Facile route to fabricate large-scale silver microtubes

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Abstract

Large-scale uniform Ag microtubes with high length diameter ratios have been first successfully synthesized by a facile approach, using low-cost super fine glass fibers as templates. The samples were characterized by SEM and XRD. The investigations showed that calcining or adding of PEG-1000 and alcohol could greatly improve the mechanical strength of the sample. Especially the products exhibited favorable catalytic properties during the degradation of Rhodamine B by NaBH₄.

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1. Introduction

The discovery of carbon nanotube has opened a challenging new field in materials science [1]. This results in the extensive scientific interests in tube-like micro- and nanotextures of other substances. These micro- or nanohollow structures are expected to find uses as the paths for gases and fluids or reservoirs for catalysts, and applications in sensors, fuel cells, and separation systems [2–5]. The current synthetic techniques to produce aligned nano/microtubes are mainly hydrothermal method [6], sol–gel process [7], CVD growth [8], etc. However, the yields of nano/microtubes in these methods are limited, and it should be low-cost and short cutting to the large-scale production of these materials in industry. So the problems of exploring simple and inexpensive routes for fabricating nano/microtubular frameworks still remain to be solved.

On the other hand, metal tubular structures with hollow interiors, such as Pt, Te and Bi, exhibit a range of interesting properties superior to their solid counterparts [9–11], thus making them attractive from both scientific and technological viewpoints. In particular, silver is one of the most useful materials...
materials in the fields of catalysts, microelectrodes, surface-enhanced Raman spectroscopy (SERS) [12–14], etc. Its nano/microstructures with morphologies of cubes, wires, rods, spheres, triangular plates, and dendrites have already been fabricated [15–18]. However, heretofore relative little work has been concerned on fabricating the tubular structures of Ag. In
In this letter, we first report on a facile and versatile approach to fabricate large-scale Ag microtubes using low-cost super fine glass fibers as templates. Here the surface of super fine glass fibers can be directly coated by a perfect layer of Ag and we can successfully get large-scale metallic Ag microtubes by dissolving the templates with hydrofluoric acid (HF). This method is simple and the products have higher length diameter ratios which may have advantages for many applications.

2. Experimental

All the reagents were analytical grade and used as received without further purification. Commercial amorphous super fine glass fibers with average diameter of 1.8 μm were adopted as the templates. A typical experimental procedure was described as follows. Firstly, the fibers were washed with ethanol and nitric acid to get rid of the impurity. After rinsed with distilled water for three times, the fibers were dried at room temperature. Secondly, 0.1 g of glass fibers was immersed in 4 ml of 0.12 mol l⁻¹ freshly prepared silver–ammonia aqueous solution. Then 2 ml of 0.12 mol l⁻¹ glucose aqueous solution was mixed with the silver–ammonia solution and the reaction has been kept for 12 h at room temperature. After removing the excess AgNO₃ solution by washing with distilled water under ultrasonic, the fibers coated by Ag were cut to bare the ends. Then the well defined Ag microtubes were freed from the templates by dissolving with 24 wt.% HF for 24 h. At last, the samples were separately washed twice with 48 wt.% HF and distilled water to fully get rid of the remaining silicon. To improve the mechanism properties of the microtubes, two means have been adopted here. One method was calcining the sample at 450 °C at a rate of 240 °C h⁻¹ and keeping at this temperature for 8 h. The second method was adding polyethylene glycol (PEG, average Mw 1000) and ethanol to the coating solution. 0.1 g of PEG and 0.5 ml of ethanol were added to 2 ml of 0.12 mol l⁻¹ glucose aqueous solution. After PEG was fully dissolved, 4 ml of 0.12 mol l⁻¹ silver–ammonia was added. Then 0.1 g of washed glass fibers was added to the mixed solution to begin coating. The conditions and the process of reaction and removing silicon were similar to the previous steps.

3. Results and discussion

Fig. 1 shows the SEM image of the amorphous super fine glass fibers and its frequency distribution of diameters. The fiber diameter mainly distributes in the range of 1–3 μm. Fig. 2 gives typical SEM images of glass fibers coated by Ag and Ag microtubes released from the templates. By contrasting the surfaces of the fibers in Fig. 1(a) with the fibers in Fig. 2(b), it can be observed that the glass fibers are coated by Ag. The tubular morphologies of the fibers after removing the templates are clearly demonstrated in Fig. 2(c). The open ends of the fibers, indicated by the arrows, clearly demonstrate the hollow structure of the resulting product. From the magnified image [Fig. 2(d)], it can be observed that the walls of the microtubes are composed of coalesced Ag nanoparticles (about 50–80 nm) and their thickness is around 200 nm. Simultaneously, the hollow structures can be further proved by the sonicated sample. As shown in Fig. 2(e), the hollow structure can be clearly observed from the broken microtubes by ultrasound vibration. Significantly, these breaks can fitly prove that the Ag tubes are unblocked throughout the whole length. That is to say the templates (at least 2–5 cm long) are completely removed by HF. To prove that silicon is clearly removed during the process of dissolving the templates and washing the remainders, Fig. 2(f) gives its XRD pattern, which indicates that the product is pure Ag phase (JCPDS 4-0783).

Simultaneously, the calcined sample coated by Ag, as shown in Fig. 3(a), exhibits obvious bends. This may be caused by the combined action of the stress enhancement between the Ag nanoparticles on the surface of the glass fiber and the distortion of the glass fiber itself. Notably, the Ag
microtubes [Fig. 3(b)] freed from these calcined fibers at 450 °C appear to have better mechanical strength than the uncalcined fibers. On the other hand, it is noticeable that the adding of PEG-1000 and ethanol in the reaction has not only changed the morphology of the surface of the microtube but also enhanced the mechanical strength of the products. From the cross section in Fig. 3(d), we can observe that the surfaces of these samples are much smoother than the surfaces of the previous products. In addition, we have not found a large amount of breaks in these products under ultrasound. This indicates that the addition of PEG-1000 and ethanol during reaction has enhanced the force between the Ag nanoparticles. This may be due to the restriction of PEG and ethanol to the growth of Ag nanoparticles. We observe that the XRD result of silver microtubes obtained by this method is similar to Fig. 2(f) and no new peaks appear except the peaks of silver, indicating PEG is clearly removed.

Finally, we investigate the catalytic properties in the degradation of Rhodamine B (RB) by NaBH₄. The progressions of the catalytic reduction of the dye are followed by the changes of absorptions at the wavelength of the absorbance maximum (λmax) of RB. In this experiment, the volume of the reaction aqueous solution is 50 ml. The concentrations of RB and NaBH₄ are separately 2.0×10⁻⁵ mol l⁻¹ and 1.0×10⁻² mol l⁻¹. The amount of Ag catalyst is 40 mg in each catalytic reactions. Fig. 4(a) shows the evolution of the UV-visible spectra of RB during catalytic reductions. Fig. 4(a) depicts using directly reduced Ag microtubes by glucose as catalyst and Fig. 4(b) shows using PEG–ethanol aiding grown Ag microtubes as catalyst. Consistent with previous results [19], the reduction of RB by NaBH₄ is insignificant without catalyst. However, these two degradation reactions are completed within a few minutes after adding the above two Ag microtubes. Besides this, these two catalysts exhibit no deactivation or poisoning during the reactions. Fig. 4(c) indicates that each catalytic reaction has an induction period. The directly reduced product by glucose (without PEG added) has a longer induction period, which may be caused by the larger diameter of the Ag nanoparticles composed of its tubular structures.

4. Conclusions

In conclusion, we have demonstrated a facile approach to fabricate large-scale Ag microtubes using low-cost super fine glass fibers as templates. The products have higher length diameter ratios and uniform morphologies of tubular structures. By calcining the product or adding PEG-1000 and alcohol during the reaction, the mechanical strength of the Ag microtubes can be greatly improved. Simultaneously, these products show good catalytic properties in the degradation of Rhodamine B. By further modifying the reaction conditions, opportunities exist not only for Ag, but also for other materials.

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References