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Template free and large-scale fabrication of silica nanotubes with centrifugal jet spinning

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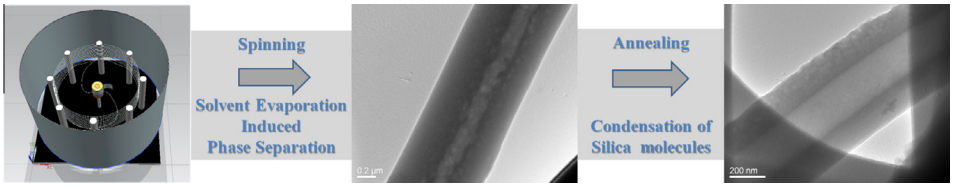
HIGHLIGHTS

- Centrifugal jet spinning is an efficient and low cost nanofiber fabrication method.
- CJS production rate is 500 times higher comparing to electrospinning method.
- Dual solvent evaporation induced phase separation created hollow structured fibers.
- Large amount of silica nanotubes were obtained with controlled morphologies.
- The silica nanotube wall thickness is tunable with current method.

GRAPHICAL ABSTRACT



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ABSTRACT

Silica nanotubes are widely used in nanotechnology because of their unique properties. In this paper, silica nanotube fibers with wall thickness less than 100 nm and outer diameters ranging between 300 nm and 500 nm are fabricated using the centrifugal jet spinning (CJS) technique with two steps: spinning and annealing. Polyvinylpyrrolidone-silica (PVP-silica) composite fibers are initially spun with engineered spinning solutions. By controlling the degree of tetraethyl orthosilicate (TEOS) hydrolysis, unreacted excess TEOS is introduced into spinning solutions to form a dual-solvent system with ethanol. Because of the differential vapor pressures of TEOS and ethanol as well as their differential solubility of PVP and dispersion of silica, dual-solvent evaporation induces phase separation in the spinning solution. This promotes the formation of hollow structure in PVP-silica fibers during spinning. Silica nanotube fibers are obtained with subsequent thermal annealing of PVP-silica composite fibers. The diameter and wall thickness of the silica nanotubes can be controlled by tuning the content of TEOS in the initial spinning solutions. The mechanism of tubular structure formation is also explained and examined with the help of elemental analysis. The method used in this paper can provide a new direction for efficient and large-scale fabrication of nanomaterials with controlled morphologies.

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1. Introduction

Hollow silica nanostructures have unique physicochemical properties which make them attractive building blocks in the field of nanotechnology because of their surface effects, size effects, and quantum confinement effects [1–7]. The presence of Si-OH moieties on silica surfaces has enabled straightforward functionalization of edges, as well as inner and outer surfaces of the hollow nanostructures by silane chemistry [2,6,8,9]. Their unique optical, electrical, and mechanical properties, as well as their hydrophilic nature and biocompatibility have resulted in their application as nanocontainers, nanoreactors and encapsulation of optically-active molecules [1–7,9,10]. Owing to the high rigidity of the silica structure and the ease of forming colloidal suspensions, hollow silica nanostructures are particularly well suited for catalysis (e.g., for enzyme immobilization) [10], separations (e.g. nanofiltration) [11], sensing [12], nanofluidics and drug/gene delivery [2,7].

Traditional methods to synthesize hollow silica nanostructures include, hydrothermal synthesis, chemical vapor deposition, metallic template sol–gel method, and reverse-micro-emulsion-mediated sol–gel method [13–17]. Other popular approaches to synthesize hollow silica nanostructures involve using organic molecules (e.g. long-chain alkyl silane), assemblies and supramolecular systems (e.g. peptide fibrils) as templates to create hollow structure [14,15,18]. These methods share the disadvantages of low productivity, low efficiency, introduction of impurities and high equipment/process cost [14]. Thus, alternative methods that can enable direct, facile and highly efficient synthesis of hollow silica nanostructure will promote its applications in many engineering fields.

In this paper, we present a relatively easy, inexpensive and highly efficient route to fabricate silica nanotube fibers. Large amounts of highly purified silica nanotube fibers are directly fabricated from centrifugal jet spinning (CJS) technique without using templates. Only two steps (spinning and annealing) are involved in this fabrication process. Hollow polyvinylpyrrolidone-silica (PVP-silica) composite fibers are fabricated using the CJS. With subsequent thermal annealing, high purity silica nanotube fibers can be obtained easily. In order to create hollow PVP-silica fibers, the composition of the spinning solution is carefully tuned to create a stable dual-solvent system. During spinning, phase separation of spinning solution induced by dual-solvent evaporation is exploited to form hollow structures in PVP-silica fibers. Utilizing solution phase separation to create hollow/porous structures has been explored by many studies for making porous polymer membrane as well as dry-spun hollow/porous polymer fibers [19–27]. Different techniques are developed over years such as non-solvent induced phase separation (NIPS) [21,25,26], vapor-induced phase separation (VIPS) [19,20,24] and thermally induced phase separation (TIPS) [22,27]. However, the application of these techniques to fabricate hollow ceramic structures is rarely studied, mainly because of the difficulty in formulating a stable uniform spinning solution with ceramic precursors. Herein, we are applying the mechanism of non-solvent evaporation induced phase separation to large-scale fabrication of hollow ceramic fibrous structures through CJS with a ceramic precursor in the spinning solution. In this study, TEOS is used as a precursor of silica. To generate hollow silica structure, the degree of TEOS hydrolysis is controlled to introduce unreacted/excess TEOS in spinning solution and form a dual-solvent system containing two solvents (TEOS and ethanol) with two different solutes (silica and PVP). It is noteworthy that TEOS and ethanol have different vapor pressures, TEOS is a non-solvent for PVP while allowing for dispersion of silica, and that ethanol is a good solvent for PVP but results in poor dispersion of silica. Since TEOS has a low solubility for PVP as well as lower vapor pressure in comparison to ethanol, differences in the evaporation rate of the two solvents induces phase separation in the spinning solution. This could result in a concentration gradient of solute (PVP and silica) which produces hollow structures in the PVP-silica composite fibers. Subsequent thermal annealing of PVP-silica hollow fibers can decompose PVP and condense the silica network to form high purity silica nanotubes.

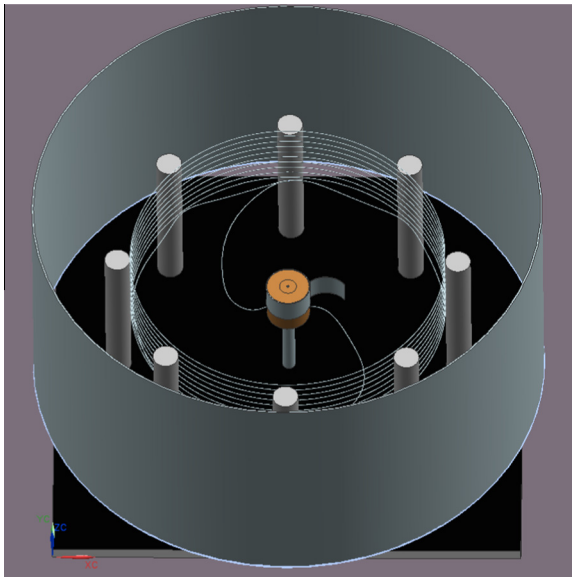

Fig. 1. Schematic drawing of Centrifugal Jet spinning system.

The CJS technique used in this study is a micro-/nanofiber spinning technique that can be used for both ceramic and polymeric materials [28–30]. The configuration of the CJS system is shown schematically in Fig. 1. A DC motor is used to power a hollow chamber with two orifices on chamber wall. Spinning solution is ejected from orifices and extended into thin liquid jets by centrifugal force. Successful spinning requires appropriate viscoelastic properties of spinning solution to form a continuous liquid jet before its solidification upon evaporation of solvent. The flexible air tape on the spinning chamber and the encircling aluminum sheet are used to facilitate fiber collection. The influence of spinning solution viscosity, chamber rotational speeds, solvent volatility, chamber wall thickness, collection distance and orifice sizes on morphology of obtained fibers are reported elsewhere [28,29]. To form the PVP-silica composite fibers, formulated spinning solutions are continuously fed into the chamber at a set flow rate. After ejection from the orifice, the liquid jets are thinned and extended by shearing to form PVP-silica fiber after evaporation of TEOS and ethanol. PVP-silica composite fibers are collected in-between the rods at the periphery of CJS set-up. In this paper, we focus on fabrication of silica nanotube fibers with controlled dimensions by utilizing dual-solvent evaporation induced phase separation within the jet. Synthesis of silica nanotubes with the CJS technique can open a new window for large-scale and highly efficient fabrication of silica nanotube as well as other ceramic fibers with interesting nanostructures.

2. Experimental method

2.1. Materials fabrication

2.1.1. Synthesis of spinning solution

All chemicals are purchased from Sigma–Aldrich and used in this study without further purification. To prepare sol–gel precursor for centrifugal jet spinning of silica hollow nanostructure,