METAL AND CERAMIC NANOFIBERS

CROSS-REFERENCE

[0001] This application claims the benefit of U.S. Provisional Application Nos. 61/528,895, filed August 30, 2011, and 61/636,095, filed April 20, 2012, both of which are incorporated herein by reference in their entireties.

BACKGROUND OF THE INVENTION

[0002] Ceramic and metallic nanofibers have potential for applications in a wide variety of fields, including high performance filtration, chemical sensing, biomedical engineering and renewable energy. Previous methods for producing ceramic or metallic nanofibers include the electrospinning of sol-gel precursors with or without a polymer binder. However, the nanofibers produced by the sol-gel method have many disadvantages, such as low performance and poor coherence, which makes them unsuitable for many applications.

SUMMARY OF THE INVENTION

[0002a] According to an aspect of the present invention, there is provided a process for producing one or more nanofiber, the process comprising electrospinning a fluid stock, the fluid stock comprising metal precursor(s) and polymer, the weight to weight ratio of the precursor(s) to polymer being at least 1:2; and the fluid stock being aqueous.

[0002b] According to another aspect of the present invention, there is provided a nanofiber comprising metal precursor(s) and polymer, the weight to weight ratio of the precursor(s) to polymer being at least 1.5:1.

Provided herein are nanofibers and processes for producing nanofibers. In some instances, the nanofibers are metal, metal oxide, and/or ceramic nanofibers. In some embodiments, the nanofibers are high quality nanofibers, high performance nanofibers, highly coherent nanofibers, highly continuous nanofibers, or the like. In some embodiments, the nanofibers are coherent, are long, have few voids and/or defects, and/or have other advantageous characteristics such as flexible control of metal and/or ceramic crystal sizes. In some instances, the nanofibers are produced by electrospinning a fluid stock comprising a high concentration of ceramic or metal precursor in the fluid feed stock. In some instances, the fluid stock further comprises well mixed or substantially uniformly distributed precursor in the fluid stock. In some embodiments, the fluid stock is converted to a nanofiber comprising few voids, few defects, long or tunable lengths, and the like.

[0004] Provided in certain embodiments herein is a process for producing one or more nanofiber, the process comprising electrospinning a fluid stock, the fluid stock comprising metal precursor(s) and polymer, and

a. the weight to weight ratio of the precursor(s) to polymer being at least 1:2;
b. the fluid stock being aqueous;
c. the precursor(s) being present in the fluid stock in a concentration of at least 200 mM; or
d. any combination thereof.

[0005] In specific embodiments, the fluid stock is (1) a solution; (2) a substantially uniform dispersion (e.g., of the precursor(s)); or (3) a substantially homogenous dispersion (e.g., homogeneous dispersion of the precursor(s)). In further or alternative embodiments, the weight-to-weight ratio of the precursor(s) to polymer

in the fluid stock is at least 1:2 (e.g., over 1:2) and the fluid stock is aqueous. In specific embodiments, the weight-to-weight ratio of the precursor(s) to polymer is at least 1:1. In further or alternative embodiments, the fluid stock is prepared by combining reagent precursor(s), reagent polymer(s) and water to form the fluid stock comprising the precursor(s)

[0011] ~~In one aspect,~~There is also described herein ~~is~~ a process for producing a nanofiber. In some embodiments, the process includes electrospinning a fluid stock. The fluid stock comprises metal and/or ceramic precursor and polymer. In one embodiment, the weight to weight ratio of the precursor to polymer is at least 1:2. In some embodiments, the polymer is water soluble.

[0012] ~~In one aspect,~~There is also described herein ~~is~~ a process for producing nanofibers, the process comprising electrospinning a fluid stock, the fluid stock comprising metal precursor(s) and polymer. In some embodiments, the fluid stock is (1) a solution; (2) a substantially uniform dispersion (e.g., of the precursor(s)); or (3) a substantially homogenous dispersion (e.g., of the precursor(s)).

[0013] ~~In one aspect,~~There is also described herein ~~is~~ a method for producing a nanofiber, the method comprising electrospinning a first fluid with a second fluid, at least one of the first or second fluids being an aqueous fluid. In some embodiments, the first and second fluids are electrospun about the same or similar axis. In some embodiments, the first fluid is an aqueous fluid comprising water, a water soluble polymer, and metal precursor. In some embodiments, the second fluid is a second aqueous fluid, comprising water, a water soluble polymer, and a second metal and/or ceramic precursor, wherein the water soluble polymer of the second fluid is the same or different than the water soluble polymer of the first fluid.

[0014] ~~In one aspect,~~There is also described herein ~~is~~ a method for producing a nanofiber, the method comprising multi-axially electrospinning an aqueous fluid stock and a second fluid. In some embodiments, the aqueous fluid stock comprises water, a water soluble polymer, and metal and/or ceramic precursor. In some embodiments, the second fluid is a second aqueous fluid stock. In some embodiments, the second fluid is a gas. In some embodiments, the second fluid at least partially surrounds the aqueous fluid stock. In some embodiments, the aqueous fluid stock at least partially surrounds the second fluid.

[0015] ~~In one aspect,~~There is also described herein ~~is~~ a process for producing a nanofiber, the process comprising electrospinning a fluid stock comprising metal precursor, ceramic precursor, or combination thereof wherein: (a) the fluid stock is aqueous; (b) the concentration of the precursor in the fluid stock is at least 200 mM; or both (a) and (b).

[0016] In some embodiments, the fluid stock further comprises a water-soluble polymer. In some embodiments, the precursor binds to the water-soluble polymer. In some embodiments, the electrospinning step comprises multi-axially electrospinning the fluid stock with a gas or a second fluid stock. In some embodiments, the fluid stock comprises a non-aqueous solvent. In some embodiments, the fluid stock comprises tetrahydrofuran (THF) and polystyrene (PS).

[0017] ~~In one aspect,~~There is also described herein ~~is~~ a process of producing a nanofiber, the process comprising electrospinning a fluid stock into an electrospun material, the fluid stock comprising polymer and precursor, the precursor comprising (i) metal precursor, (ii) ceramic precursor, or (iii) a combination thereof, and: (a) the weight to weight ratio of the precursor to polymer being at least 1:2; (b) the fluid stock is (1) a solution; (2) a

substantially uniform dispersion; or (3) a substantially homogenous dispersion; (c) the concentration of the precursor in the fluid stock is at least 200 mM; or (d) a combination thereof.

[0018] In some embodiments, the fluid stock is an aqueous fluid stock.

[0019] In some embodiments, the process further comprises removing the polymer from the electrospun material.

[0020] In some embodiments, the process further comprises calcination of the precursor to metal, metal oxide, metal alloy, ceramic, or a combination thereof.

[0021] In some embodiments, calcination of the metal and/or ceramic precursor(s) is performed under inert, oxidative, or reductive conditions.

[0022] In some embodiments, the metal is selected from the group consisting of Ag, Cu, Ni, Fe, Co, Pb, Au, Sn, and Al.

[0023] In some embodiments, the ceramic or metal oxide is selected from the group consisting of Al_2O_3, ZrO_2, Fe_2O_3, CuO, NiO, ZnO, CdO, C, Ge, Si, SiO_2, TiO_2, V_2O_5, VO_2, Fe_3O_4, SnO, SnO_2, CoO, CoO_2, Co_3O_4, HfO_2, $BaTiO_3$, $SrTiO_3$, and $BaSrTiO_3$.

[0024] In some embodiments, the fluid stock comprises the precursor associated with the polymer by covalent or non-covalent interactions.

[0025] In some embodiments, the association of the precursor with the polymer provides a fluid stock comprising precursor uniformly dispersed therein.

[0026] In some embodiments, the polymer and precursor taken together comprise about 1 weight % to about 20 weight % of the fluid stock.

[0027] In some embodiments, the metal precursor comprises a metal-ligand complex.

[0028] In some embodiments, the metal-ligand complex is a metal acetate, metal nitrate, metal chloride, or metal alko-oxide.

[0029] In some embodiments, the polymer is a thermally degradable or chemically degradable polymer.

[0030] In some embodiments, the polymer is polyvinyl alcohol, polyvinyl acetate, polyvinyl ether, polyvinyl pyrrolidone, polyglycolic acid, polyethylene oxide, hydroxyethylcellulose (HEC), ethylcellulose, cellulose ethers, polyacrylic acid, polyisocyanate, or any combination thereof.

[0031] In some embodiments, the process of electrospinning the fluid stock comprises electrospinning the fluid stock with a second fluid stock about the same or similar axis to produce a layered nanofiber.

[0032] ~~In one aspect,~~There is also described herein ~~is~~ a nanofiber comprising a metal, a metal oxide, a metal alloy, a ceramic, a metal precursor, a ceramic precursor or a combination thereof, and: (a) the nanofiber is at least 1 μm (e.g., at least 50 μm) long on average; (b) the nanofiber has an aspect ratio of at least about 5 (e.g., at least 10, at least 100, at least 1000, or the like); (c) the nanofiber comprises a segment comprising a continuous matrix of a metal, a metal oxide, a metal alloy, a ceramic, or a combination thereof; (d) the nanofiber has a specific surface area between 1 m^2/g and about 1000 m^2/g; or (e) a combination thereof. In some embodiments, the nanofiber

comprises at least 33% (w/w) of a metal, a metal oxide, a metal alloy, a ceramic, a metal precursor, a ceramic precursor or a combination thereof.

[0033] In some embodiments, the metal is selected from the group consisting of Ag, Cu, Ni, Fe, Co, Pb, Au, Sn, and Al.

[0034] In some embodiments, the ceramic or metal oxide is selected from the group consisting of Al_2O_3, ZrO_2, Fe_2O_3, CuO, NiO, ZnO, CdO, C, Ge, Si, SiO_2, TiO_2, V_2O_5, VO_2, Fe_3O_4, SnO, SnO_2, CoO, CoO_2, Co_3O_4, HfO_2, $BaTiO_3$, $SrTiO_3$, and $BaSrTiO_3$.

[0035] In some embodiments, the nanofiber comprises a conductive material, wherein the nanofiber has an conductivity of at least about 10% when compared with the conductivity of the conductive material when formed into a sheet.

[0036] ~~In one aspect,~~There is also described herein ~~is~~ a process for producing a nanofiber, the process comprising electrospinning about the same or similar axis a first fluid stock with a second fluid stock, the first fluid stock being aqueous and comprising a first polymer.

[0037] In some embodiments, the first polymer is water soluble.

[0038] In some embodiments, the second fluid is aqueous.

[0039] In some embodiments, the second fluid stock comprises a second polymer, and the first and second polymers are optionally the same.

BRIEF DESCRIPTION OF THE DRAWINGS

[0040] The novel features of the invention are set forth with particularity in the appended claims. A better understanding of the features and advantages of the present invention will be obtained by reference to the following detailed description that sets forth illustrative embodiments, in which the principles of the invention are utilized, and the accompanying drawings of which:

[0041] FIG. 1 illustrates a schematic of the process and system of the disclosure.

[0042] FIG. 2A illustrates an exemplary mechanism of precursor-polymer bonding. FIG. 2B illustrates an FTIR study of the effect of Ni precursor loading on the saturation of –OH bonds in PVA.

[0043] FIG. 3 illustrates micrographs and an x-ray diffraction plot of Ni nanofibers from electrospinning of Ni-Ac/PVA (2:1) feed.

[0044] FIG. 4 illustrates micrographs and an x-ray diffraction plot of NiO nanofibers from electrospinning of Ni-Ac/PVA (2:1) feed.

[0045] FIG. 5 illustrates micrographs and an x-ray diffraction plot of Cu nanofibers from electrospinning of Cu-Ac/PVA (2:1) solution.

[0046] FIG. 6 illustrates micrographs and an x-ray diffraction plot of CuO nanofibers from electrospinning of Cu-Ac/PVA (2:1) solution.