

Preparation of Hollow Nickel Microtubes by Electroless Plating

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We demonstrate a novel method for the fabrication of hollow metal microtubes by the template-based synthesis without using an oxidative burning procedure. Amphoteric azopyridine carboxylic acid of low-molecular-weight organic molecules dissolved in alkaline aqueous solution was self-organized by neutralization to grow into well-defined organic crystalline fibers of supramolecular assemblages with several micrometers in diameter. The microfibers were available as templates of nickel electroless plating. When the nickel-plated organic hybrids were immersed in an alkaline solution, hollow nickel microtubes were successfully obtained by dissolving the fibrous templates. This method has a distinctive advantage consisting of no-VOC processes not to generate volatile organic compounds, when compared with previous fabrication methods resorting to an oxidative burning procedure to remove organic fibrous templates.

Key words: self-organization, hollow microtube, electroless plating, metallization, nickel

1. INTRODUCTION

The hollow nickel tubes with micropores (pore size 0.1 to 100 μm) or nanopores (1 to 100 nm) are promising for wide applications including electrodes used in display devices¹ and efficient electro catalysts in fuel cells,^{2, 3} due to their large surface area. These hollow tubes are typically made by the template-base synthesis consisting of the nickel electroless plating of organic fibrous materials as templates and the removal of the organic templates from nickel-coated organic hybrids after the plating. The organic fibrous templates such as lipid tubule,⁴ polypropylene fiber^{2, 3} and carbon nanotube^{5, 6} have been used up to date. Accordingly, the process of oxidative burning of templates under high temperatures is adopted, and the organic template is removable from the nickel-coated fibrous hybrids. Since the burning process involves the consumption of large energy and the emission of volatile organic compounds (VOC) mainly including carbon dioxide, other methods consisting of environmentally benign no-VOC procedures have been highly required from the industrial standpoint.

Amphoteric azopyridine carboxylic acid indicated in Figure 1 has unique property of their microscopic self-organized morphology.^{7, 8} The amphoteric organic compounds dissolved in alkaline aqueous solution can form well-defined shaped self-assemblages through neutralization by atmospheric acidic substance such as carbon dioxide. Especially, organic crystalline microfibers are formed from azopyridine carboxylic acids bearing an alkyl substituent tethered to the azopyridine skeleton. Moreover, the macroscopic fibrous morphology of their length and diameter is readily tunable by external stimuli such as heat, pH-change, and light irradiation⁸ and change in partial chemical structure of the alkyl substituent.⁹ We noticed a series of azopyridine carboxylic acids for the fabrication of hollow nickel tubes as the following reasons. First, the azopyridine carboxylic acids are capable of tuning their macroscopic organized

morphology by their chemical structures and external stimuli.^{8, 9} Secondly, it is anticipated that fibrous template bodies composed of the organic components are removable easily from the nickel-coated hybrid materials in alkaline aqueous solution by dissolving them. Therefore, all procedures consisting of the template fabrication, the nickel electroless plating, and the removal of template bodies will be performed in environmentally benign aqueous systems without using the oxidative burning procedure to remove the fibrous template bodies.

In this study, we demonstrate a novel method to fabricate hollow nickel microtubes by the template-based synthesis using the organic fibrous template formed from azopyridine carboxylic acid. This method has a distinctive advantage consisting of no-VOC procedures.

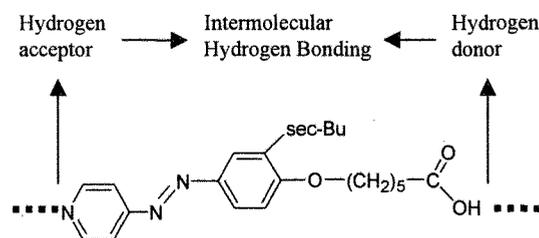


Figure 1. Chemical structure of sb-APC.

2. EXPERIMENT

2.1 Preparation of template microfibers

Organic microfibers used in this study were prepared in a similar manner described in our previous paper.⁸ Azopyridine carboxylic acid with a *sec*-butyl group, sb-APC (Figure 1)⁹, in a powder state was dissolved in a NaOH aqueous solution of $3.0 \times 10^{-3} \text{ mol dm}^{-3}$. The solution was placed in a vial, which was capped with an aluminium foil with small holes to contact air and kept standing for one week under atmospheric condition, to

allow spontaneous deposition of sb-APC microfibers.

2.2 Catalyzation

The catalyzation of sb-APC microfibers for nickel electroless plating was performed in a typical manner of sensitization and catalyzation. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.5 g) was placed in a 100 cm^3 volumetric flask, to which was added HCl (0.2 ml) of 1 mol dm^{-3} . The solution was diluted with deionized water up to 100 cm^3 . The diluted solution was used as a sensitization solution for plating. PdCl_2 (26 mg) was dissolved in an aqueous solution (100 ml) containing 1 mol dm^{-3} HCl (0.05 ml). The PdCl_2 solution was used as a catalyzation solution for plating. The sb-APC microfibers self-organized in aqueous solution were filtered with a PTFE membrane filter of $1 \mu\text{m}$ pore size. The filtered microfibers were rinsed with deionized water thoroughly and treated with the sensitization solution of SnCl_2 for 2 min. After rinsing with deionized water, the microfibers were subsequently contacted with the catalyzation solution of PdCl_2 for 5 min, followed by a rinse with deionized water.

2.3 Nickel electroless plating

Catalyzed sb-APC microfibers were immersed in a nickel electroless bath at 30°C for suitable time, and then nickel-coated microfibers were filtered. A typical chemical composition of the plating bath was summarized in Table 1. After filtration of the plating bath, multiple rinses with deionized water and natural drying, nickel-coated hybrid microfibers were collected.

Table 1. Chemical composition of nickel plating bath.

Chemical	Concentration (mol dm^{-3})
$\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$	0.05
H_3BO_3	0.19
CH_3COONa	0.03
$(\text{NH}_4)_2\text{SO}_4$	9.8×10^{-3}
pH at 30°C (adjusted by CH_3COOH)	5.5
Bath temperature	30°C

2.4 Fabrication of hollow nickel microfibers

The nickel-coated hybrid microfibers were immersed in an aqueous NaOH solution (5 cm^3) of 1.0 mol dm^{-3} for 24 h, to dissolve the organic sb-APC fibrous template. Hollow nickel microfibers were collected by filtration with a PTFE membrane filter of $0.2 \mu\text{m}$ pore size and rinsing with deionized water.

3. RESULTS AND DISCUSSION

3.1 Catalyzation of organic microfibers

When the aqueous alkaline solution dissolving the azopyridine carboxylic acid with a *sec*-butyl group, sb-APC, kept standing for about one week under atmospheric condition, fibrous materials were self-organized in the solution. Neutralization by acidic substance included in air causes the formation of intermolecular *head-to-tail* hydrogen bonds between pyridyl and carboxyl groups of sb-APC. The sb-APC

was self-assembled as microfibers of supramolecular polymeric assemblages.⁹ The crystalline organic microfibers were approximately $8 \mu\text{m}$ in diameter and $700 \mu\text{m}$ in length in average as shown in Figure 2(a). For catalyzation and plating of the microfibers, we first investigated chemical and thermal stability of the microfibers in aqueous solution. The microfibers of sb-APC were completely soluble in acidic solutions below pH 1 and in alkaline solutions over pH 12. Even in neutral deionized water, the microfibers were completely soluble in hot water. These results come from the fact that the microfibers are supramolecular polymers of amphoteric sb-APC chained by intermolecular hydrogen bonds between its pyridyl and carboxyl groups. Therefore, a suitable condition resorting to pH and temperature is required for the catalyzation and plating processes.

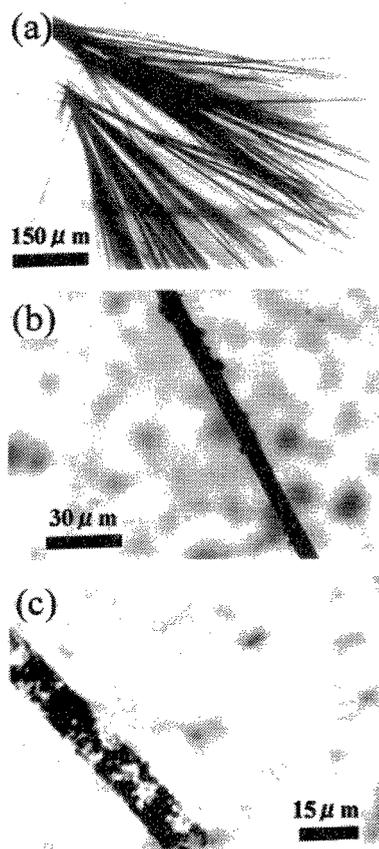


Figure 2. Photographs of (a) sb-APC template microfibers, (b) microfibers after nickel plating, and (c) hollow nickel microtubes after removing templates.

Tin-palladium (Sn-Pd) catalysts¹⁰ are commonly used for nickel electroless plating. The methods for preparation of the plating catalysts are categorized into two types. One type is the stepwise method consisting of the sensitization of plated surfaces with SnCl_2 , followed by catalyzation with PdCl_2 to allow the formation of reduced Pd metal, and the activation with HCl to remove oxidized Sn^{4+} clusters. Another type is the single step method based on direct physicochemical adsorption of Pd colloids on plated surfaces that are prepared by reduction of PdCl_2 with SnCl_2 in advance.

In this study, we attempted these two methods for the catalyzation of organic sb-APC microfibers. However, the macroscopic morphology of microfibers was broken into small powdery materials in the single step method under strongly acidic conditions (results not shown). Moreover, the diameter of Pd colloids prepared by the reduction of PdCl₂ with SnCl₂ was not uniform in a micrometer scale so that it was difficult to obtain nickel-coated microfibers with smooth surface morphology.

Thereupon, we adopted the stepwise catalyzation method to avoid the formation of micrometer-scale Pd colloids. Even after the treatment of sb-APC microfibers with the SnCl₂ sensitization solution and the PdCl₂ activation solution, the fibrous morphology of microfibers was almost maintained. Elongation of the sensitization and catalyzation time often caused to make the diameter of microfiber more slender. This implies that the microfibers were gradually dissolved under the acidic condition.

3.2 Plating of organic microfibers

The sb-APC microfibers after the treatment by the stepwise catalyzation were immersed in a nickel plating bath containing 0.05 mol dm⁻³ Ni(H₂PO₂)₂ at 30 °C for 2 h. The color of microfibers turned from yellow to metallic color. Figure 2(b) shows a photograph of microfiber after the plating by means of optical microscopy in a transmission mode. Dark microfibers enlarged in their diameter were observed. Outermost surfaces of the plated fibers were smooth. When compared with the microfibers before the plating [Figure 2(a)], the plated microfibers obviously prevent the transmission of visible light. This indicates that the microfibers were completely metallized and coated by nickel metal. The thickness of the plating was estimated to be 1.0 μm by subtraction of an average diameter of microfibers before the plating. The plating behaviors mentioned above clearly suggested that the Sn-Pd catalyst caused nickel electroless plating of sb-APC microfibers. It is anticipated that the SnCl₂ is adsorbed on pyridyl and/or carboxyl groups of microfiber surfaces by coordination and the reduced Pd metal induced the nickel electroless plating.

Figure 3 shows optical microscopy images of nickel-coated sb-APC microfibers prepared by nickel electroless plating baths with different Ni(H₂PO₂)₂ concentration of (a) 0.05, (b) 0.10 and (c) 0.15 mol dm⁻³. When the dilute plating bath containing 0.05 mol dm⁻³ Ni(H₂PO₂)₂ was used, smooth plated surfaces of sb-APC microfibers were observed. On the other hand, use of more concentrated plating baths caused deterioration of fibrous morphology after the nickel plating as indicated in Figure 3(b) and 3(c). The plated microfibers with a lot of metal particles were generated in more concentrated plating baths. These observations clearly indicate that the concentration of Ni²⁺ ion affected the resulting surface morphology of the nickel-coated microfibers. A suitable plating rate of nickel electroless plating is an important factor for the coating of sb-APC microfibers.

The surface morphology of nickel-coated microfibers was remarkably dependent on pH conditions of the dilute nickel plating bath containing 0.05 mol dm⁻³ Ni(H₂PO₂)₂. Figure 4 shows photographs of plated

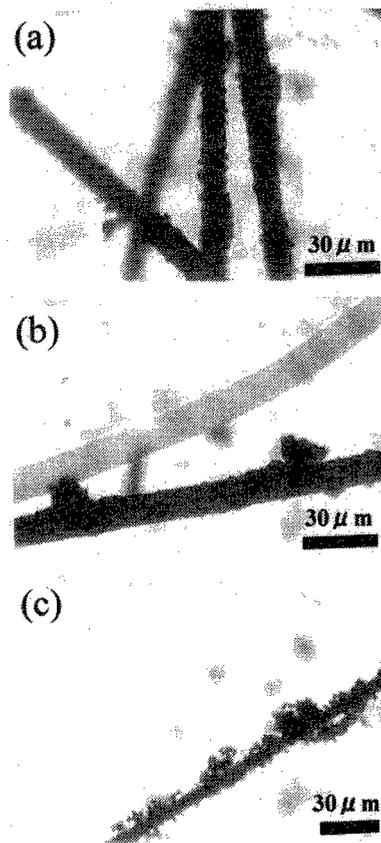


Figure 3. Photographs of sb-APC template microfibers after nickel plating prepared by plating baths with different Ni(H₂PO₂)₂ concentration of (a) 0.05, (b) 0.10 and (c) 0.15 mol dm⁻³.

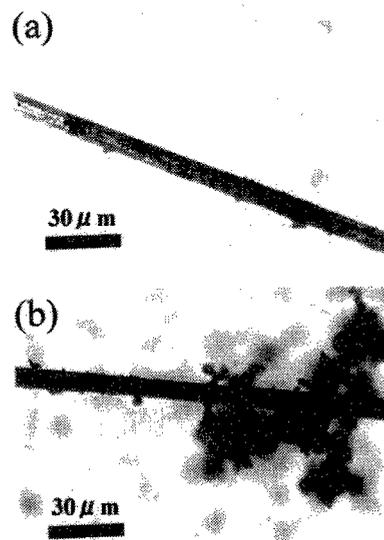


Figure 4. Photographs of nickel-coated microfibers prepared in the plating bath with a pH value of (a) 5.0 and (b) 6.0.

microfibers prepared in different plating baths varying a pH value by addition of small amount of NaOH or HCl. The plated microfibers with coarse surface morphology were obtained, when the plating baths of pH 5.0 [Figure 4(a)] and pH 6.0 [Figure 4(b)] were used. In the

slightly acidic condition at pH 5.0, the metallization was not complete due to a slower plating rate. Conversely, a higher plating rate in more neutralized solution at 6.0 deteriorated the surface morphology of coated microfibers by emergence of metal particles. It was found that the use of plating bath of pH 5.5 is most suitable for the nickel plating in order to obtain nickel-coated fibers exhibiting homogenized surface morphology as shown in Figure 2(b).

3.3 Removal of organic fibrous template

To remove the organic fibrous templates from the nickel-plated hybrid microfibers, the plated materials were dispersed in an alkaline aqueous solution of pH 12 adjusted by addition of NaOH. The colorless solution was immediately changed to yellow one, indicating that the self-organized organic microfibers were dissolved due to the cleavage of chained intermolecular hydrogen bonds forming the supramolecular polymers. Figure 2(c) shows a photograph of nickel-plated materials after the removal of organic templates. The morphology of the nickel fibers was not almost deteriorated by the immersion in the alkaline solution. A prominent feature of the plated materials compared with that before the removal of organic templates is that the center of microfibers exhibits improved transmission of visible light. This observation clearly suggests that the inside of nickel microfibers is in a hollow situation by removing the organic fibrous templates.

Previous studies on the template-based synthesis of hollow nickel microtubes using lipid tubules and polymer microfibers must resort to the oxidative burning procedure for the removal of templates, which consumes large energy for burning and causes the emission of carbon dioxide. In our procedures, the self-organized microfibers formed by chained intermolecular hydrogen bonds between the amphoteric azopyridine carboxylic acids were readily removable by the immersion in the alkaline aqueous solution at room temperature. Therefore, no emission of volatile organic compounds can be achieved for the fabrication of hollow nickel microtubes.

4. CONCLUSION

We developed the novel method for the fabrication of hollow nickel microtubes by the template-based synthesis using fibrous materials self-organized from low-molecular-weight organic molecules. Since the organic fibrous materials as templates for the plating are composed of chained intermolecular hydrogen bonds, self-assembly and disassembly of the resulting supramolecular materials can be controlled easily by adjusting pH and temperature conditions in media dispersing the microfibers. These novel procedures will play important roles for the preparation of advanced materials for electronics and optics as environmentally benign procedures from industrial standpoints.

Nickel electroless plating to obtain a nickel layer exhibiting high electrical conductivity is usually performed at temperatures around 70 °C. Copper electroless plating is carried out at strong alkaline solutions in industry. The morphology of fibrous materials formed from azopyridine carboxylic acid used in this study is deteriorated in these severe pH and

temperature conditions. We are under investigation to look for more chemically and thermally stable fibrous templates from a series of azopyridine carboxylic acids that endure severe fabrication conditions for these electroless plating.

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