J Mater Sci (2008) 43:1664–1668
DOI 10.1007/s10853-007-2389-9

YBCO nanofibers synthesized by electrospinning a solution of poly(acrylic acid) and metal nitrates

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Received: 8 September 2007 / Accepted: 6 December 2007 / Published online: 11 January 2008
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Abstract A versatile approach to the synthesis of YBCO (high temperature superconductor ceramics) nanofibers via electrospinning a polymer precursor solution is reported. The aqueous polymer precursor solution consists of poly(acrylic acid) (PAAc) and a mixture of yttrium nitrate, barium nitrate, and copper nitrate, henceforth termed (Y,Ba,Cu)–N. The conductivity of the polymer precursor solution at 27.1 °C was 14.70 mS/cm, its zero shear viscosity was 52.00 cP, and its pH was 1.88. Typical YBCO nanofibers were 50–100 nm in diameter and around of 10 μm length. The nanofibers also contain relatively small amounts of yttrium oxide and copper yttrium oxide.

There is a great interest in developing nanoscale ceramic materials for advanced technology applications [1–4]. The ceramic materials of interest include high temperature superconductor ceramics (HTSC), boron nitride, silicon nitride, barium titanate, and lead zirconate titanate (PZT). One of the most actively studied HTSC materials is YBCO ($YBa_2Cu_3O_{7-\delta}$) [5]. YBCO has numerous advantages compared to other ceramic superconductors: it is the only known stable four-element compound with a critical temperature (T_c) above 77 K; it includes neither toxic elements nor volatile compounds; it is easy to produce single-phase YBCO; it is less anisotropic than other HTSC materials; it carries higher current densities at higher magnetic fields [6]. The critical temperature of YBCO is approximately 90 K and the critical magnetic field can be as high as 300 T. For thin-film applications, the critical current density (J_c) is an important parameter and, in the case of YBCO, it is typically greater than 1 MA/cm^2 [6]. Owing to its excellent properties, much attention has been focused on trying to produce YBCO in the easiest and least expensive manner possible, making it advantageous for a multitude of applications such as superconducting quantum interference devices (SQUIDs) and for high frequency applications. Several processing approaches for producing ceramic nanowires have been investigated including laser ablation, chemical vapor deposition, and a solution method [7]. The procedure for producing nanowires and its cost effectiveness, however, is far from being trivial. Developing a method for producing large quantities of nanowires remains a great challenge.

Recently, it was demonstrated that polymer/metal-salt precursors can provide a simple and flexible way to produce YBCO films [5, 8–14]. Polymers are of great interest in HTSC research and development: they can be used as thickening agents for HTSC precursor solutions [15], in HTSC composites [16], or as complexing agents for metal ions for the production of shapeable HTSC [5, 17–19]. It was shown that the precursor processing technique can affect the structure of the resulting ceramics [12]. However, the production of HTSC nanofibers using polymer/metal-salt precursors has not been investigated and the preparation of large-scale, long nanofibers presents a great challenge. Electrospinning has been widely investigated for preparing long nanofibers of polymers [20–22], ceramics [23], and carbon [24–26].

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In this manuscript, a versatile approach to the synthesis of YBCO nanofibers via electrospinning a polymer precursor solution is reported. The aqueous polymer precursor solution consists of poly(acrylic acid) (PAAc) and a mixture of yttrium nitrate, barium nitrate, and copper nitrate, henceforth termed (Y,Ba,Cu)–N, in which the atomic ratio Y/Ba/Cu is 1/2/3. The conductivity of the polymer precursor solution at 27.1 °C was 14.70 mS/cm, its zero shear viscosity was 52.00 cP, and its pH was 1.88. Adding the metal nitrates to the PAAc solution increased the ion concentration and, hence, its conductivity. The ions also shield the electrostatic repulsion between the partially charged PAAc molecules, making the PAAc molecules more compact [28], and increasing molecular entanglement.

Experimental

HTSC nanofiber synthesis

The polymer solution was made from poly(acrylic acid) (PAAc) which was supplied by Aldrich (average $M_v \sim$ 450,000 g/mol). Yttrium nitrate pentahydrate [$Y(NO_3)_3 \cdot 5H_2O$] was supplied by Aldrich, barium nitrate [$Ba(NO_3)_2$] was supplied by Merck, and copper nitrate 2.5 hydrate [$Cu(NO_3)_2 \cdot 2.5H_2O$] was supplied by Riedel de Haën. The solvent used was deionized water. All materials were used as received. The atomic ratio Y/Ba/Cu atoms was 1/2/3 in the mixture of nitrate salts [(Y,Ba,Cu)–N]. The HTSC precursor consisted of PAAc containing (Y,Ba,Cu)–N with a PAAc/(Y,Ba,Cu)–N mass ratio of 2/1. The precursor solution was made by adding one part of a 5% aqueous solution of (Y,Ba,Cu)–N to two parts of a 5% aqueous PAAc solution. The conductivity and pH of a solution was determined using a conductivity meter (PCT 402, Extech) and a pH meter (PH/Ion Model 510, Eutech Instruments), respectively. The solution viscosity was measured using a programmable viscometer (Brookfield DV-II+).

The electrospinning took place from a hypodermic needle with an inner diameter of 0.5 mm attached to a 1 mL syringe. The flow rate was 1–3 mL h^{-1}. The positive terminal was connected to the tip of the needle and the solution was spun onto the edge of a grounded collector disc (for more details cf. Refs. [27, 28]). The strength of the electrostatic field was 1.1 kV cm^{-1} and the distance between the tip and the edge of the disc was 18 cm. The linear speed at the edge of the disc collector was $V = 8.8$ m s^{-1}. All the experiments were performed at room temperature ($\sim$24 °C), and at a humidity of about 50%. As-spun nanofibers were deposited on flat pieces of Al_2O_3 which were attached to the edge of the collector disc. Nanofibers were collected in two batches: individual oriented fibers were produced using a short collection period, nanofibers mats for X-ray analysis were produced using a long collection period. The nanofibers were dried in a vacuum oven before pyrolysis.

The precursor nanofibers were pyrolyzed in a tube furnace using the following process. (1) In a nitrogen environment: from room temperature to 450 °C at 5 °C/min, holding at 450 °C for 2 h, heating to 700 °C at 5 °C/min, and holding at 700 °C for 2 h. (2) In an oxygen environment from 700 to 950 °C at 10 °C/min, holding for 3.5 h, slow cooling to 450 °C at 3 °C/min, holding at 450 °C for 3 h, followed by slow cooling to room temperature.

HTSC nanofiber characterization

The as-spun and pyrolyzed nanofibers were observed using high-resolution scanning electron microscopy (HRSEM) (LEO high-resolution SEM equipped with an in-lens SE detector) using a voltage of 3 keV and a working distance of 4 mm. The phases were identified using X-ray powder diffraction (XRD) (Philips PW 1840 X-ray with a Ni-filtered Cu Kα X-ray beam excited at 40 keV and 40 mA). TEM analysis was done using Tecnai G^2 T20 S-Twin TEM at 200 keV (or 120 keV) with a LaB6 electron source and an FEI Super Twin objective lens. This microscope is equipped with BF (bright field) and DF (dark field) STEM (scanning transmission electron microscopy) detectors. The TEM samples were prepared by sonicating the nanofibers in ethanol and placing a drop on a copper grid covered with lacey carbon.

Individual as-spun polymer precursor nanofibers from short collection times are seen in Fig. 1a, b (scanning electron microscope (SEM) micrographs). Typical as-spun nanofibers are 1.5 cm long with diameters of 400–600 nm. Most of the as-spun nanofibers are oriented in the same direction, as seen in Fig. 1a. It can be seen in Fig. 1b that the nanofibers have a relatively uniform diameter, although some beading, resulting from a Rayleigh instability [29], can be seen in Fig. 1b. Nanofibers following pyrolysis in oxygen at 950 °C for 3.5 h can be seen in Fig. 1c (SEM micrograph) and d (transmission electron microscope (TEM) bright field (BF) micrograph). Following pyrolysis the nanofibers exhibit a frankfurter-like structure with diameters between 50 and 150 nm (Fig. 1c, d). The pyrolyzed nanofibers are typically 5–10 μm long. This significant reduction in nanofiber length can be associated with the significant volume loss and the embrittlement that take place during pyrolysis. The individual segments in Fig. 1d are clearly faceted, indicating that they are crystalline in nature.

The X-ray diffraction (XRD) pattern from a pyrolyzed mat of nanofibers produced using a long collection time is

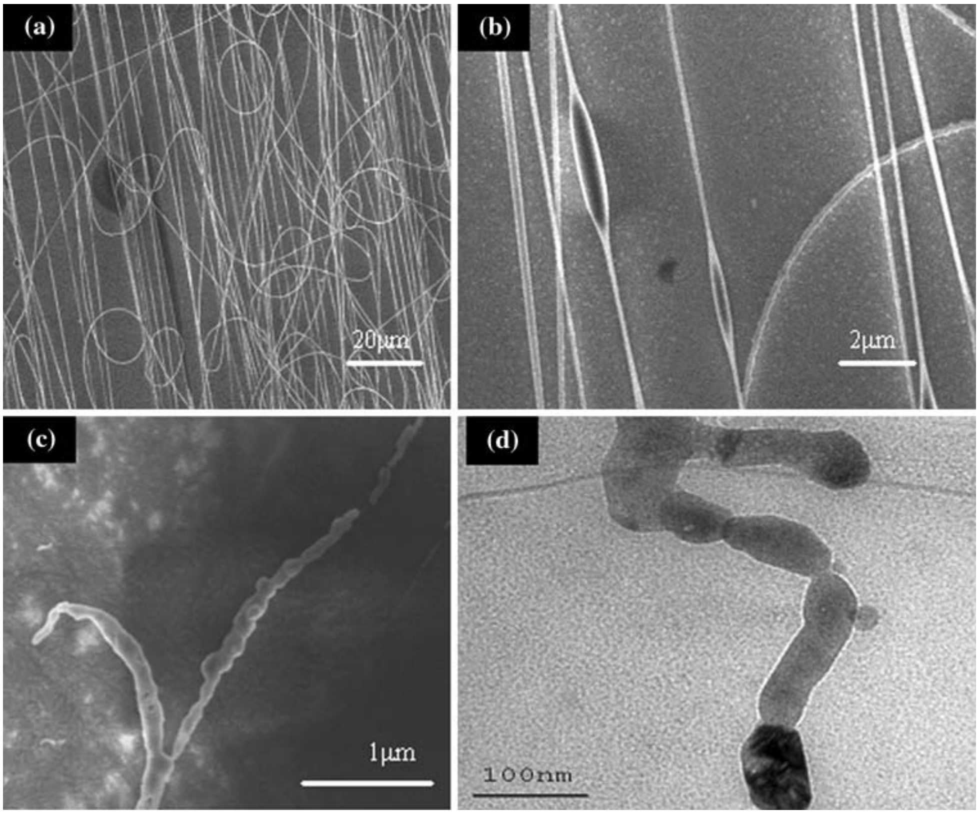

Fig. 1 (**a** and **b**) SEM images of as-spun polymer precursor nanofibers; (**c**) SEM image of a pyrolyzed nanofiber; and (**d**) TEM BF image of a pyrolyzed nanofiber

shown in Fig. 2. All the peaks can be indexed to YBCO *d*-spacings such as: (103), (113), and (020) at 2.727, 2.233, 1.943 Å, respectively (from the Joint Committee on Powder Diffraction Standards (JCPDS) # 39–0486). The X-ray results also show that there are relatively small amounts of Y_2O_3 and $Cu_2Y_2O_5$ present. Such contaminant phases may not be present in the nanofibers from the pyrolysis of individual fiber from short collection times. The presence of such contaminant in the mats may result from their significantly greater thickness, as has been seen for the production of YBCO through the pyrolysis of films of various thicknesses [12].

The pyrolyzed nanofiber in Fig. 3a (TEM BF micrograph) exhibits a distinct rod-like structure that was used for further analysis. The selected area electron diffraction (SAEDP) of the rod-like structure is presented in the insert in Fig. 3a. Indexing of the SAEDP is consistent with [4,5,−2] zone axis for the orthorhombic $YBa_2Cu_3O_{6.8}$. This assignment was confirmed through *d*-spacing values taken from the diffractions of the sample at the inset of Fig. 3a and comparison to JCPDS # 39–0486. The DF (dark field) micrograph in Fig. 3b was taken from a single diffraction spot. The fact that the entire rod-like structure is bright in Fig. 3b while the rest of the nanofibers are dark indicates that the rod-like structure is a single crystal. Thus, pyrolysis of nanofibers produced by electrospinning a precursor solution can be used to produce single crystals of YBCO. Modifications of the synthesis procedure and pyrolysis conditions that might help produce longer single crystal nanofiber units are currently being investigated.

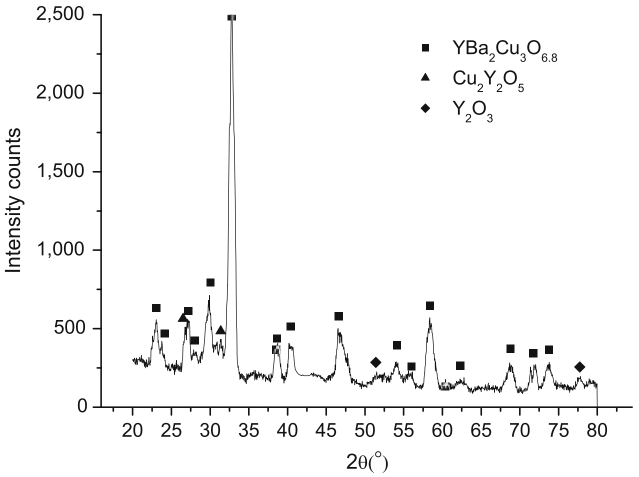

Fig. 2 XRD pattern from a pyrolyzed mat of nanofibers

Figure 4a and b shows TEM micrographs of pyrolyzed nanofibers. The lattice image clearly observed in Fig. 4b indicates that these nanofibers are highly crystalline. The lattice fringe spacings of 2.47 and 2.23 Å correspond to the {112} and {113} planes in the orthorhombic structure of YBCO. Figure 4c shows the electron diffraction pattern

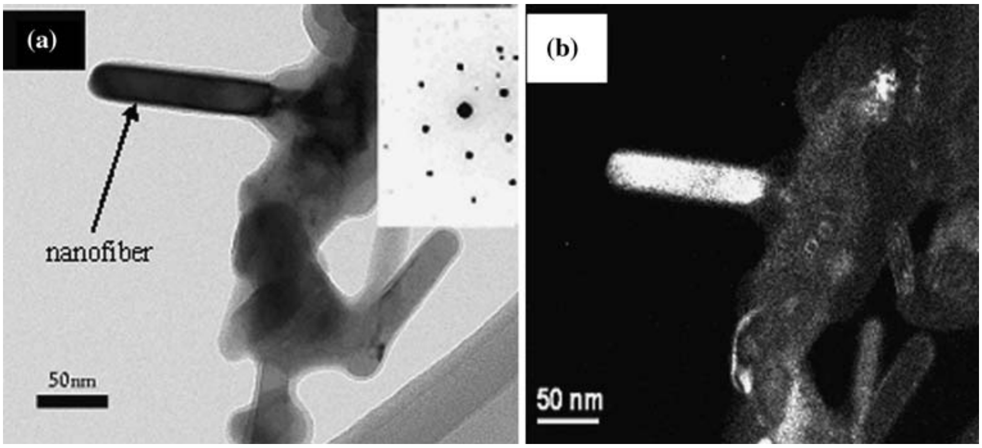

Fig. 3 (**a**) TEM BF micrograph of a pyrolyzed nanofibers (inset: SAEDP at the zone axis of a single nanofiber); (**b**) TEM DF micrograph of the pyrolyzed nanofiber seen in (**a**)

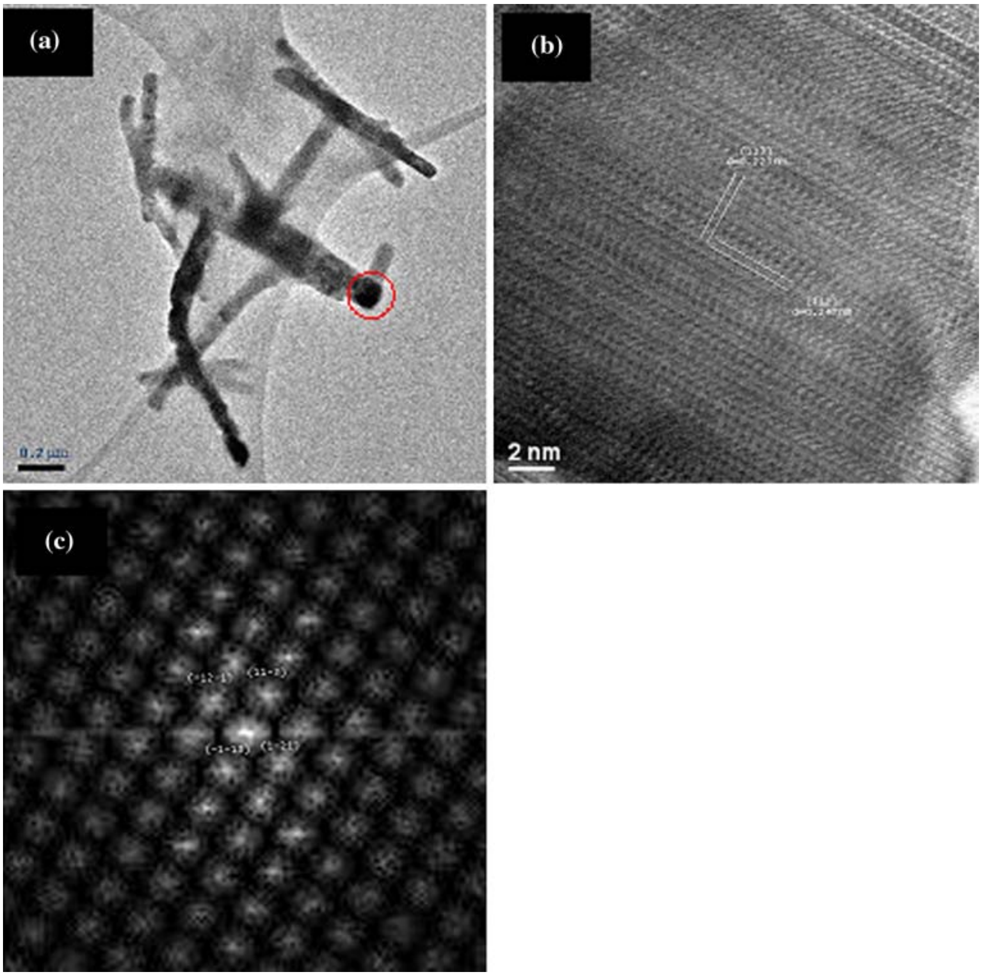

Fig. 4 Microstructure of pyrolyzed nanofibers: (**a**) TEM micrograph of individual nanofibers; (**b**) lattice image of a single crystalline nanofibers; and (**c**) FFT electron diffraction pattern obtained from (**b**)

obtained by fast Fourier transform (FFT) of the lattice image in Fig. 4b. The indices of the electron diffraction spots are based on the orthorhombic structure of YBCO.

In summary, YBCO nanofibers were synthesized by pyrolyzing nanofibers generated by electrospinning a polymer precursor solution containing poly(acrylic acid) and a mixture of metal nitrates. Typical YBCO nanofibers were 50–100 nm in diameter and around of 10 μm length. The nanofibers also contain relatively small amounts of yttrium oxide and copper yttrium oxide. Thus, it has been demonstrated that electrospinning offers a simple method for synthesizing high aspect ratio nanofibers of ceramics with complex structures. There are many potential applications for such YBCO nanofibers. Currently, detailed studies are in progress to prepare nanoscale devices using these nanofibers.

Acknowledgement We gratefully acknowledge the financial support by Russell Berrie Nanotechnology Institute.

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