Preparation of Copper Tubes with a Submicron Pore

Daisuke Ishii, Masaru Nakagawa*, Takahiro Seki[†] and Tomokazu Iyoda
Chemical Resources Laboratory, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
Fax: +81-45-924-5247, e-mail: mnakagaw@res.titech.ac.jp
[†]Department of Applied Chemistry, Graduate School of Engineering, Nagoya University,
Chikusa, Nagoya 464-8603, Japan

We demonstrated a novel method for the fabrication of copper submicron tubes by the template-based synthesis using an amphoteric organic compound of azopyridine carboxylic acid. The amphoteric compound with a pyridyl group and a carboxy group, which is soluble in alkaline aqueous solutions due to dissociation of the carboxy group, was organized by neutralization to allow the growth of hydrogen-bonded supramolecular fibrous assemblages with about 500 nm in diameter. Thus obtained submicron fibers were available as templates of nickel-assisted copper electroless plating under a weak alkaline condition. The characteristics of copper tubes after removal of the template by immersion in alkaline solutions were investigated with regard to their chemical composition and morphology by inductively coupled plasma spectrometry (ICP), energy dispersive X-ray (EDX) analysis, X-ray diffraction (XRD) analysis and scanning electron microscope (SEM) observation.
Key words: self-organization, submicron tube, electroless plating, copper, hydrogen bond

1. INTRODUCTION

Metal tubes possessing submicron-sized pores are promising materials applicable to chemical adsorbents and catalysts due to their large surface area and their easy handling. Compared with electroplating, electroless plating is a suitable method to fabricate such tubular materials, because the electroless plating based on autocatalytic reactions in an aqueous solution is available to any kinds of matters regardless of their conductivity and shapes. Therefore, metal tubes have been fabricated by the template-synthesis through the electroless plating. First, organic or inorganic fibers used as templates are prepared by spinning polymers [1] or self-organizing rod-like molecular assemblages from surfactants [2]. Secondly, the templates are coated through electroless plating to form metallized hybrid materials. Finally, the templates are removed by thermal calcination or extraction to dissolve the templates, and the metal tubes were obtained.

Polymer fibers are more readily available than glass fibers because of lowering temperature on their processing by spinning. However, it is difficult to obtain micro-fibers smaller than 10 µm in diameter. In the case of using rod-like micells formed from surfactants, the shape of micells is significantly affected by additives during a plating procedure. Moreover, the removal of organic templates such as polymers and rod-shaped micells by an oxidative burning procedure is accompanied with the emission of carbon dioxide which causes a greenhouse effect. It is more desirable from a standpoint of saving energy and environmental benignity that the metal tubes with a submicron pore could be obtained without a heating procedure in both cases of the preparation and removal of fibrous templates.

Our group has recently proposed the use of hydrogen-bonded materials composed of amphoteric azopyridine carboxylic acids, indicated in Figure 1, as fibrous templates [3]. The amphoteric compounds are soluble in alkaline aqueous solutions due to cleavage of
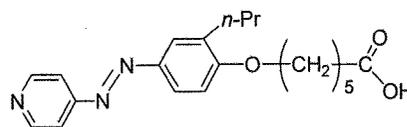
Figure 1. Chemical structure of *p*-APC.

intermolecular hydrogen bonds arising from dissociation of carboxy moiety. When the aqueous solution containing the compounds is neutralized by acidic substances, ionized amphoteric compounds are reorganized by the formation of intermolecular hydrogen bonds, to give supramolecular polymeric fibers with a submicron size in diameter. We demonstrated that nickel tubes are successfully obtained by nickel electroless plating using the hydrogen-bonded supramolecular templates and then facile removal of the amphoteric templates with an alkaline aqueous solution [4]. This method has two distinctive advantages as follows: (1) The fibrous shapes of templates are scarcely affected after immersion in the nickel plating solution. (2) The fibrous templates can be prepared and removed without heating procedures.

In this study, we attempt to fabricate the copper tubes by the template-synthesis using the amphoteric compound. Copper electroless plating is usually carried out with formaldehyde as a reducing reagent at high temperature over pH 12. Such a common copper plating method is unusable because the fibrous shapes formed from the amphoteric compounds could not be maintained under severe conditions. We report here that the copper tubes could be prepared by nickel-assisted copper electroless plating. The method to fabricate copper tubes and their characteristics examined by ICP, EDX, XRD and SEM are described.

2. EXPERIMENT

2.1 Preparation of hydrogen-bonded fibrous templates

Hydrogen-bonded fibrous templates used in electroless plating were prepared in a similar manner described in our previous paper [5]. The amphoteric compound of 6-[2-propyl-4-(4-pyridylazo)phenoxyl] hexanoic acid (*p*-APC) [3], indicated in Figure 1, was dissolved in an aqueous solution containing NaOH of 3.0 x 10^{-3} mol dm^{-3}, to prepare a transparent yellow solution containing *p*-APC of 1.0 x 10^{-3} mol dm^{-3}. The solution was placed in a vial, which was capped with an aluminium foil with small holes to contact with air and kept standing for several days under air to allow spontaneous formation of *p*-APC fibers.

2.2 Fabrication of copper tubes

The catalyzation of *p*-APC fibers for copper electroless plating was performed in a single-step activation. An aqueous solution of 1.0 x 10^{-3} mol dm^{-3} PdCl$_2$ was prepared and subjected to centrifugal separation at 2000 rpm for 5 minutes. A supernatant solution was used as a catalyzation solution for copper plating. The obtained *p*-APC fibers were filtered with a PTFE membrane filter of 1.0 μm pore size. The filtered fibers were rinsed with deionized water thoroughly and treated with the catalyzation solution containing PdCl$_2$ for 24 hours. Catalyzed fibers were filtered with a PTFE membrane filter, followed by a rinse with deionized water. The catalyzed fibers were immersed in a copper electroless plating bath at 30 °C for 24 hours, and then copper-coated hybrid fibers were filtered with a PTFE membrane filter. A chemical composition of the copper plating bath was summarized in Table 1. After removal of the plating bath by filteration and multiple rinses with deionized water, the copper-coated fibers were immersed in an alkaline aqueous solution containing 1.0 mol dm^{-3} NaOH for 24 hours, to dissolve the hydrogen-bonded fibrous templates. After multiple rinses with deionized water until no *p*-APC could be detected, copper tubes were collected by filteration.

Table 1. Chemical composition of copper plating bath.

Reagent	Concentration (mol dm^{-3})
CuSO$_4$·5H$_2$O	0.024
H$_3$BO$_3$	0.5
sodium citrate	0.052
NaH$_2$PO$_2$·H$_2$O	0.27
NiSO$_4$·6H$_2$O	0.002
pH at 30°C (adjusted by NaOH)	8.5
bath temperature	30°C

2.3 Physical measurements

SEM and EDX measurements were carried out with a Hitachi S-3000N natural-SEM. SEM images of copper tubes were observed with a Hitachi S-800 FE-SEM. Chemical composition of copper tubes was determined with a Shimadzu ICPS-8100. X-ray diffraction was measured by a Phillips PW-3050.
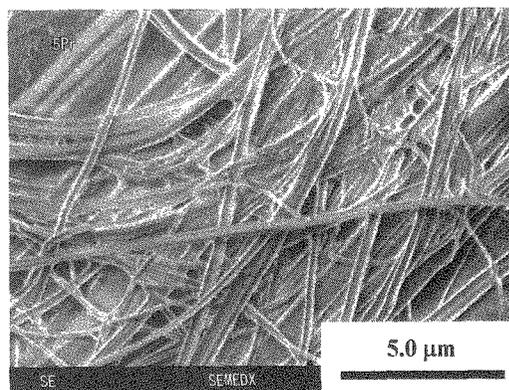
Figure 2. Natural-SEM image of *p*-APC fibers.

3. RESULTS AND DISCUSSION

3.1 Catalyzation of hydrogen-bonded fibers

When an aqueous alkaline solution of *p*-APC was left to stand for several days under air condition, the yellow solution was changed to a yellow suspension. Neutralization of the alkaline solution with carbon dioxide included in air causes the formation of a chain of intermolecular hydrogen bonds between pyridyl and carboxyl groups of *p*-APC [5]. Figure 2 shows a natural-SEM image of the suspended materials formed from *p*-APC. It was found that *p*-APC was self-organized into well-defined fibers of approximately 500 nm in diameter. Each submicro-fiber was not in an aggregated state, but in a dispersed state. Thus obtained *p*-APC submicron fibers were completely soluble in acidic aqueous solutions below pH 1 and in alkaline solutions over pH 12 [4]. Even in a neutral solution, the submicron fibers were decomposed into molecular species at a boiling point of water and under high ionic strength [3]. Therefore, it is necessary to find suitable conditions of pH, temperature and ionic strength in both catalyzation and plating processes characteristic of the hydrogen-bonded fibrous templates.

At first, we attempted two catalyzation methods using the tin-palladium (Sn-Pd) catalyst via a single-step approach [6] and the sensitizer-accelerator (SnCl$_2$-PdCl$_2$) catalyst via a two-step approach [7], in which the treatment with a SnCl$_2$ solution was followed by that of a PdCl$_2$ solution. After these catalyzation procedures were performed, copper electroless plating of *p*-APC submicron fibers was carried out by using several copper plating baths with different chemical compositions. However, SEM observation revealed that no copper-coated fiber was formed, although a lot of metal grains were formed.

We attempted the other catalyzation method reported by Yoshiki et al. [8]. They demonstrated that copper could be plated on an etched ZnO substrate by using only an aqueous solution of PdCl$_2$. When *p*-APC fibers were immersed in an acidic solution of 1.0 x 10^{-3} mol dm^{-3} PdCl$_2$ for 24 h, the initial yellow color of *p*-APC fibers turned to darken yellow. Then, the fibers were further immersed in copper electroless plating bath with a chemical composition containing a small amount of NiSO$_4$ as summarized in Table 1. It was found that
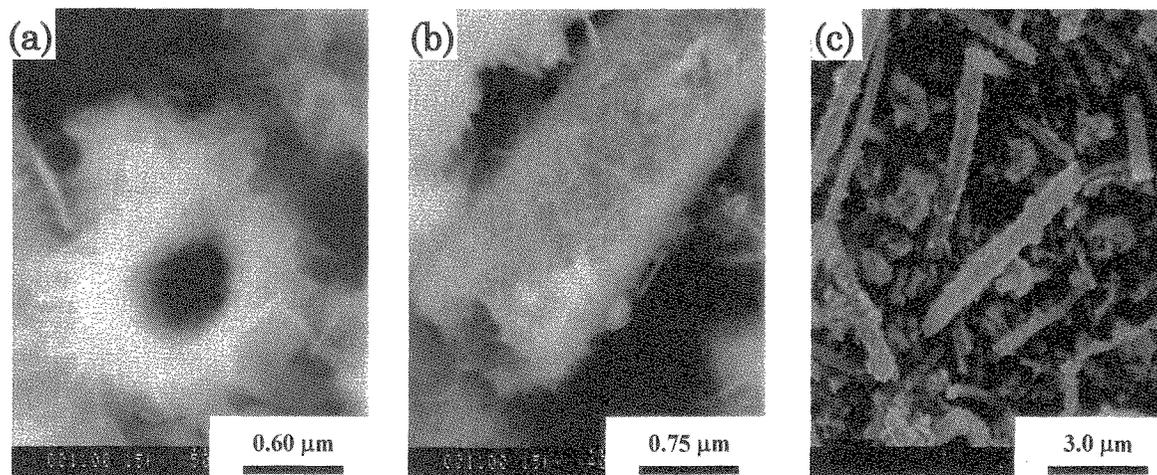
Figure 3.   FE-SEM images of copper tubes meda of p-APC fibrous templates.   (a) Cross section of copper tubes. (b) Side section of copper tubes.   (c) Cross and side sections of copper tubes under low magnification.

copper plating occurred as the fibrous morphology was maintained.   Thus plated fibers had a lot of metal grains.   The metal grains could be removed from copper-coated fibers by using a supernatant PdCl$_2$ solution after configuration as a catalyzation solution.

3.2 Copper-coating mechanism of p-APC fibers

The copper electroless plating of hydrogen-bonded p-APC submicron fibers was induced by the treatment of a supernatant PdCl$_2$ solution, followed by the immersion in a plating bath containing a small amount of NiSO$_4$. In the former catalyzation methods using either the Sn-Pd catalyst or the SnCl$_2$-PdCl$_2$ catalyst, it is well known that Pd^{2+} ions are reduced to Pd$^{(0)}$ by Sn^{2+} ions, then Pd$^{(0)}$ works as a catalytic center of electroless plating. However, Sn^{2+} ions as reducing reagents were not used at all in the latter catalyzation method using a PdCl$_2$ solutions.   According to the discussion reported by Yoshiki et al. [8], it is anticipated that Pd^{2+} ions chemically adsorbed on surfaces of the hydrogen-bonded p-APC submicron fibers were reduced to activated Pd$^{(0)}$ species by NaH$_2$PO$_2$ which is also a reducing reagent included in the copper electroless plating bath.   Taking the chemical structure of p-APC into consideration, carboxy and/or pyridyl groups located at a surface of the p-APC fibers might act as coordination sites of Pd^{2+} ions.   This speculation is under investigation by XPS measurements.

It is anticipated that the following reactions occurred in the copper plating process, assuming that Pd^{2+} ions were initially adsorbed on the hydrogen-bonded p-APC fibers.

$$Pd^{2+} + 2H_2PO_2^- + 2OH^- \rightarrow Pd^{(0)} + 2H_2PO_3^- +H_2 \quad (1)$$
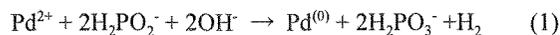
At first, the reduction of Pd^{2+} ions adsorbed on a surface of the p-APC fibers by H$_2$PO$_2^-$ causes the formation of Pd$^{(0)}$ catalytic centers for nickel electroless plating.

$$Ni^{2+} + 2H_2PO_2^- + 2OH^- \rightarrow Ni^{(0)} + 2H_2PO_3^- +H_2 \quad (2)$$
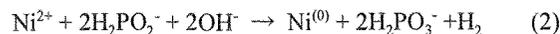
Secondly, the Pd$^{(0)}$ catalysts bring about the deposition of Ni metal from Ni^{2+} ions.

$$Ni^{(0)} + Cu^{2+} \rightarrow Ni^{2+} + Cu^{(0)} \quad (3)$$
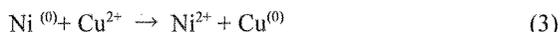
Thirdly, Cu^{2+} ions are reduced to Cu$^{(0)}$ metal by Ni$^{(0)}$ according to ionization tendency.

$$Cu^{2+} + 2H_2PO_2^- + 2OH^- \rightarrow Cu^{(0)} + 2H_2PO_3^- +H_2 \quad (4)$$
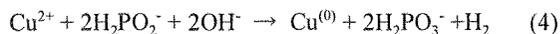
Finally, the Cu$^{(0)}$ deposition is induced one after another by a Cu$^{(0)}$ self-catalyst effect.

Under the plating condition containing no NiSO$_4$, copper coating of the hydrogen-bonded p-APC fibers was unsuccessful.   This result clearly indicated that nickel-assisted copper electroless plating took place in the plating process.

3.3 Preparation and characterization of copper tubes

The copper-coated hydrogen-bonded fibrous templates were immersed in an aqueous NaOH solution of pH 12 to remove the p-APC template fibers.   As soon as the copper-coated fibers were immersed in the alkaline solution, the color of aqueous solution turned to yellow.   This indicates that the hydrogen-bonded p-APC fibers were dissolved due to disassembly of intermolecular hydrogen bonds forming supramolecular polymers.

Figure 3 shows FE-SEM images of copper tubes obtained after the treatment with the alkaline solution. We found that copper submicron tubes were formed though our preparation method.   The copper tubes were composed of tangled needle-like materials.   An inner diameter of the copper tubes was approximately 500 nm, which was well consistent with the diameter of p-APC submicron fibers used as templates (see Figure 2).   The copper tubes tended to undergo a charge-up effect during the SEM observation, implying that the copper tube is less electroconductive than copper metal in a crystalline state.

The whole and local parts of chemical compositions of the copper tubes were investigated by ICP and EDX

Table 2. Composition ratio of copper tubes by ICP analysis. (unit: wt%)

Cu-Concn.	Ni-Concn.	Pd-Concn.	P-Concn.
95.0	2.5	1.7	0.4

Table 3. Composition ratio of (a) copper tubes and (b) metal grains by EDX analysis. (unit: wt%)

	Cu-Concn.	Ni-Concn.	Pd-Concn.	P-Concn.
a	97.1	1.8	1.0	0.1
b	91.3	3.3	5.0	0.3

analyses, respectively. The ICP and EDX results were summarized in Tables 2 and 3. The ICP analysis revealed that the copper tubes were composed from copper (Cu) of 95 %, palladium (Pd) of about 2% as a primary catalyst, nickel (Ni) of about 2 % as a secondary catalyst, and a trace amount of phosphorus (P). This result was well consistent with the chemical composition of copper tubes as indicated in Table 3(a). However, different chemical compositions were observed when the local part of spherical grains adsorbed on a surface of copper tubes was examined by EDX (Table 3(b)). An excess amount of palladium was contained in the grain materials, in comparison with the copper tubes.

Crystal structures of the copper tubes prepared by this copper electroless plating were investigated by XRD measurement. A broad peak was observed mainly in the range of $8° < 2\theta < 90°$, with small peaks at $2\theta = 33.6, 35.3, 38.4, 48.8, 62.8$ and $66.8°$ (data not shown). These diffraction peaks were not ascribed to a general crystalline phase of copper metal, appearing at $2\theta = 43.5, 51.5, 74.0,$ and $90.0°$ [9]. This result also indicates that thus obtained copper tubes are in a different state from crystalline copper metal.

4. CONCLUSION

We described here that novel copper tubes with a submicron pore were obtainable through the template-synthesis using a hydrogen-bonded fibrous material as a template for electroless plating. It was found that nickel-assisted copper electroless plating with $PdCl_2$ was suitable for the plating process under the mild condition without deterioration of supramolecular fibrous templates. It is anticipated that the copper submicron tubes with a rough surface morphology exhibit high adsorption ability toward gas and high catalytic activity for chemical synthesis. Moreover, the copper tubes will be applicable as templates for the fabrication of novel submicron tubes of the other metals such as Au, Pd, Pt and forth, by further electroless plating and electroplating.

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