thus, an individual run lasted about 8–33 h with short intermittent interruptions of the run for periodic cleaning of the clogged needle-tip from time to time.

Fig. 3. Photographic timeline of the progress of the electrospinning process and fiber growth in the case of 1:1 aqueous YSZ–ethanolic PVP solution (flow rate, 0.03 ml/h; applied voltage, 12–15 kV), shots were taken after: (a) 26 min; (b) 50 min; (c) 103 min; (d) 104 min, from the start of the spinning process.
After spinning was complete, small fraction of the fibers collected on ceramic plates were separated for characterization by Raman, TG–DSC and SEM. The ceramic dish with the remaining fibers was directly placed in a PID-controlled programmable box furnace and fired to remove the polymeric component and to form the desired solid solutions, viz. 8YSZ and 10GDC. In the case of 8YSZ, fibers were fired up to 1500 °C for 1 h, while the GDC samples were fired up to 1000 °C for 2 h in two stages according to the schedule shown in Fig. 1. The small heating rates were chosen so as to ensure the removal of organic components without destroying the nanofibrillar morphological features in the end products and also to avoid the disintegration of the ceramic fibers; as such, ceramics exhibit rather poor thermal shock resistance, even in bulk. After the furnace was cooled, samples were collected for characterization by various analytical techniques.

3. Results and discussion

In order to test the feasibility of making ceramic fibers by this technique, prior to the electrospinning of the YSZ or GDC polycer composites, first a 5 wt.% aqueous solution of zirconyl chloride was mixed with 15 wt.% HMWPVP in equal volumes, homogenized and spun. Fig. 2 shows the scanning electron micrographs of the ZrOCl₂·PVP composite fibers collected on a ceramic plate. Several inches long fibers with uniform diameter were formed.

Fig. 3 shows the progress of the spinning process in real-time and the increase in the amount of the YSZ–PVP composite fibers formed.

With the 25 gauge needle, a more uniform, almost cotton like distribution of fibers was observed. Using the 23 gauge needle, longer fibers were observed along with twisting and braiding during the spinning process. It should be pointed out that at the verge of fiber formation, the liquid droplet at the tip of the needle split into several elongated dried strands, which individually transformed into thin fibers. The scanning electron micrographs (acquired on a Philips XL30 FEG SEM) on the as-electrospun composite fibers from the YSZ–PVP solution are shown in Fig. 4. Identical morphological features of individual fibers with large aspect ratio can be easily seen.

The fibrillar attributes observed in the as-spun YSZ–PVP composite were virtually retained in the samples that were fired at 1500 °C for 1 h and furnace cooled, as per the heating schedule shown in Fig. 1. This is evident in the SEM pictures shown in Fig. 5.
Fig. 6 shows the comparative Raman spectra (LabRam, Jobin-Yvon Horiba Inc., using 633 nm excitation laser) of PVP in ethanol and the fired YSZ–PVP composite in the range of 200–1200 and 200–1600 cm\(^{-1}\) wavenumbers, respectively. The Raman shifts at \(\sim 745, 880\) and 1053 cm\(^{-1}\) in Fig. 6a belong to ethanol [15].

As can be seen, there is no trace of the polymer remnant in the fired sample. The slightly displaced Raman lines at 260, 322, 463/467 and 640 cm\(^{-1}\) represent zirconia that contains Y\(_2\)O\(_3\) phase, whose mild signatures at 302, 348 and 367 cm\(^{-1}\) [16–18] can also be observed in the Raman spectrum shown in Fig. 6b. The shift in the Raman lines from those for pure ZrO\(_2\) and Y\(_2\)O\(_3\) phases is a manifestation of the incorporation of the latter in the zirconia lattice and the stabilization of the former [19]. It is also worth pointing out that the bands characteristic of monoclinic zirconia phase [20] are totally absent. One might speculate the presence of carbon as an impurity in the fired sample, resulting from the degradation and carburization of PVP upon heat-treatment of the as-spun composite fibers. It is rather hard to detect carbon, if formed, by XRD, but it is possible to identify it easily in Raman spectrum since carbon is strongly Raman active. The D and G peaks of carbon occur around 1360 and 1560 cm\(^{-1}\), respectively [21]. However, as seen from Fig. 6b, such strong absorptions are entirely absent, thereby confirming the total combustion of the organic part of the composite.

The formation of crystalline YSZ phase in the YSZ–PVP composite fired at 1500 °C is corroborated by the XRD signature collected at room temperature, using a Scintag XDS-2000 diffractometer with monochromatic Cu K\(\alpha\) radiations and Ni
filter at a scan rate of $1^\circ (2-\theta)/\text{min}$. The X-ray diffraction is shown in Fig. 7, which excellently matches the JCPDS-ICDD Card #30-1468 for the cubic solid solution 8YSZ. The energy dispersive spectrum (EDS) collected on the fired YSZ sample (whose microstructure is illustrated in Fig. 5) distinctly identifies Zr and Y as the elemental component in the fiber and is shown in Fig. 8.

4. Conclusions

The technique of electrospinning has been successfully employed to fabricate several inches long 1-D ceramic fibers consisting of phase pure yttria-stabilized zirconia and gadolinia-doped ceria from a polymeric solution containing appropriate metal cations in the desired mole ratios. The polymeric component aided in obtaining the required viscosity of the base mixture. The structural and microstructural artifacts of the resulting fibers were investigated by Raman spectroscopy, SEM–EDS and XRD techniques.

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References