

Fabricating of silver and copper nano/microtubes using nano-scale glass fibers as templates

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Received: 13 January 2009 / Accepted: 27 March 2009 / Published online: 15 April 2009
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Abstract In this paper, large-scale uniform silver and copper nano/microtubes with high length diameter ratios have been successfully synthesized by a facile approach, using low-cost nano-scale glass fibers as templates. The tubular structures can be obtained by reducing of Ag and Cu ions on the surface of the fibers, along with removing the templates. The samples are characterized by SEM and XRD. Results show the tubular structures are very uniform and the tubular walls are composed of densely coalesced crystalline nanoparticles of 30–50 nm.

Introduction

Metallic nanostructures are attracting increasing interest due to their important applications in sensing [1], catalysis [2], surface-enhanced Raman scattering (SERS) [3], optoelectronics [4], optics [5] and information storage [6]. Because the intrinsic properties of nanostructures can be tailored through controlling their size, shape, composition, crystallinity and structure (e.g., solid or hollow), great effort has been paid to control their shape during growing process. Now, all kinds of metallic nanostructures with different morphologies have been successfully prepared, such as nanorods, nanowires, nanoplates, nanocubes, nanoprisms and nanoshells [7–20].

Among all these metallic nanostructures, metal tubular structures with hollow interiors, such as Pt, Ni, Au, exhibit

a range of interesting properties superior to their solid counterparts [21–23], which makes them attractive from both scientific and technological viewpoints. Silver and copper are of particular interest, because they show high electrical conductivity and play important roles in the fields of catalysts, microelectrodes, SERS, electronics, resins and thermal conducting [24–28], etc. Their nano/microstructures with the morphologies of particles, cubes, wires, rods, spheres, triangular plates and dendrites have already been fabricated [29–32]. In addition, their hollow nanostructures are expected to be used in some important special fields, such as drug delivery, biological labeling, catalysis and high-performance SPR [33, 34]. However, heretofore relative few methods have been concerned on fabricating their tubular hollow structures because of the difficulty in preparing them. Cao et al. [35] synthesized Cu nanotubes by using surfactant of CTAB in hydrothermal system. Liu's group synthesized silver multiwall nanotubes using another kind of nanotube as template [36]. Though these tubular structures are successfully obtained, their synthesis needs either rigorous condition or relatively complicated steps. Including this, their applications may be restricted by their lower length diameter ratios. In this paper, we for the first time report a facile and versatile approach to fabricate large-scale silver and copper tubular structures using low-cost nano-scale glass fibers as templates. Here, the surface of glass fibers can be coated with uniform films of Ag or Cu, and large-scale metallic nano/microtubes of Ag or Cu can be fabricated by dissolving the templates of glass fibers with hydrofluoric acid (HF). Results indicate that this is a simple method for preparing metal tubular structures. The products show high length diameter ratios, and this advantage may be useful for many applications and even for some special fields such as microflow system [37].

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Experimental

All the reagents were analytical grade and used as received without further purification. Commercial amorphous nano-scale glass fibers with average diameter of 750 nm were adopted as the templates. They were cleaned and pretreated before coating with Ag or Cu. A typical experimental procedure was described as follows. Firstly, 0.2 g of the fibers was washed with ethanol and nitric acid to get rid of the impurity. Then, the fibers were dried at room temperature after rinsed with distilled water for three times. Secondly, 1.13 g of SnCl_2 , 25 mL of 12 M HCl and 25 mL of H_2O were mixed to form a sensitize reagent. After the solution was aged for 24 h, the template fibers were sensitized by immersing in it for 5 min. Thirdly, the template fibers were activated by immersing in 0.06 M AgNO_3 solution for 5 min after washed with distilled water. Next, Ag and Cu were coated on the surface of the fibers.

Then, 0.07 g of AgNO_3 was dissolved in 3 mL of H_2O , and 0.07 g of KOH was added to form precipitate immediately. After that, about 0.1 mL of ammonia was slowly dropped into the solution to dissolve the sediment. Then, 0.08 g of polyethylene glycols (PEG-1000) was added to 2 mL of 0.1 M glucose solution and it was mixed with the above solution. Then, 0.1 g of glass fibers were immersed into the mixed solution to began coating silver. The reaction had been kept for 12 h at room temperature.

On the other hand, the coating of copper on the surface of glass fibers was realized by the redox reaction of Cu^{2+} with reducing reagent and the specific process was described as follows. Fehling's solutions was used here and it was a mixture of solution A and solution B. Solution A was prepared by massing 7.0 g of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ ($M = 249.78$) and dissolving it in 100 mL of distilled water. Solution B was prepared by dissolving 29.0 g of $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ ($M = 282.2$) and 15.0 g of NaOH ($M = 40.01$) in 100 mL of distilled water. Then, 2 mL of solution A and 2 mL of solution B were mixed to form a solution with the color of bronze blue. After that, 1 mL of 40%

glyoxal was added into the solution and 0.1 g of activated glass fiber was immersed to begin coating. The reaction was kept by a warm water bath for 5 h, and the temperature was 50 °C.

The fibers coated with Ag and Cu were cut to bare the ends after removing the excess reacting solution by washing them with distilled water under ultrasonic. Then, the well-defined Ag and Cu nano/microtubes were separately freed from the templates by dissolving with 24 wt% HF for 24 h. At last, the samples were separately washed with 48 wt% HF and distilled water for several times to fully get rid of the remained silica.

Results and discussion

Figure 1 shows the SEM images of the amorphous super fine glass fibers and its frequency distribution in diameters. They are generally very long, and the ratio of length to diameter is difficult to be measured. Macroscopical state of coated fibers is similar with freshly prepared electrospinning nanofibers [38]. The fibers are very fine, whose diameters mainly distribute in the range of 700–850 nm.

Figure 2 gives typical SEM images of the glass fibers coated by Ag and the Ag microtubes which are released from the templates. Because the glass fibers have small diameters, they appear sol-like when they are just immersed into the solution. During the coating process, they slowly precipitate within several hours and become light gray, which indicates that silver is continuously growing on them. Previously, we attempted to directly grow silver on the glass fibers that were not activated, but the results were not favorable. Silver reduced not on the template but in solution and mostly on the inner wall of beaker. So the coating process must be started with modifying glass fiber with silver nanoparticle seeds that are reduced by Sn^{2+} . Additionally, PEG-1000 should be added to reduce the surface tension of reaction solution on the surface of the fibers.

Fig. 1 a SEM of amorphous nano-scale glass fibers. b Diameter distribution of the fibers

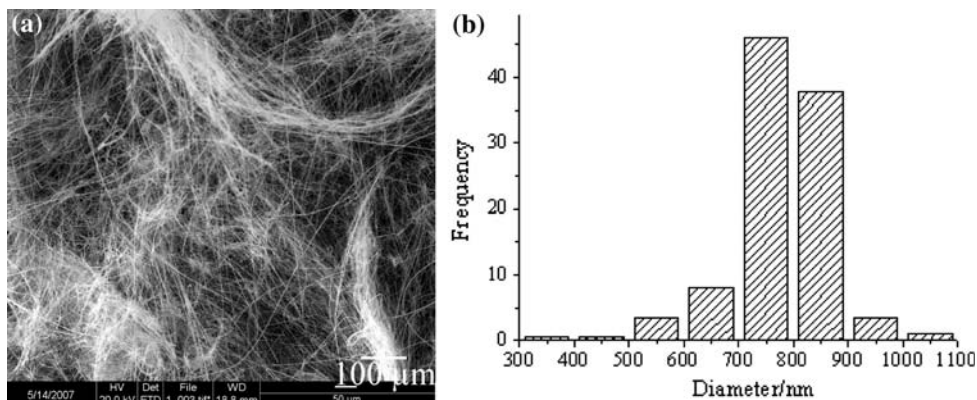
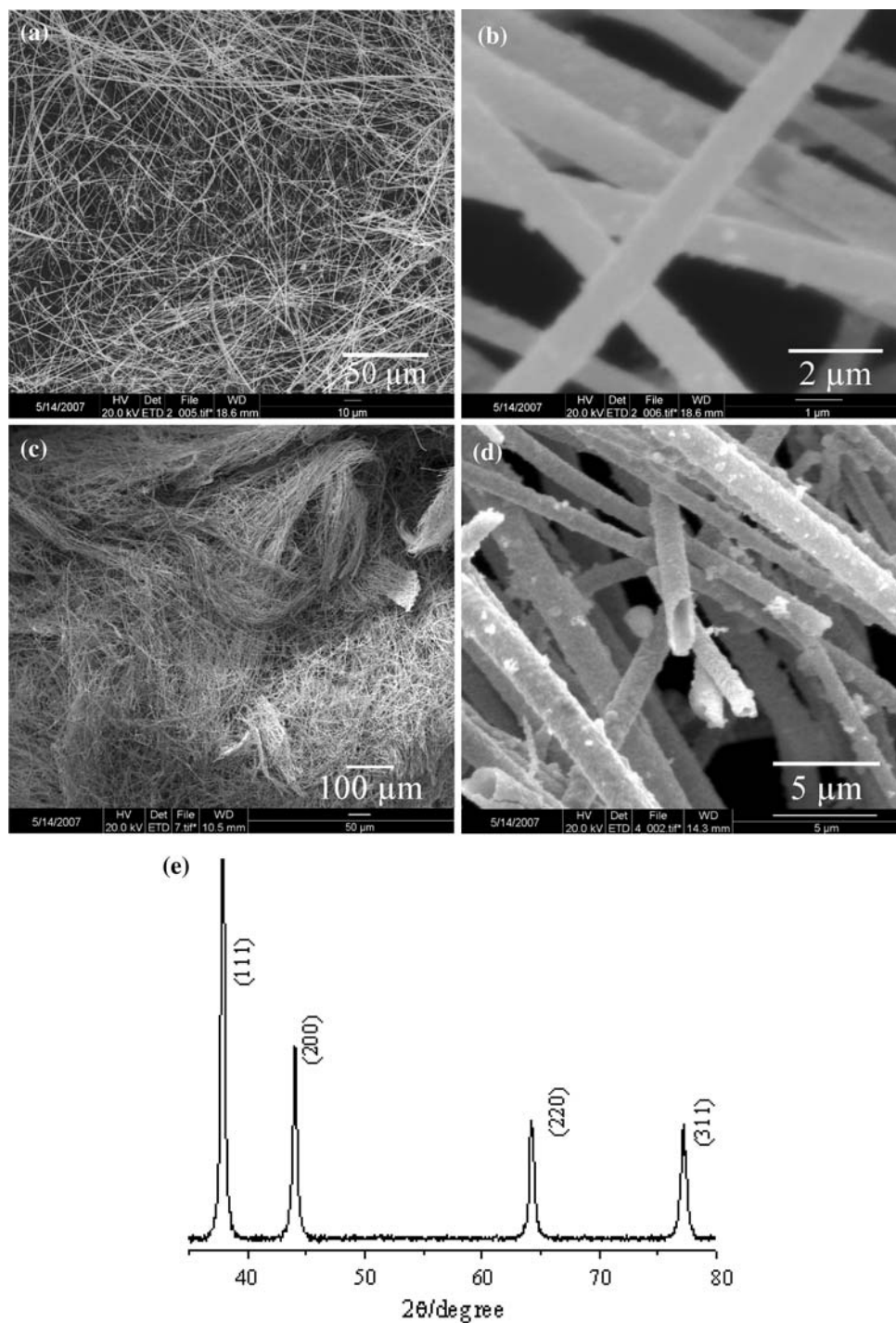


Fig. 2 Typical SEM images of **a, b** the super fine fibers coated by Ag, **c, d** Ag microtubes released from the templates, **e** XRD pattern of the Ag sample



By contrasting the surfaces of the fibers in Fig. 2a with the fibers in Fig. 1a, we can observe that the glass fibers are coated by Ag. A magnified SEM picture (Fig. 2b) shows that nanoparticles densely coat on the fibers and the fibers are 100% covered. When removing the templates, the reaction that treating the coated fibers with 24 wt% HF after cutting them is not drastic. Low concentration of microbubbles appears immediately, which indicates that

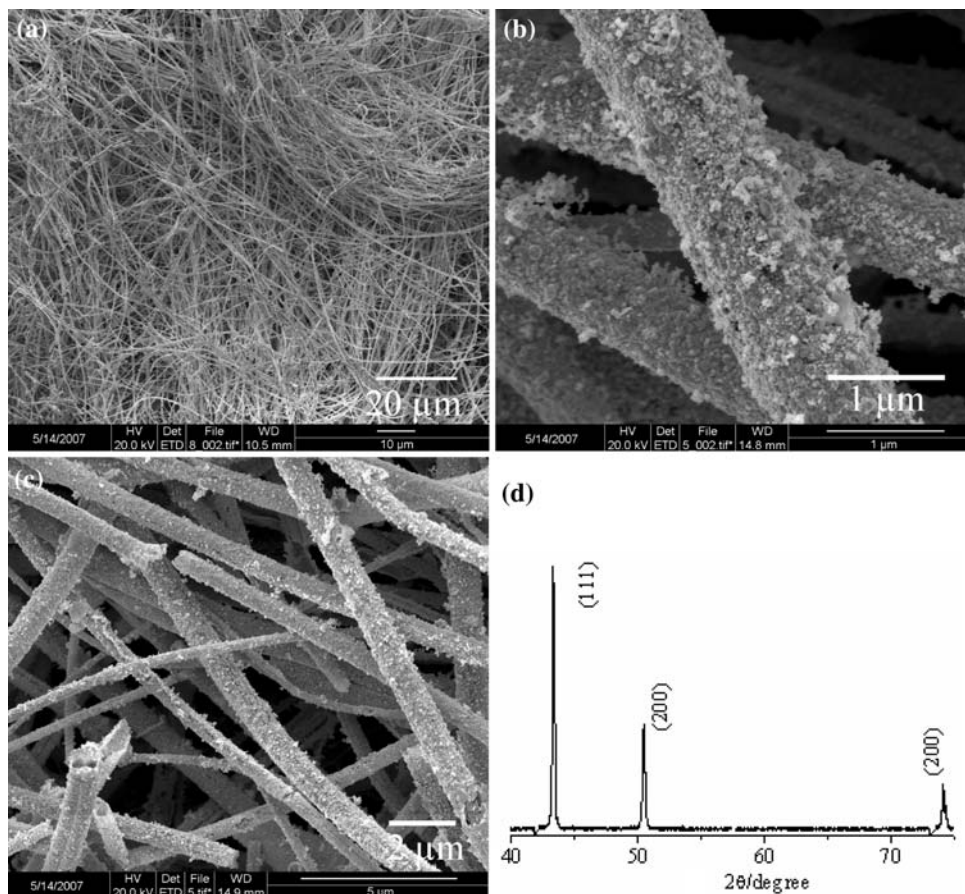
SiF₄ is released. Enough time ensures the completely removing of silica component. As the backbones of coated fiber are dissolved, the hollow tubular fibers become more flexible, which can be judged by Fig. 2c. The space between fibers becomes smaller. In other words, loosening of backbones make their distribution more compact. There may be two mechanisms of eroding the cores. One is that HF enters the channels by diffusing from the ends. Another

possibility may be HF directly penetrates into the fiber core through the silver walls. Associated effects accelerate the formation of Ag microtubes. The tubular morphologies of the fibers after removing the templates are clearly demonstrated in Fig. 2d. The open ends of the fiber clearly demonstrate the hollow structure of the resulting product. We can also observe from the image that the walls of the microtubes are composed of coalesced Ag nanoparticles (about 30 nm) and their thickness is around 200 nm. Thus to obtain pure samples, enough washing with HF solution is necessary. Otherwise, rudimental SiF_4 in the channels cannot be washed off and may further hydrolyze to form solid silicate on the sample surfaces or end faces. To prove that silica is clearly removed during the process of dissolving the templates and washing the remainders, a typical XRD pattern for the as-prepared Ag nanoclusters is shown in Fig. 2e. Three sharp diffraction peaks that are the characteristics of a face-centered cubic (fcc) crystalline structure are seen in the curve, which indicate the tubular structures are composed of highly crystalline silver. These diffraction peaks can be attributed to the (111), (200), and (220) planes (JCPDS, File No. 04-0783).

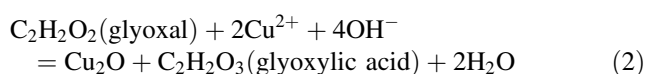
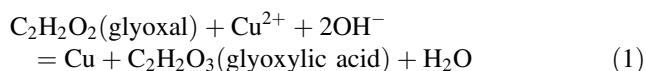
Figure 3 gives the typical SEM images of Cu coated fibers and Cu microtubes after getting rid of silica. Similar

to the morphologies of silver coated fibers, these fibers are successfully coated with a layer of copper (Fig. 3a). Though the surfaces are not as smooth as the above silver encapsulated ones, copper nanoparticles still densely accumulated on the substrate of glass fibers (Fig. 3b). It can be seen the thickness of the Cu microtube is about 210 nm. The XRD result indicates that the copper layer is also highly crystalline. Three peaks correspond to the (111), (200), and (220) planes (JCPDS, File No. 04-0836), which consist with previously reported XRD patterns of copper nanoclusters [39]. Moreover, no peaks of Cu_2O had been detected in the XRD curve. In this circumstance, the reducing agent adopted here is glyoxal. It possesses not only high reactivity, but also cross-linking abilities. These characteristics make glyoxal to be a favorable reducer for growing continuous Cu film on the surface of the glass fibers. Glyoxal is a kind of aldehyde that is oxidized to a carboxylic acid which is called glyoxylic acid. Here, the main chemical process of coating may be explained as follows. There are two feasibilities for the products of oxidation-reduction reaction. On the one hand, the Cu^{2+} cation might be deeply reduced by glyoxal with large concentration to form Cu film on the surface of glass fibers (Eq. 1). On the other hand, the products may be both Cu

Fig. 3 Typical SEM images of **a, b** the super fine fibers coated by Cu, **c** Cu microtubes released from the templates, **d** XRD pattern of the Cu sample



and Cu₂O (Eqs. 1 and 2) at the same time. Actually, even a small amount of Cu₂O generated, it will finally change into Cu. The reason is that hydrofluoric acid is used in the process of dissolving template. It is well known that Cu₂O is not stable in acid medium. If the Cu₂O is dissolved in acid solution, Cu⁺ cation will be released from Cu₂O. Because the Cu²⁺ is more stable than the Cu⁺, disproportionation of Cu⁺ will occur in the solution (Eq. 3). The standard equilibrium constant of Eq. 3 is $K = 1.70 \times 10^6$ at 298 K, which indicates almost all the Cu⁺ will change into Cu. In addition, residual Cu²⁺ can be washed by solution. So the layer on the surface of glass fiber is composed of pure copper.



Conclusion

In summary, we have demonstrated a facile approach to fabricate large-scale tubular silver and copper nano/microtubes using low-cost super fine glass fibers as templates. Results show that the products are composed of pure silver or copper. This work provides a method to fabricate metallic tubular structures with higher length diameter ratios and uniform morphologies. By further modifying the reaction conditions, opportunities exist not only for Ag and Cu, but also for other materials such as Au.

Acknowledgements This work was financially supported by the National Natural Science Foundation of China (No. 60437020) and Natural Science Foundation of Harbin Engineering University (No. 002110260748).

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