Three-Dimensional Interconnected Silica Nanotubes Templated from Hyperbranched Nanowires**

*Jia Zhu, Hailin Peng, Stephen T. Connor, and Yi Cui**

Inorganic nanofluidic devices, such as nanopores,[1–3] nanochannels,[4–10] and nanotubes (NTs)[8,11–17] have been actively studied in bioseparation, bioanalysis, fluidic transistors, power generation, and fast mass transport. Compared to biological nanopores, inorganic nanofluidic devices have been demonstrated to be robust, to have easily tuned surfaces and to be integrable into arrays. One of the most powerful nanofluidic device fabrication methods is templating against a porous membrane[16,17] or chemically synthesized or lithographically patterned nanowires (NWs).[11,14] NTs or nanochannels made in this way have controllable dimensions, with diameters down to several nm and lengths up to tens of μm. Herein, we exploit hyperbranched PbSe NWs[18,19] as templates to produce 3D interconnected hyperbranched silicon dioxide (silica) NTs by simple coating and etching steps. The obtained NTs with a thick enough shell retain the orientation of the original hyperbranched arrays and are either parallel or perpendicular to each other. These hyperbranched NTs afford interesting opportunities for constructing new 3D nanofludic devices.

The fabrication process for silica hyperbranched NTs is shown in Figure 1. Hyperbranched PbSe NWs were grown on Si (100) substrates using vapor transport growth. Each hyperbranched PbSe NW exhibits 90° orientation between branches because of the epitaxial relationship. The details of hyperbranched NW growth can be found elsewhere.[18] The samples with hyperbranched NWs were then coated by plasma enhanced chemical vapor deposition (PECVD) of silica. The deposition temperature was 350 °C. The growth rate for a silicon oxide layer based on thin-film deposition on silicon (100) substrate is around 6 nm min^{-1}. Silica layers with different thickness (30 nm and 80 nm) were deposited on different samples of hyperbranched NWs to evaluate the effect of silica thickness on the morphologies of the final silica NTs.

[*] Prof. Y. Cui, Dr. H. Peng
Department of Materials Science and Engineering
Stanford University
476 Lomita Mall, Stanford, CA 94305 (USA)

J. Zhu
Department of Electrical Engineering
Stanford University
350 Serra Mall, Stanford, CA 94305 (USA)

S. T. Connor
Department of Chemistry
Stanford University
333 Campus Drive, Stanford, CA 94305 (USA)

DOI: 10.1002/smll.200801083

A scanning electron microscopy (SEM) image of PbSe NW hyperbranches with 30-nm SiO_2 is shown in Figure 2a. The sample was then put in freshly prepared aqua regia solution (Note: aqua regia is dangerous and must be handled with great care). The aqua regia solution started to bubble immediately after the sample was dipped into it, indicating the etching of PbSe (Note: this step might produce toxic gases such as H_2Se, and so must be conducted within laboratory fume hood). Aqua regia is believed to diffuse through the pinholes of silica layer. After around 20 min, the bubbling stopped. The sample was taken out, flushed with de-ionized water for 20 min, and blown dry by nitrogen gas. It was then examined with SEM. As shown in Figure 2b, the order of the original hyperbranch was deformed after the aqua regia etch. Zoomed-in SEM images from different parts of the same hyperbranch are shown in Figure 2c and d. The middle of each branch looks transparent under SEM, suggesting that PbSe is etched away, resulting in

Figure 1. Flowchart of the fabrication process for interconnected silica nanotubes from hyperbranched PbSe nanowires.

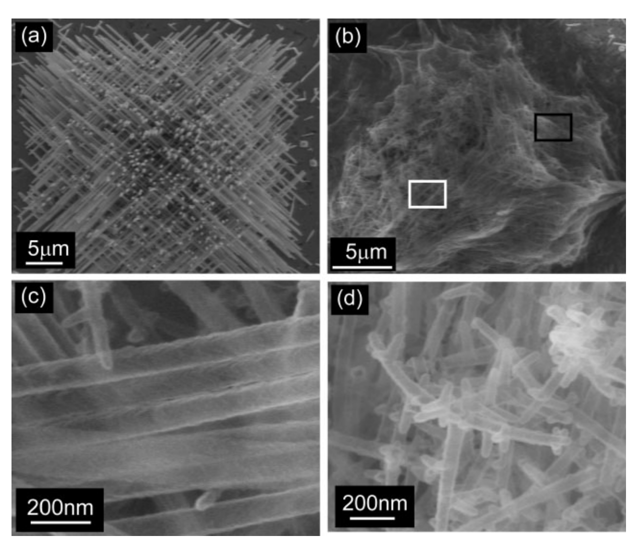

Figure 2. a) An SEM image of PbSe hyperbranched nanowire coated with 30-nm SiO_2. (b) Interconnected SiO_2 nanotubes with a 30-nm-thick shell. c) and d) High resolution SEM images of interconnected SiO_2 tubes taken from white and black box of (b), respectively.

the hollow NT structure. Because of the flexibility of the 30-nm-thick silica shell, the whole structure bends toward the substrate surface by the surface tension force during the solution drying process. Even though the whole hyperbranch was significantly deformed, the silica shell still remained interconnected (Figure 2c and d).

Compared with the flexibility of 30-nm-thick silica NTs, PbSe hyperbranches with an 80-nm-thick silica coating did not show any morphology change with aqua regia etching, which is presumably because of the larger mechanical strength of a thicker shell. NTs with 80-nm-thick shells are too thick to have differential contrast under SEM. However, it is possible to identify the hollow nature of a NT if it has an open end. Therefore, a PbSe hyperbranch coated with 80-nm-thick silica was cut through the center by a focused ion beam (FIB), followed by aqua regia etching. Figure 3a shows the PbSe NW network after FIB cutting but before etching. The same hyperbranch after etching was shown in Figure 3b. The network coated with 80-nm-thick silicon oxide did not collapse as the one with 30-nm-thick silica. Figure 3c and d are the zoomed-in pictures taken from two places close to the FIB cut location. Several NTs with an open end that resulted from the FIB cut clearly indicate that all the NWs have already turned into NTs.

To reveal their interconnected nature, we have studied the hyperbranched silica NTs with transmission electron microscopy (TEM). PbSe hyperbranched NWs with different thickness of silica coating were mechanically transferred to copper grids. A low-magnification TEM image of a hyperbranch with nominally 30-nm-thick silica coating is shown in Figure 4a. A zoomed-in image (Figure 4b) reveals that the surface of hyperbranched NW is coated with silica but has variation in thickness on different faces, which is believed to result from the shadow effect during PECVD coating.

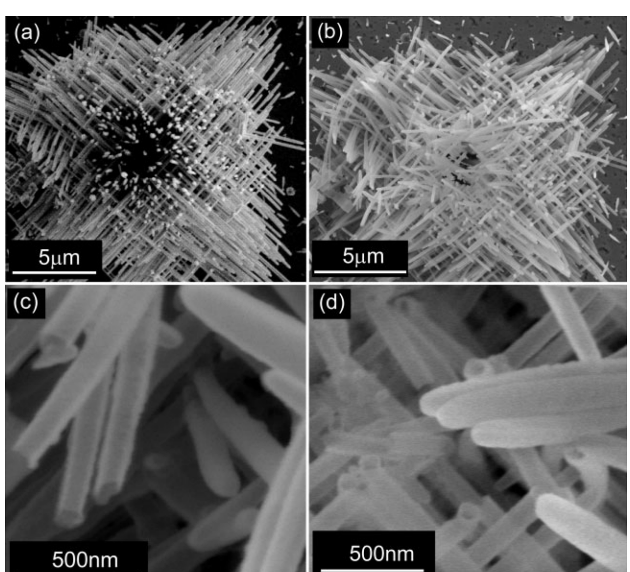

Figure 3. a) An SEM image of a hyperbranched PbSe hyperbranched nanowire with 80-nm SiO_2 shell after FIB cut. b) Interconnected SiO_2 nanotubes with 80-nm shell and after aqua regia etching. c) and d) high resolution SEM images of SiO_2 tubes with open end from (b).

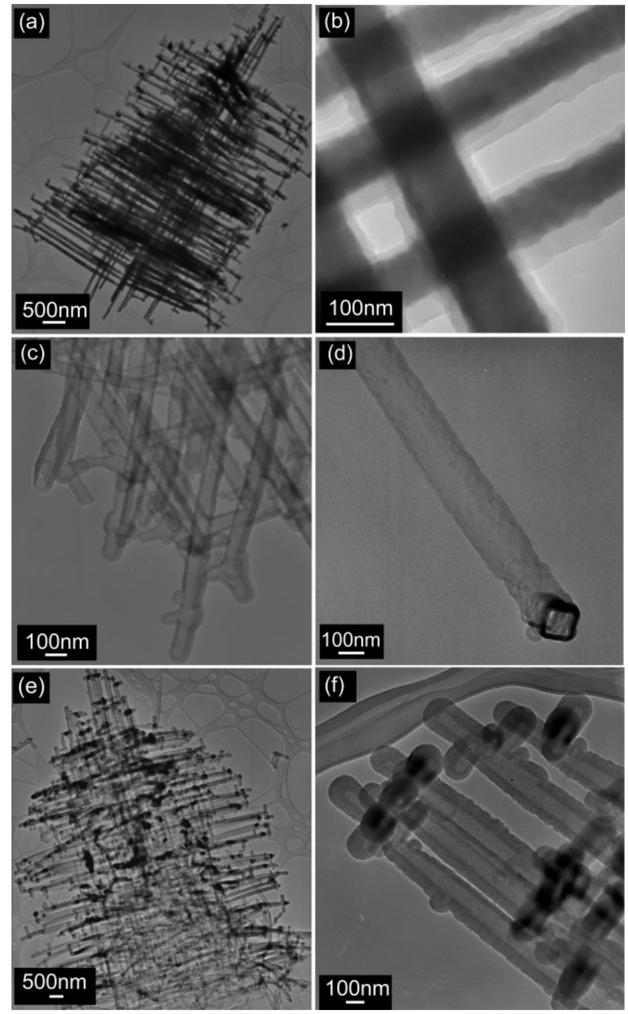

Figure 4. a) and b) TEM images of a hyperbranched PbSe hyperbranched nanowire with 30-nm SiO_2 coating. c) A TEM image of hyperbranched nanotubes with an 30-nm-thick silica shell. d) A TEM image of silica nanotube with open end. e) and f) TEM images of nanotubes network with an 80-nm-thick silica shell.

Figure 4c shows hyperbranched silica NTs with 30-nm-thick shells after the aqua regia etching, in which NTs appear to be interconnected. Figure 4d shows a 30-nm-thick silica tube with open end. The cross section of the tube still remains square, same as the cross section of most of PbSe NWs.[18] The silica NT hyperbranch with 80-nm shell thickness formed after aqua regia etch is shown in Figure 4e. The NT appears to retain mostly the orientation of the original PbSe hyperbranched NW, forming 3D interconnected hyperbranched tubes, which is different from the deformed structures of NTs with 30-nm-thick silica shells. Like hyperbranched PbSe NWs, the NT branches are perpendicular or parallel to each other. The deviation from the three orthogonal directions was caused by the transfer from the growth substrate to a copper TEM grid. A higher magnification TEM image, as shown in Figure 4f, indicates that PbSe was totally etched away while the silicon oxide shells were left behind.

In conclusion, 3D interconnected silica NTs networks with a high degree of branching and good structural regularity were obtained by templating against hyperbranched PbSe NWs.

These interconnected NTs network provides a new platform for 3D nanofluidic applications.

Keywords:
hyperbranched structures · nanotubes · nanowires · templates

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Received: July 27, 2008
Revised: September 10, 2008
Published online:

