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Synthesis of very small diameter silica nanofibers using sound waves

Panos Datskos,[a] Jihua Chen,[b] and Jaswinder Sharma*[a]

Silica nanofibers of an average diameter ≈ 30 nm and length ≈ 100 µm have been synthesized using an unprecedented strategy: sound waves. A new phenomenon, spinning off the nanofibers at silica rod tips, is also observed.

Synthesis of small diameter fibers is of fundamental interest and of practical implications in fields such as aerospace, lightweight materials, protective armor, tissue engineering, and filtration.[1] Fibers can be made of a range of materials, including carbon, silica (glass), polymers and cellulose.[1] Each type of fiber has its niche applications based upon their individual properties. Among these fibers, silica fibers have attracted scientists for decades because of their high tensile and compressive strength and low production cost.[2a] Stabilized silica fibers of small diameter are also sought after for water desalination since a small diameter results in a small pore-sized mesh.[2b] Small diameter also reduces the number and size of surface defects, which are the main source of fiber tensile strength deterioration.[3] Consequently, an increase in tensile strength is observed with a decrease in diameter in many fibers.[4] Silica fibers with a small diameter are also desired in silica fiber reinforced lightweight materials because this small diameter adds minimal weight to the composites.

There are two main types of silica fibers: continuous (long) and discontinuous (nonwoven).[1,2] Electrospinning and glass drawing are the main techniques for silica fiber production.[1,2] In electrospinning, a droplet of viscoelastic polymer solution having silica precursors is subjected to a high voltage electrostatic field to achieve the nonwoven silica fibers. In glass drawing, silica precursors melted at high temperatures are passed through platinum or other precious metal bushings to make continuous long fibers. Although nonwoven silica fibers of diameter ≈ 80 nm have been synthesized using

electrospinning, obtaining fibers below 50 nm diameters is challenging due to spinneret nozzle clogging.[5] Solution phase synthesis of helical silica nanofibers of ≈ 80 nm diameter has also been reported.[5] By flame-heated fiber drawing silica wires down to 50 nm have been reported.[5] Similarly, by employing gallium as a catalyst at high temperature and pressure, silica wires down to 20 nm, and by using electron beam lithography well aligned nanowires of about 50 nm diameter can be obtained.[5] However, low throughput, small lengths, time consuming processes and need of expensive instruments is hindering their widespread use. Therefore, to make silica fibers below 50 nm, an inexpensive technique with a potential for scale up is still required.

To further decrease the diameter of silica nanofibers beyond the limit of conventional synthesis techniques, herein, we report a new strategy, use of sound waves, for the synthesis of silica nanofibers of an average diameter ≈ 30 nm. The main features of this approach are (1) it does not require any electrospinning, glass drawing, or heating; (2) synthesis is inexpensive, quick, and without any special sample preparation requirements; (3) use of sound waves in silica nanofiber synthesis is a new approach; and (4) spinning off the nanofibers from silica rod tips is an unprecedented phenomenon.

In a typical experiment, polyvinylpyrrolidone (PVP; MW = 40,000, 0.5 g) was dissolved in pentanol ($C_5H_{11}OH$; 5 mL) in a glass vial by sonication. Water (140 µL), sodium citrate ($Na_3C_6H_5O_7$; 50 µL; 0.18 M), absolute ethanol (C_2H_5OH; 475 µL), and ammonium hydroxide (NH_4OH; ≈30%; 100 µL) were added to the glass vial and sonicated for a few minutes. Finally, 50 µL of tetraethyl orthosilicate (TEOS) was added to the above reaction mixture and sonicated [40 kHz; 4 hr.; bath sonicator: Branson 2510 ultrasonicator; power setting: 100 watt (set by the manufacturer)]. The schematic of the synthesis

process and SEM images of the silica nanofibers are shown in Fig. 1a,b. SEM images showed a bendable rather than stiff nature of the nanofibers. The length (30–100 μm) and diameter (20–65 nm) of nanofibers changed from batch to batch depending upon the sample position in the sonication bath. Thin and long fibers were obtained by placing the sample at hot spots in the sonication bath (more synthesis details; S1, ESI†). Nanofibers did not grow alone but grew on the tips of silica rods (Fig. 1c; nanofibers and rods exist in the same solution and some nanofibers are still attached to the rod tips). In the absence of sonication, only silica rods were obtained by mixing the above reagents, indicating that sonication caused the nanofiber formation. [6]
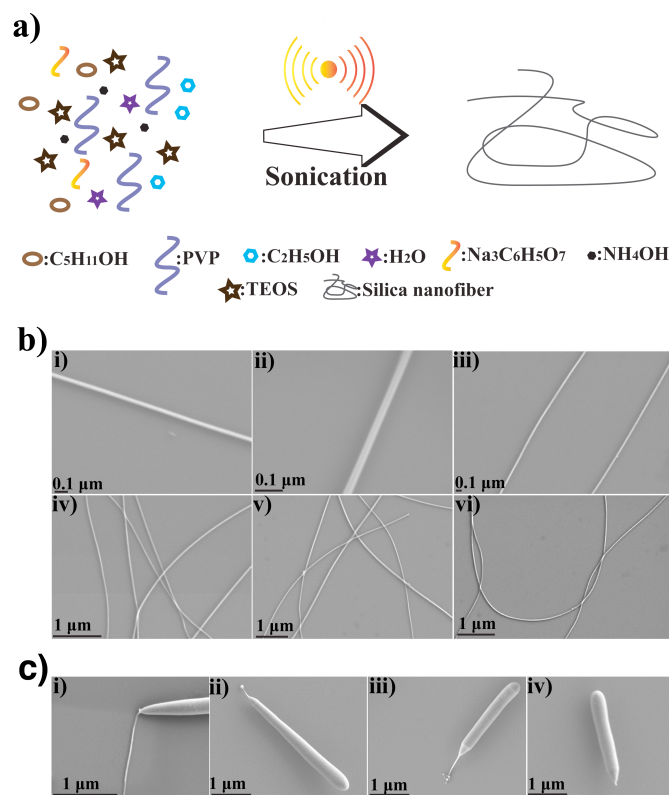

Fig. 1 a) Schematic showing the synthesis of silica nanofibers, b) Scanning Electron Microscopy (SEM) images of silica nanofibers (i–iii zoom in and iv–vi zoom out images), and c) SEM images showing the initiation of silica nanofiber growth on the rod tips.

Sonication involves the use of ultrasound waves (20 – 40 kHz) for creating cavitation bubbles having high temperatures (≈ 4725 ºC), pressures (≈ 1000 bar), and heating-cooling rates (≈ 10^{10} Ks⁻), which can not be achieved by other traditional energy sources. These enhanced temperatures and pressures provide the activation energy for the chemical reactions.[7] Nanomaterials ranging from particles, wires, belts, and rods have been synthesized using sonication.[7]

The exact mechanism of nanofiber formation is not clear, however, there are three possibilities. First, the modified local reaction conditions (enhanced temperature and pressure) might have lead to the directional growth by increasing reaction rates.[7c] Additionally, as observed in our previous work,[6c] an increase in temperature might have decreased the size of the emulsion droplet, and thus led to the growth of very thin rods, i.e., nanofibers. It must be noted that silica rods grow from an emulsion droplet made of PVP attached to water and citrate molecules in pentanol phase.[6a] If the increased temperature was the cause of nanofiber formation, there should be direct formation of nanofibers without any initial silica rod formation. Therefore, this assumption seemed implausible.

Second, since the nanofibers grew at the tips of initially formed rods (Fig. 1c), it appeared that the rods acted as a microrotor (spinneret) and the torque produced by the sound waves resulted in rotational motion in the rods, and thus spinning off nanofibers at the rod tips. Sound waves are known for creating motion in objects, especially cylindrical objects, through phenomena called microstreaming or acoustic streaming.[8] From SEM images, it appeared that nanofibers could grow on almost all rods irrespective of the original length and diameter of the rod. Generally, nanofibers started growing earlier (small rod length) on small diameter rods compared to the large diameter rods (large rod length). Tapering of the rod diameter before nanofiber growth indicated (1) either the rod has reached that specific length to experience the required torque or (2) the rod came in the path of sound waves and started spinning. Additionally, some rods didn't get tapered, and thus seemed to not spin nanofibers indicating neither of the two above phenomenon occurred in their case.

Third, it has been observed that once rods reached a certain length, the shear force caused by magnetic stirring could destabilize and shrink the emulsion droplet, which resulted in further rod growth with reduced diameter.[6a] Similar to the magnetic stirring induced shear force, we think that sonication resulted in destabilization and shrinkage of the emulsion droplet to such an extent that further growth resulted in silica nanofibers. Since the working principle of magnetic stirring (tangential shear force) and sonication (cavitation) are totally different, it appeared that this hypothesis did not contribute significantly to the nanofiber growth in our case. Though all these assumptions may have played a role in nanofiber formation, but exact mechanism is still not known.

To find if nanofibers could grow on preformed rods, we first let the rods grow for 24 hr. followed by sonication for another 4 hr. No nanofiber formation and tapering of the preformed rods occurred. It is reasonable since almost no TEOS was left for deposition to make the nanofibers after 24 hr. We added another equivalent of TEOS to preformed rods followed by sonication. We observed few silica nanofibers and also tapering of the rods (S3, ESI†). Similarly, if rods were sonicated after 3 hr. of initial growth, few small nanofibers were observed (S4, ESI†). These experiments indicate that (1)

silica nanofibers can be grown even after some initial rod growth provided the emulsion droplet is attached and TEOS is available, and (2) without TEOS, polymer alone does not form nanofibers on the preformed rods. A long sonication before TEOS addition did not change the outcome, and smooth rods, similar to when TEOS was added without any sonication, were formed. This showed that sonication didn't result in polymer template formation in which TEOS has deposited afterwards and formed the nanofibers (S5, ESI†).

Energy Dispersive X-Ray (EDX) studies revealed that nanofibers were made of silica (Fig. 2a sample, 2b background), and an absence of any peak for nitrogen showed that washings removed any adhering PVP. Peaks for C, O, Cu, and Na were from carbon coated copper grids. The removal of most PVP molecules by washings with water and ethanol, indicated that PVP made either an external template[9a] or only helped in defining the original emulsion droplet.[6a] Selected area electron diffraction studies (Fig. 2c; inset) showed that nanofibers were amorphous.
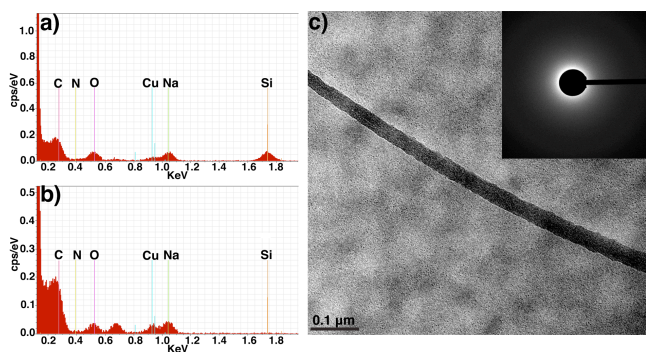

Fig. 2. a) EDX spectrum of silica nanofibers, b) EDX spectrum of background, and c) Transmission Electron Microscope (TEM) image and selected area electron diffraction pattern (inset) of silica nanofibers.

To further investigate if nanofibers were made of silica, we annealed the nanofibers at 500 °C for 1 hr. to burn any PVP if present.[9b] The subsequent SEM studies showed no change in the nanofiber diameter, and thus proved that the nanofibers were made of silica and not of PVP, though PVP played a crucial role in nanofiber formation (Fig. 3a). We assume, the bead like structures observed adhering to the nanofibers after annealing at 500 ºC might be contaminations remaining because of insufficient washings. Lack of formation of any nanofibers in the absence of TEOS further confirmed that PVP alone couldn't form any nanofibers (S6, ESI†).

Transmission Electron Microscopy (TEM) studies showed that some nanofibers were hollow (Fig. 3b) with a groove of ≈ 15 nm diameters. The exact mechanism of this hollowness is not clear, however, we assume that initial nanofiber nucleation occurred in such a way that TEOS has deposited on the sides leaving a hole in the center, and a hollow groove grew from this initial hole. Though we achieved a good separation of nanofibers from the rods by centrifugation (nanofibers being

light in weight stay in supernatant), complete removal of the rods remains a challenge. We performed the synthesis at a small scale (50 µL of TEOS) and anticipate that by using high power ultrasonicator and large reaction vessel, the synthesis process can be easily scaled up.
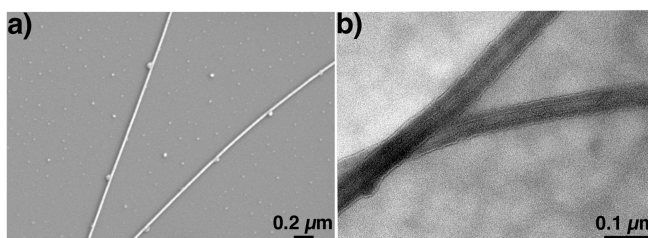

Fig. 3. a) SEM image showing silica nanofibers after annealing at 500 ºC for 1 hr., and b) TEM image showing hollow silica nanofibers.

In conclusion, we have demonstrated a new strategy to synthesize silica nanofibers of very small diameter (≈ 30 nm). This strategy did not require any sophisticated instruments or high temperatures. This work also demonstrated an extraordinary phenomenon: spinning off the nanofibers at silica rod tips. These silica nanofibers have the potential for obtaining high strength polymer ceramic and metal ceramic composites, which will have further implications in aerospace, lightweight automobiles, and protective armor. We expect that this research will further open up new opportunities for solution-phase synthesis of nanofibers of glass and other materials. Efforts to understand nanofiber formation mechanism and increase the length of nanofibers are in progress.

Notes and references

[a]Nanosystems, Separations, and Materials Research Group, Energy and Transportation Science Division, Oak Ridge National Laboratory, One Bethel Valley Road, Oak Ridge, TN 37831, USA, E-mail: sharmajk@ornl.gov.
[b]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, One Bethel Valley Road, Oak Ridge, TN 37831, USA

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