

FACILE FABRICATION OF LARGE SCALE MICROTUBES WITH A NATURAL TEMPLATE — KAPOK FIBER*

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Abstract A newly natural fine template, kapok fiber, for microtube preparation was reported. Large scale microtubes with high length/diameter ratio and controllable wall thickness and morphology have been successfully fabricated with this template. It is a widely available, low-cost, environmental friendly and fine structured natural template for microtubes. Its thin wall thickness is only about 1–2 μm that means the whole template material is tiny and easy for removing. Even there is any residue the amount can be ignored. When the template is covered with a shell component, hollow structured microtube could be obtained by removing the thin inner template, and its shape could be the same as that of the original template (positive copy of the template's shape). The products have high length/diameter ratio and uniform tubular structure. By further modifying the fabricating methods, facile fabrication not only exists for polypyrrole (PPy) in electrochemical deposition, but also for many other organic and inorganic materials. The surface morphology and wall thickness of the resultant microtubes can be easily modulated by controlling the processing conditions. This natural fiber is predicted to be a fine template for fabricating large scale microtubes with large cavity and high length/diameter ratio.

Keywords: Biomaterials; Kapok fibers; Templates; Microtubes.

INTRODUCTION

Due to the development of nanosciences and technology, studies about nanotubes (*e.g.* nano carbontubes) were so focal and popular recently. However, actually the safe and high cost of nano-size materials have aroused increasing worry^[1, 2]. Alternatively, microtubes similarly with small size but large specific surface area are also endowed with many excellent properties, *e.g.* super-heat-exchange conductivity. They are expected to be applied as encapsulating agents, liquid carriers, release controlling agents, catalyst carriers, adsorbents, absorbents, micro-reactors, sensors and separation systems, *etc.*^[3–6]. Furthermore, compared with nanotubes, microtubes have their own advantages, such as easy and low-cost for fabrication, safe and environmental friendly for use.

There are numerous methods for fabricating microtubes, such as extrusion^[7], self-assembly^[8], direct solution synthesis^[9, 10]. However, the yields of microtubes obtained by these methods are limited. And in industry, it should be low-cost and short-cut enough for large scale production. Therefore, the problem of exploring simple and low-cost route for fabricating microtubular frameworks still remain to be solved. Currently, the template method is one of the extensively adopted methods for its facile, simple, controllable and

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universal applicable traits. However, finding novel and general template which can be used as structure-directing agent is still an attractive challenge. Although many artificial materials like porous anodic aluminum oxide or polymer membranes, and micrometer glass or composite polymer fibers have been used as fine templates for microtubes, the working procedure for making these templates is an energy consuming and environmental polluting process^[4–6, 11, 12]. As the environmental problem becomes one of the severe troubles that human being is confronted with, more and more researchers have paid considerable attention to the rational development and utilization of natural materials for agricultural and industrial processes. Recent years some researchers have focused on adopting natural materials like bacteria^[13], collagen fibers^[14], wood cells, cellulose^[15], tobacco mosaic viruses^[16], human hairs^[17] and spider silk as microtube templates^[18–21]. However, these previously reported natural templates almost have their own shortcomings, like the keratinization of human hairs, the spiral twist of cellulose, the linear limit of bacteria and viruses, and the deficiency of spider silk.

Kapok fiber is natural and has a shape of round microtube with smooth surface and thin wall, whose diameter is about 10 μm and length is in several centimeters^[22]. It is abundantly produced, and utilized locally as stuffing, buoyancy material, oil-absorbing material or blending material with other cellulose fibers. Therefore, it is a wildly available, low-cost, environmental friendly, fine structured and natural template for microtubes. The thin wall thickness of kapok fibers is only about 1–2 μm that means the whole template material is tiny and easy for removing. Even there is any residue, the amount can be ignored. In this communication, for the first time, we use kapok fiber as a newly natural fine template for microtube preparation. With this natural fine template, large scale microtubes with high length/diameter ratio and controllable wall thickness and morphology were successfully fabricated for several kinds of materials.

EXPERIMENTAL

Materials

Natural kapok fiber produced in Sichuan province, China was used. It was washed thoroughly with acetone and distilled water several times to remove ashes, then dried at room temperature. All the reagents were of analytical grade and used as received without further purification.

Preparation of Microtubes

The Ag and Ni microtubes were prepared with chemical deposition procedure^[23, 24]. The SiO_2 microtubes with smooth or rough surfaces were obtained by a sol-gel process described in previous reports^[25, 26]. A typical polypyrrole (PPy) electrochemical deposition procedure was adopted^[27]. The PPy coated kapok fibers were slurry-washed with copious amounts of deionized water, then immersed in 75% H_2SO_4 aqueous solution to remove kapok template. The samples should slurry-washed with copious amounts of deionized water again and dried in vacuum overnight before the calcination procedure. They were finally heated from room temperature to 800°C at a rate of 10 K/min under N_2 atmosphere, and calcined at this temperature for 1 h to remove the organic components. Then the carbon microtubes were freed from the templates. For microtubes with other different materials, the conditions and the processes for removing kapok templates were similar to the previous steps.

Characterization

Scanning electron microscopy (SEM) observations were carried out on a Hitachi S-4300 cold-field emission SEM (Hitachi Japan) operated at 15.0 kV. The Pt coating time before SEM observations was 45 s. The chemical nature of the original kapok fiber, a pure PPy specimen, the controlled PPy/kapok composite fibers, and the resultant carbon microtubes after calcination was inspected by Fourier transform infrared spectroscopy (FTIR, Equinox 55, Bruker, Germany), with a resolution of 4 cm^{-1} . The thermal stability of the resulted PPy/kapok composite fibers was examined by thermogravimetric analysis (TGA, PerkinElmer, U.S.A.). Samples for TGA studies were heated from 30°C to 1000°C with a heating rate of 10 K/min and under a nitrogen flow rate of 300 mL/min.

RESULTS AND DISCUSSION

Fabrication of PPy Microtubes

Figures 1(a) and 1(b) show the typical SEM images of the natural cotton fiber and natural kapok fiber, respectively. It is obviously that each natural cotton hair is a thin flattened tubular cell with pronounced helical superstructure. However, the natural kapok fiber presents ideal round tube with smooth thin wall. Figures 1(c) and 1(d) give the SEM images of kapok fibers electrochemically coated with polypyrrole (PPy) and PPy microtubes released from template by dissolving kapok fibers in H_2SO_4 aqueous solution. The SEM micrograph in Fig. 1(c) for the composite PPy-coated kapok fibers clearly showed that every kapok fiber was homogeneously coated with a skin layer of PPy, as compared with the micrograph in Fig. 1(b) for uncoated kapok fibers. The tubular hollow structure and morphology of the resulted microtubes after removing the templates are clearly demonstrated in Fig. 1(d). As shown in the SEM images, hollow structure can be clearly observed from the microtubes broken by ultrasound vibration. Furthermore, these breaks can fitly prove that the obtained microtubes are unblocked throughout the whole length. That is to say the template (at least 1–2 cm long) is completely removed by H_2SO_4 aqueous solution and the obtained microtube almost has the same structure as the original template.

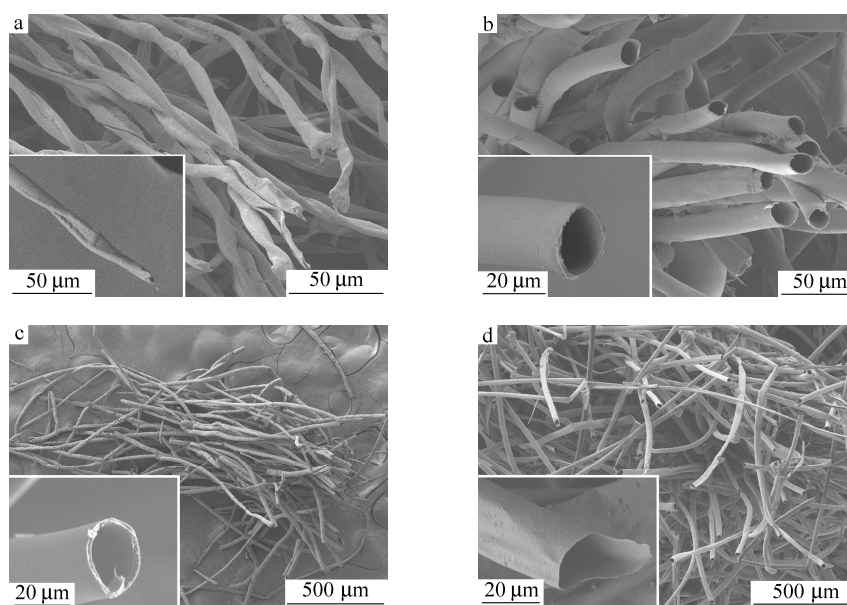


Fig. 1 SEM images of (a) natural cotton fibers, (b) natural kapok fibers, (c) kapok fibers electrochemistry coated with PPy and (d) PPy microtubes released from the templates

Facile Fabrication of Carbon Microtubes

Calcination is one of the most frequently employed ways for removing template materials in general template method. The natural kapok fiber consists of 64% cellulose, 13% lignin, 8.6% water, 1.4%–3.5% ashes, 4.7%–9.7% water-soluble substances, 2.3%–2.5% xylan and 0.8% waxes^[28]. Therefore, it can easily be burned and removed at temperatures above 350°C. Take advantage of this property, more conveniently, a new chemical approach for obtaining carbon microtubes can be developed by direct pyrolysis of the composite fibers. The basic idea is to utilize a thermally removable polymer fiber, like kapok fiber, as the growing template for a thermally more stable material such as conjugated PPy. The detailed process can be described as follows: the resultant composite fiber which consists of a thermally more stable PPy skin layer and a natural kapok fiber core was then subjected to a thermal treatment; the natural template was thermal degraded, while the PPy skin layer was simultaneously carbonized to form a carbon microtube. Small shrinkage was noticed by comparing the obtained carbon microtubers with the original composite microtubes. The wall thickness of the resultant hollow

carbon microtubes was directly proportional to the thickness of the original PPy layer. However, a minimum thickness of the PPy coating was required to provide sufficient mechanical strength for the microtubes to maintain their round shape after removing the template. The numerical value was estimated to be about 100 nm by SEM. Most interestingly, it also provides a feasible approach for the preparation of two- or three-dimensional well-organized carbon microtube assembly with suitable woven fabrics or structure.

The Fourier transform infrared spectroscopy (FTIR) spectra for natural kapok fibers, a pure PPy specimen, the PPy-coated kapok fibers and the carbon microtubes are displayed in Fig. 2(A), respectively. The results clearly showed that the PPy-coated kapok fibers indeed contained the IR characteristic bands for both PPy and kapok fibers. All the peaks in the IR spectra, however, disappeared completely after carbonizing treatments and left a featureless IR spectrum (d of Fig. 2A) for the resultant carbon microtubes. This result indicated that all the carbonyl and other characteristic functional groups have been essentially eliminated. The residual carbons have formed highly symmetrical carbon-carbon bonds which are IR inactive. This result further implies the presence of a carbon matrix with an extensive network structure^[4].

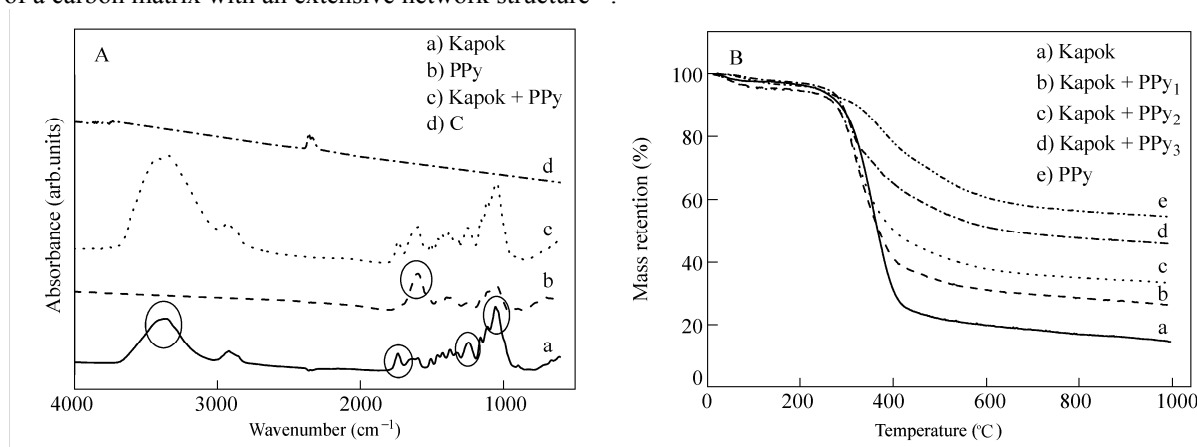


Fig. 2 (A) FTIR spectra for (a) kapok fibers, (b) pure PPy, (c) PPy-coated kapok fibers and (d) the resultant carbon microtubes; (B) Thermogravimetric analysis traces for (a) kapok fiber, (b–d) PPy/kapok composite fibers with a progressive increase in PPy coating thickness and (e) undoped PPy powder

The result that PPy is thermally more stable than natural kapok fibers is also confirmed by thermogravimetric analysis (TGA), as displayed by curves (e) and (a) in Fig. 2(B), respectively. The results showed that the mass retention at 1000°C for undoped PPy (60%) was much higher than that for natural kapok fibers (13%). As the thermally less stable kapok fibers were coated with PPy, the resulted composite fibers also showed a tendency for higher weight retention. The TGA traces (b–d) in Fig. 2(B) are for a series of composite fibers with an increasing time of PPy coating treatments. The results indicated that composite fibers with a relatively thicker PPy layer displayed a relatively higher mass retention after annealing at 1000°C. The on-set decomposition temperature was measured to be about 260°C by TGA. Meanwhile, the PPy skin layer also starts to decompose at its decomposition on-set temperature (*i.e.* 310°C for undoped PPy powder), with the formation of active intermediates^[4]. It is believed that these intermediates may induce efficient crosslinking of the highly π -bond-conjugated PPy, thus forming the initial three-dimensional network of the final carbon microtube wall.

Fabrication of Microtubes for Other Organic and Inorganic Materials with Different Methods

Normally, organic molecules, inorganic compounds, polymers, and organic or inorganic particles all can be candidates for the shell component, if they may firmly attach to the template surface. After the template is covered with a shell component, hollow structure is created by removing the inner template. Its shape could be the same as that of the original template. Currently, this template has already succeeded in preparing different microtubes with different approaches, *e.g.* metal microtubes, like silver (Ag) and nickel (Ni) microtubes with chemical deposition, silicon dioxide (SiO₂) microtubes with surface sol-gel process, poly(acrylonitrile) (PAN) microtubes with solution wetting method.

In addition, both of the wall thickness and the surface morphology of the resultant microtubes can be feasibly controlled, as shown in Figs. 3 and 4, respectively. It can be clearly observed from the SEM images that as the preparing conditions (concentration, reacting time, applied voltage, *etc.*) changed, the wall thickness of the resultant microtubes can be feasibly controlled.

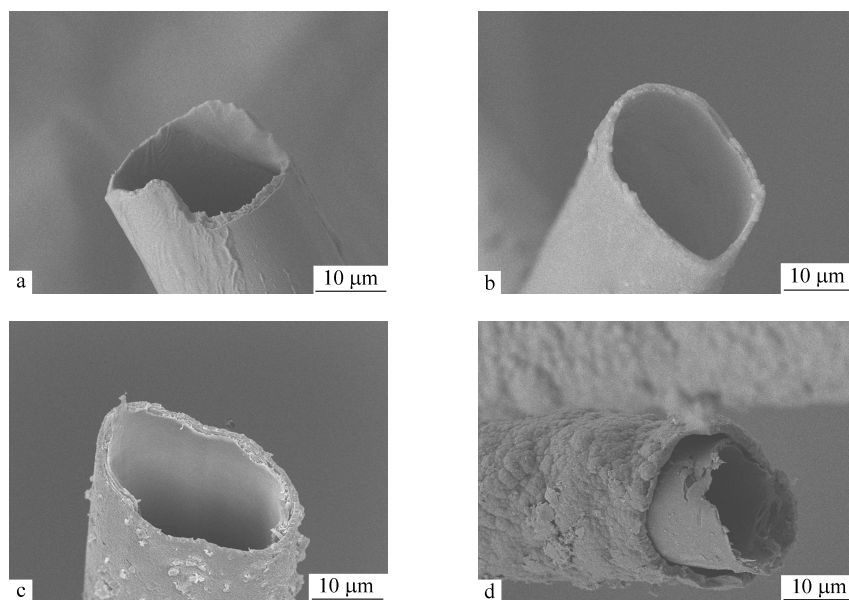


Fig. 3 SEM images of PPy/kapok composite fibers with a progressive increase in PPy coating thickness from (a) to (d)

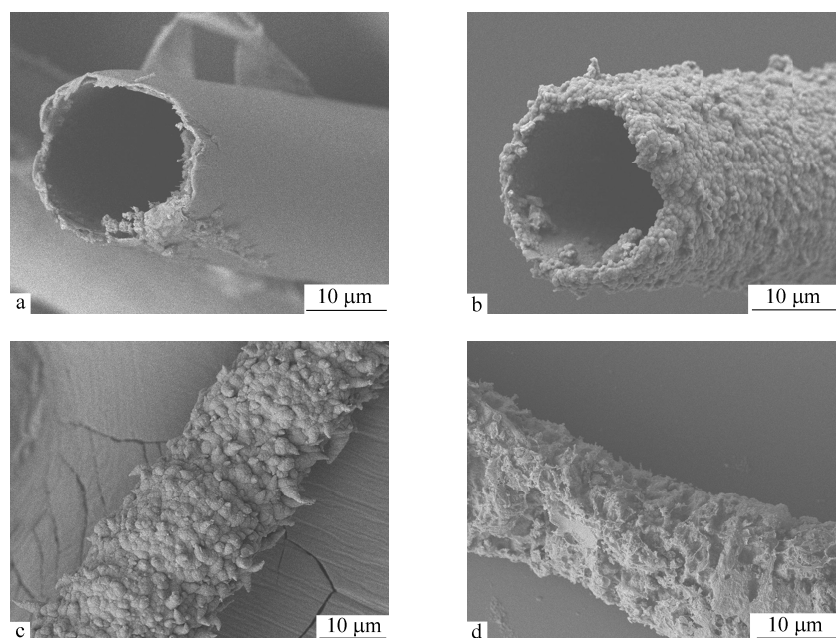


Fig. 4 SEM images of the resultant microtubes with controllable surface roughness
 a) SiO₂ microtube with smooth surface; b) SiO₂ microtube with rough surface; c) PPy microtube with rough surface; d) Carbon microtube with rough surface

Large scale Ag and Ni microtubes can be obtained by chemical deposition method followed with template dissolving process in H_2SO_4 aqueous solution. The surface sol-gel process is a useful and effective approach for manufacture. Stepwise hydrolysis and dehydration of tetraethylorthosilicate $[(\text{EtO})_4\text{Si}]$ produce SiO_2 in aqueous solution is a typical surface sol-gel process^[23]. Smooth crystalline SiO_2 thin films (anatase phase) on organic polymer templates can be successfully obtained in solutions of pH 1–3. Since solutions in this pH region gradually became supersaturated with SiO_2 produced by the stepwise reactions, thin films of crystalline SiO_2 were prepared through heterogeneous nucleation on various kinds of hydrophilic substrates^[24]. Alternatively, the rough sample can be obtained using alkaline solution, which has many potential applications, *e.g.* catalysts carrier. Furthermore, PPy microtubes and the accordingly obtained carbon microtubes both with rough surfaces are fabricated by controlling different preparation conditions (as shown in Fig. 4).

As for micrometer-sized tubes with relatively large inner diameter, it would be easier for reactants to flow through their cavities. The inner surface can be modified *via* treatment with various chemicals that render the inner surface active with desired affinity and selective separation (or extraction) of interested compounds. Likewise, desired transition metal complexes (with size often larger than 2–3 nm) would also be embedded on the inner surface of microtubes for imparting specific catalytic functions. It is envisaged that, with its large inner diameter, the throughput of the tubular micro-reactor would be acceptable for practical applications.

CONCLUSIONS

In summary, we have successfully fabricated large scale microtubes by using low-cost, abundantly available and super fine natural kapok fiber as template. The products have high length/diameter ratio and uniform tubular structure. By further modifying the reaction conditions, opportunities exist not only for PPy in electrochemical deposition, but also for many other organic and inorganic materials with different fabricating methods, *e.g.* chemical deposition and surface sol-gel process. The surface morphology and wall thickness of the resultant microtubes can be easily modulated by controlling processing conditions. The implication of the current results is at least twofold. First, fine microtubes can be fabricated in large scale using appropriate bio-templates. Second, appropriate utilization of natural material instead of artificial material will present us a low-cost, environmentally benign and efficient route to prepare desired products. Work involving the use of many other materials as skin layers with various different preparing methods is under progress.

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