

Hyperbranched Polymer-Assisted Hydrothermal In situ Synthesis of Submicrometer Silver Tubes

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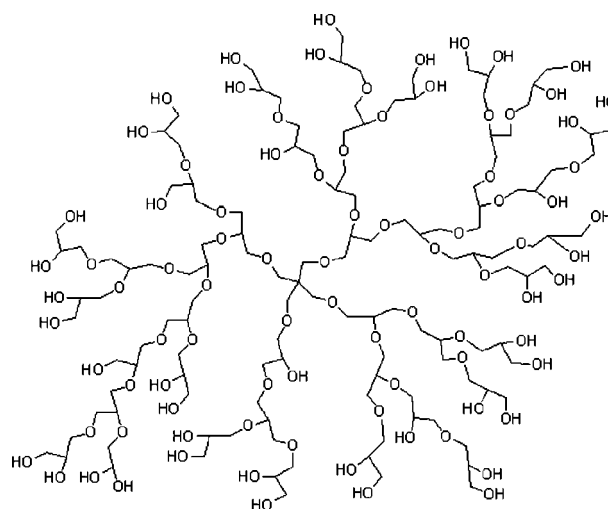
ABSTRACT: We produced silver tubes with an outer diameter of 1 μm , wall thickness of 200 nm, and length of hundreds of micrometers by hydrothermal treatment of aqueous solutions of AgNO_3 and hyperbranched polyglycidol (HPG) at 165 $^\circ\text{C}$. The surfaces of the silver tubes were chemically modified by HPG, which was confirmed by FTIR of the silver tubes. Ostwald ripening of small Ag crystals with surface passivated by HPG was perhaps the key to the controlled formation of silver tubes. DSC analysis showed a melting peak at about 198 $^\circ\text{C}$ for the silver tubes. The solution-phase approach to synthesize silver tube is facile for large-scale fabrication.

Introduction

Since the discovery of carbon nanotubes by Iijima in 1991,¹ nanotubular materials have been the focus of intensive study because of their unique physical properties that are substantially different from their bulk counterparts (for example, low density, large specific surface area, and surface permeability). Nanotubular materials may find applications as gas and fluid paths or capsule agents for catalysis, fuel cells, sensors, and separation systems. Various methods have been demonstrated to process a broad range of materials into nanotubes, including the new class of nanotubes of metal oxides,^{2–4} metals (Au, Ni, Pd, and Pt),^{5–8} and polymers (polyaniline and polythiophene).^{9,10} Among these nanotubular materials, silver, which exhibits the highest electrical and thermal conductivity among all metals, is particularly interesting to investigate. There are considerable reports on silver nanostructures ranging from nanoparticles, nanocubes, and nanoprisms to nanorods, and nanowires. Xia et al.'s work has contributed greatly to the guiding law of silver nanostructures.¹¹ However, the challenge of synthetically controlling metal nanotubes has been met with limited success.

Silver nanotubes have been synthesized by different kinds of techniques, for example, using solid electrolyte thin films under direct current electric field treatment,¹² and template techniques.^{13–19} Among various methods for preparing the silver nanotubes, the template method is a versatile and inexpensive technique. Diverse templates have been used toward the synthesis of the silver nanotubes, including “hard” templates such as porous anodic aluminum oxide templates,¹³ functionalized silica rods,¹⁴ a silanetreated nanoporous alumina membrane template,¹⁵ pristine porous alumina membranes,¹⁶ and Ag nanowires;¹⁷ and “soft” templates such as organogel from a bolaamphiphile,¹⁸ and lyotropic mixed-surfactant liquid-crystal templates.¹⁹ “Soft” templates seem conducive to produce very thin but not free-standing tubes, whereas “hard” templates often result in nanotubes built of nanoparticles which perhaps lack the mechanical strength. Though the use of templates can ensure a good control over the morphology, it is perhaps an obstacle to large-scale fabrication of nanomaterials and purification.²⁰

Scheme 1. Schematic Structure of HPG



Recently, Xia et al. demonstrated a solution-phase method that generates silver nanowires by reducing silver nitrate with ethylene glycol in the presence of poly(vinyl pyrrolidone) (PVP).²⁰ PVP perhaps services as a capping agent, which can control the growth rates of various faces of silver by coordinating to the surfaces. Solution-phase methods are superior in many respects to template techniques for producing nanotubes.²¹ However, no report on producing silver tubes by a solution-phase method is found in the literature so far.

The materials as templates or capping agents in solution phase methods are generally linear polymers. Highly branched polymers including dendrimers and hyperbranched polymers are often regarded to be suitable for producing nanoparticles, e.g., nanospheres, not one-dimensional (1D) nanostructures.^{22–24} Highly branched polymers are a new class of polymers that are often used as unimolecular hosts for encapsulation of metal ions or small molecules. A highly branched polymer with many end groups is perhaps more efficient in passivating the side surface of nanorods. Here, we report a solution-phase approach to synthesize free-standing silver tubes with the assistance of hyperbranched polyglycidol (HPG) in aqueous solutions. This approach is facile for large-scale fabrication, though the silver

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Figure 1. Morphology of the hydrothermal products at 165 °C for different times of (A) 20, (B) 30, and (C) 40 h. The bar is 20 μm for A–C. The molar ratio of repeating unit of HPG to AgNO_3 was 4.2:1 for all these syntheses. The images shown in A–C were taken from the as-synthesized samples, and no centrifugation was involved.

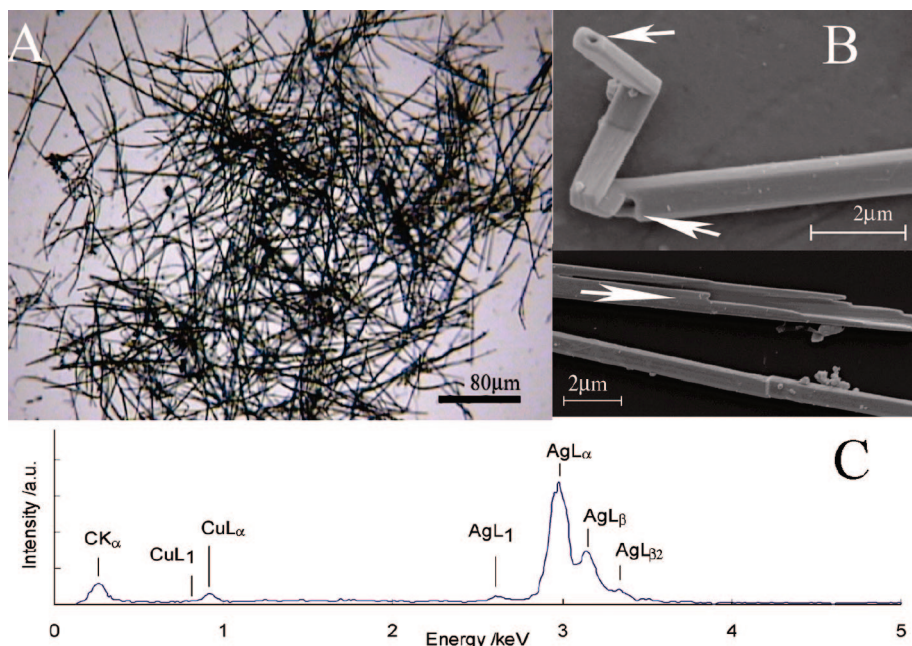


Figure 2. (A) Microscopy, (B) SEM images, and (C) EDS of the silver tubes formed hydrothermally at 165 °C for 40 h. The molar ratio of the repeating unit of HPG to AgNO_3 was 4.2:1.

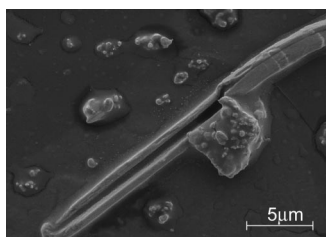


Figure 3. SEM images of the silver tubes formed hydrothermally at 165 °C in 30 h. The molar ratio of the repeating unit of HPG to AgNO_3 was 4.2:1. The image was taken from the as-synthesized samples, and no centrifugation was involved.

tubes synthesized in this work have relative big outer diameters with a nanometer-sized wall thickness. Fine control in the tube diameters is under further investigation.

Experimental Section

HPG with number-average molecular weight of 17 000 was synthesized according to A. Sunder et al.'s work.²⁵

Synthesis of Silver Tubes. A solution of AgNO_3 (0.1 g) and HPG ($M_n = 17000$, 0.15 g) in distilled water (25 mL) was charged in a Teflon-lined stainless steel autoclave (34 mL), which was sealed and maintained at 165 °C. The reaction system at 165 °C for 40 h became white floccules dispersing in pink solution. The mixture was centrifuged

at 9000 g to obtain raw products, which were purified by recentrifugation from water. All the upper centrifugal solutions were collected and vacuum-dried for the structural analysis of free-standing HPG.

Characterization of the Yield of Silver Tubes. The suspensions of the hydrothermal reactions in different time were redispersed by using supersonics, and then were watched by using high-resolution optical microscopy with digital imaging systems. The apparent yield (AY) of silver tubes was characterized by the total length of Ag tubes per mm^2 area according to the following formulas

$$\text{AY} = \frac{\text{number of Ag tubes per mm}^2 \text{ area} \times \text{average length of Ag tubes}}{\text{mm}^2}$$

where both the number of Ag tubes per mm^2 area and average length of Ag tubes were obtained from statistics of microscopy pictures.

Instruments. FTIR spectra were recorded with an Eouinos 55 Model Fourier transform infrared spectrometer. NMR (300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR) was performed on an AVANCE 300 spectrometer. XRD patterns were obtained on a Philips X'Pert PRO SUPER Model X-ray diffractometer, with symmetry reflection at 2θ values from 10 to 85°. SEM pictures were taken on JEOL (Japan) JEM-6700F field emission scanning electron microscope with an accelerating voltage of 30 kV. For the high-resolution transmission electron microscope (HRTEM) observations, a JEM-2010 transmission electron microscope was used with an accelerating voltage of 200 kV. EDS was attached to the microscopy for composition analysis. The sample for SEM or HRTEM observations was prepared by placing 10 μL of sample solution on copper grids coated with thin films of Formvar and carbon successively. DSC was performed with Perkin-Elmer Diamond

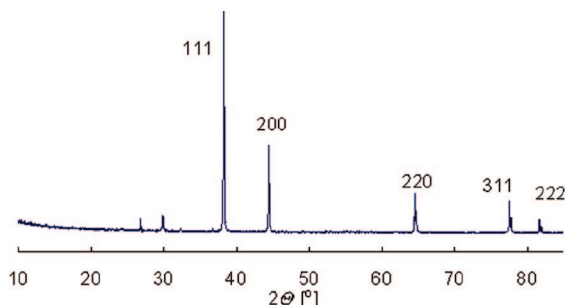


Figure 4. XRD pattern of silver tubes.

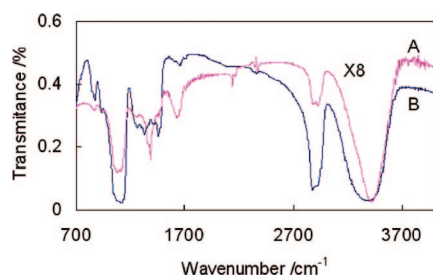


Figure 5. FTIR of silver tubes obtained (A) hydrothermally at 165 °C for 40 h and (B) pure hyperbranched polyglycerol.

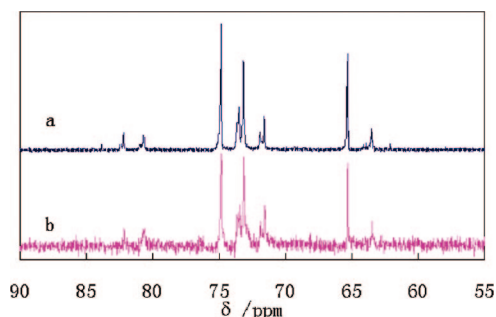


Figure 6. ^{13}C NMR of (a) the pure HPG and (b) the viscous material collected from the clear water and methanol solution phase of centrifugation.

differential scanning calorimeter under a nitrogen atmosphere at a heating rate of 10 °C/min.

Results and Discussion

HPG were water-soluble hyperbranched polyethers with numerous hydroxyl end groups, which are often synthesized by “ring-opening multibranching polymerization” of a latent AB_2 monomer, glycidol.²⁵ The schematic structure of a HPG

was illustrated in Scheme 1. The synthesis and structural characterization of HPG have been reported.^{25,26} We synthesized HPG with Pentaerythritol incorporated as the core unit according to the method reported in the literature. The number average molecular weight (M_n) of the HPG was 17 000 with a polydispersity of about 1.11. The degree of branching (DB) of HPG was measured to be 0.45 by using a quantitative ^{13}C NMR technique.²⁷ The DB value is close to 0.5 that is a theoretically approximate value for the hyperbranched polymers from AB_2 monomers.^{28,29}

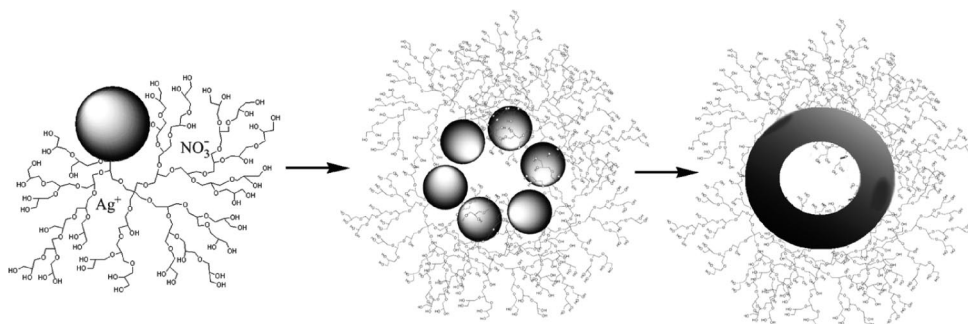
Silver tubes were synthesized by a hydrothermal method in a steel autoclave with Teflon contact-type insert. In a typical process, the autoclave containing a solution of HPG (0.15 g), AgNO_3 (0.1 g) in distilled water (25 mL) was kept at 165 °C for different time. The molar ratio of the repeating unit of HPG to AgNO_3 (RGA) was 4.2:1. The morphology of the products was monitored by high-resolution optical microscopy with digital imaging systems (Figure 1). In 20 h, only nanoparticles were obtained (Figure 1A), whereas particles with needlelike farragoes as long as 100 μm appeared in 30 h (Figure 1B). In 40 h, mainly needlelike materials as long as 1000 μm were obtained (Figure 1C). AY of the Ag tubes obtained in 30 h was about 9000 nm^2/mm^2 , whereas it increased to 210 000 nm^2/mm^2 in 40 h. The process indicated that the silver needles were perhaps formed in an Ostwald ripening process.

The needlelike materials obtained in 40 h were separated by repeated centrifugation from water and methanol suspensions, by which free-standing HPG and AgNO_3 could be removed. The needlelike materials were investigated by scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). These results were illustrated compositively in Figure 2. EDS indicated that these needlelike materials consisted of nearly pure silver element (Figure 2C). The EDS peaks of carbon and copper elements arose from copper grids. The nitrogen element at 0.39 eV vanished in the EDS spectrum.

To our surprise, the scanning electron microscope (SEM) pictures clearly showed that the silver needlelike materials were actually silver tubes of hundreds of micrometers long (Figure 2B), with an outer diameter of about 1 μm and wall thickness of about 200 nm. The silver needlelike materials obtained by a hydrothermal method at 165 °C for 20 h were also actually silver tubes, though the yield of 1D materials was much lower than that in 40 h (Figure 3).

The silver tubes' crystal structure was analyzed by XRD. The XRD patterns (Figure 4) were indexed to (111), (200), (220), (311), and (222) planes of the face-centered cubic structure (fcc) of silver with lattice constant $a = 4.083 \text{ \AA}$, which was close to the reported values of bulk silver crystals (the standard values from JCPDS 04-0783: $a = 4.086 \text{ \AA}$). Comparison of Fourier transform infrared spectra (FTIR) between the silver tubes and

Scheme 2. Ostwald Ripening of Small Ag crystals with Surface Passivated by HPG to Form Tubes



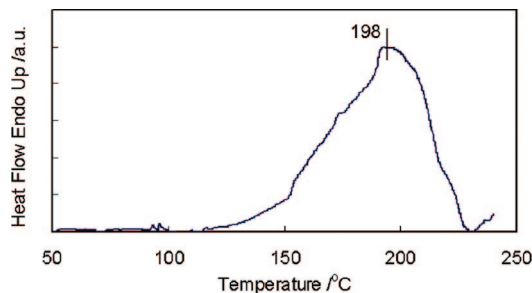


Figure 7. DSC curve of silver nanotubes formed hydrothermally at 165 °C for 40 h. The molar ratio of the repeating unit of HPG to AgNO_3 was 4.2:1.

pure HPG confirmed that after being repeated rinse, there still had signals of HPG left (Figure 5). In the FTIR of silver tubes (Figure 5A), the strong peak at about 1070 cm^{-1} arose from vibration of C–O. The O–H peak at about 3380 cm^{-1} was sharper than that in pure HPG. The strengthened peaks at 1616 and 1380 cm^{-1} indicated a strong conjugated state that was perhaps due to chemical bonding to the surface of Ag, because no any unsaturated carbon signals could be found in the ^{13}C NMR of the silver nanoneedles (Figure 6). The viscous material collected from the clear water and methanol solution phase of centrifugation was HPG whose structure including DB was the same with that of the original HPG according to comparison of ^{13}C NMR (Figure 6).

The effects of RGA on the formation of Ag tubes were also investigated. The AY of the system with RGA of 4.2:1 in 40 h was $210000\text{ nm}^2/\text{mm}^2$. However, if RGA was decreased to 2.1:1, AY in 40 h was only about $2000\text{ nm}^2/\text{mm}^2$. Though the systems with higher molar ratios were not tested yet, the systems with higher molar ratios usually formed nanoparticles according to the literature.²¹ If the RGA was kept as 4.2:1, but the concentration of HPG was doubled, AY was about $4000\text{ nm}^2/\text{mm}^2$, and mainly nanoparticles were obtained. This indicated a possible self-seeding process, and the proper seed concentration was important for the formation of Ag tubes.²¹

In an aqueous solution of AgNO_3 and HPG, Ag ions were in two states relative to HPG, nonstructural exterior ions, and nonstructural interior ions.²² Nonstructural interior Ag ions were reduced to yield HPG-encapsulated Ag nanoparticles with an average size of about 5 nm, as also reported by plenty of work in the literature. Many small Ag crystals, whose surfaces were partially passivated by HPG via both steric and chemical interactions, formed in the system initially but slowly disappeared except for a few that grew larger, at the expense of the small crystals. Ostwald ripening of small Ag crystals with surface passivated by HPG was perhaps the key to the controlled formation of tubes, as schematically illustrated in Scheme 2. The low melting point of small Ag particles was also conducive to tube-formation process. According to the literature, the melting point of Ag nanoparticles with size smaller than 5 nm was around 100 °C .^{30,31} Figure 7 illustrated the differential scanning calorimetry (DSC) curve of the tubes formed in 40 h, and found a melting peak at about 198 °C , however, the melting process began at about 120 °C . The melting behavior of silver tubes coincided with the reported characteristics of silver nanomaterials. Rodlike segments could be constructed from the cubic fcc structure of silver. One possible explanation was a 5-fold symmetry round the wire axis as proposed for silver wires and rods.³² When the crystallization process to form Ag tubes started from HPG-passivated Ag, physically chemically attached

HPG on the surface of Ag could obstruct the formation of Ag crystals round the wire axis and resulted in vacancy at the center.

In summary, we facilely produced silver tubes with an outer diameter of $1\text{ }\mu\text{m}$ and a wall thickness of 200 nm by hydrothermal treatment of aqueous solutions of AgNO_3 and HPG. The surfaces of the silver tubes were chemically modified by HPG, which could be confirmed by FTIR of the silver tubes. Ostwald ripening of small Ag crystals with surface passivated by HPG was perhaps the key to the controlled formation of silver tubes. DSC analysis showed a melting peak at about 198 °C for the silver tubes. This approach is facile for large-scale fabrication of silver tubes; however, the silver tubes synthesized in this work have relatively large outer diameters and a nanometer-sized wall thickness. Fine control in the tube diameters needs further investigation.

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