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Morphology Control of Hollow Ni-P Microfibers

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In our previous paper [*Trans. Mater. Res, Soc. Jpn.* **29**, 889 (2004)], we demonstrated that the macroscopic morphologies of hydrogen-bonded fibrous molecular assemblages formed from 6-[2-propyl-4-(4-pyridylazo)phenoxy]hexanoic acid could be controlled by four kinds of self-assembling methods. The four methods were categorized into (i) air neutralization, (ii) CO_2 neutralization, (iii) crystal growth, and (iv) air neutralization with anionic surfactant. In this paper, we investigated the shapes of hollow Ni-P microfibers obtained through electroless plating from the four types of fibrous template materials. The following results were obtained. The inner diameter (500 nm) of the hollow Ni-P microfibers was almost identical to the outer diameter of the organic template microfibers prepared by (i) air neutralization. The Ni-P nanotubes having an outer diameter of 70 – 130 nm were formed using the template fibers prepared by (ii) CO_2 neutralization. The hollow Ni-P microfibers having a range of 1 – 2 μm in inner diameter were obtained from the template fibers by (iii) crystal growth. Ni-P nanotubes with rough surfaces were successfully obtained from template microfibers prepared by (iv) air neutralization with anionic surfactant of sodium dodecyl sulfate. We demonstrated that several types of hollow Ni-P microfibers with different morphology could be fabricated from one amphoteric compound. The formation mechanisms were proposed.

Key words: template synthesis, metal, microfiber, nanofibril, morphology, self-assembly

1. INTRODUCTION

The hollow metallic microfibers have attracted attention in resent year because of their potential applications. The number of articles on the metallic tubes having an interior diameter from nanometer to micrometer has rapidly increased.[1] For example, in the case of using the hollow metallic fibers as composite fillers, there are some advantages of light weight, component material saving, and cost reduction over usual metallic fibers.[2]

We have reported that nickel-phosphorus (Ni-P)[3] and copper[4] hollow microfibers could be prepared through electroless plating of hydrogen-bonded fibrous molecular assemblage[5] as an organic template fiber. There are some advantages in the fabrication process. First, no pyrolysis process is included to cause CO_2 emission. Secondly, all of three processes consisting of template fabrication, electroless plating and template removal can be carried out in environment-friendly water systems. Thirdly, the hydrogen-bonded fibrous molecular assemblage is recyclable with a recovery of 70 ~ 80 %, because the template fabrication and removal are based on formation and dissociation of reversible hydrogen bonds composing the molecular assemblage.[6] Moreover, it is found that macroscopic organized morphologies of fibrous molecular assemblages such as diameter and entire shape can be controlled by slightly varying chemical structure of azopyridine carboxylic acids. Consequently, we can prepare rod-like or twisted hollow Ni-P microfibers having an interior diameter of 100, 500, 1000 nm through precise transcription.[6]

As another method for controlling the macroscopic morphology instead of the chemical structure alteration, we investigate the dependence of self-assembling conditions on macroscopic organized morphology formed from one amphoteric azopyridne carboxylic acid of 6-[2-propyl-4-(4-pyridylazo)phenoxy]hexanoic acid. In addition to neutralization of azopyridine carboxylate in an alkaline solution by acidic substances in air, we attempt three methods of the CO_2 neutralization method, the crystal growth method, and the air neutralization method with anionic surfactant of sodium dodecyl sulfate. The fibrous molecular assemblages having an average diameter of 100 nm, 500 nm, and 1 – 2 μm can be prepared separately from the amphoteric compound.[7]

In this paper, we demonstrated that morphology-controlled Ni-P hollow microfibers could be prepared by electroless plating using the morphology-tunable fibrous molecular assemblages made from one amphoteric compound of 6-[2-propyl-4-(4-pyridylazo)phenoxy]-hexanoic acid under different self-assembling conditions. The morphologies of hollow Ni-P microfibers were observed by scanning electron microscopy and transmission electron microscopy.

2. EXPERIMENT

2-1. Materials

6-(2-Propyl-4-(4-pyridylazo)phenoxy)hexanoic acid (Pr-APC) was prepared according to our previous paper.[8] Other regents were purchased from Kanto Chemicals, Ltd. and used as received. Deionized water was used after purification through a Mili-Q system.

2-2. Preparation of fibrous molecular assemblages as templates

Preparation of morphology-controlled fibrous molecular assemblages formed from Pr-APC under different self-assembling conditions was described in our previous report[7] in detail. Here, the self-assembling methods categorized into four methods are described briefly. The four methods consist of (i) the air neutralization method, (ii) the CO_2 neutralization method, (iii) the crystal growth method, and (iv) the SDS-containing air neutralization method.

(i) Air neutralization method: The amphoteric compound of Pr-APC was dissolved in a 3.0 mmol dm^{-3} NaOH aqueous solution to prepare a transparent solution containing 1.0 mmol dm^{-3} Pr-APC. The alkaline aqueous solution was stirred with a magnetic stirrer at room temperature under an air atmosphere for 48 h. Fibrous molecular assemblage of Pr-APC formed in the solution was used as a fibrous template material prepared by the air neutralization method.

(ii) CO_2 neutralization method: The alkaline aqueous solution containing 1.0 mmol dm^{-3} Pr-APC and 3.0 mmol dm^{-3} NaOH was stirred with a magnetic stirrer at room temperature for 1 h under an atmosphere of CO_2 gas injected from a bomb containing liquid CO_2. Fibrous molecular assemblage formed in the solution was abbreviated as a fibrous template material prepared by the CO_2 neutralization method.

(iii) Crystal growth method: To an aqueous solution (300 ml) containing the fibrous template material prepared by the air neutralization method was added 150 μl of a 1.0 mmol dm^{-3} NaOH aqueous solution so as to dissolve surfaces of the fibrous template material. The alkaline solution was stirred with a magnetic stirrer under an air atmosphere for 48 h. Thus obtained fibrous aggregate was abbreviated as a fibrous template material prepared by the crystal growth method.

(iv) SDS-containing air neutralization method: An alkaline aqueous solution containing 16.2 mmol dm^{-3} sodium dodecyl sulfate (SDS), 1.0 mmol dm^{-3} Pr-APC and 3.0 mmol dm^{-3} NaOH was stirred by a magnetic stirrer at room temperature under an air atmosphere for 72 h. Thus obtained fibrous molecular assemblage was used as a fibrous template material prepared by the SDS-containing air neutralization method.

2-3. Preparation of Ni-P hollow microfibers

The fibrous template materials dispersed in each aqueous solution were filtered and washed with deionized water. The organic fibrous template materials were immersed in an acidic aqueous solution containing 1.0 mmol dm^{-3} $PdCl_2$ for 24 h. After filtration, catalyzed fibrous template materials were immersed for 24 h in a nickel-phosphorus (Ni-P) electroless plating bath containing 0.05 mol dm^{-3} $Ni(H_2PO_2)_2$ $6H_2O$, 0.19 mol dm^{-3} H_3BO_3, 0.03 mol dm^{-3} CH_3COONa and 9.8 mmol dm^{-3} $(NH_4)_2SO_4$. Ni-P-coated fibrous template materials were filtered, washed with deionized water, and immersed in a 1.0 mol dm^{-3} NaOH aqueous solution for 24 h to dissolve the organic template materials formed from Pr-APC. Ni-P hollow microfibers were collected by filtration, washed with deionized water, and dried under a reduced pressure at 60 °C for 24 h. Ni-P hollow microfibers were obtained in a powder state.

2-4. Morphology observation

The morphology of the Ni-P hollow microfibers were observed by a Hitachi S-3000N scanning electron microscope (SEM) in a secondary electron mode. Transmission electron microscope (TEM) images and electron diffraction (ED) patterns were taken on a Hitachi H-7100 TEM operated at an accelerating voltage of 100 kV.

3. RESULTS AND DISCUSSION

3-1. Hollow Ni-P microfibers having an inner diameter of 500 nm prepared by (i) the air neutralization method

In the case of (i) the air neutralization method, an organic fibrous template material having an average outer diameter of 500 nm is formed from the amphoteric compound Pr-APC.[8] When the fibrous template material was used, Ni-P hollow microfibers with an average inner diameter of 500 nm and a Ni-P wall thickness of 70 – 90 nm could be obtained as reported in our previous paper.[6] It was worthy of note that the inner diameter of hollow Ni-P microfibers as shown in Fig. 1 was very consistent with the outer diameter of template fibers. It was found that the fibrous material prepared by the air neutralization method was available for the template-directed synthesis of hollow Ni-P microfibers by electroless plating.

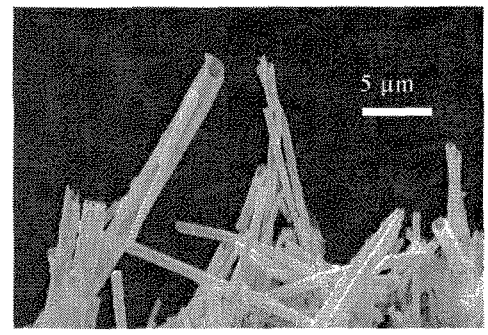

Figure 1. SEM image of Ni-P hollow microfibers fabricated by electroless plating using a fibrous template material prepared under an air atmosphere.

3-2. Hollow Ni-P microfibers having an outer diameter of 70 – 130 nm prepared by (ii) the CO_2 neutralization method

Parts (a) and (b) of Fig. 2 show the SEM image of a fibrous template material prepared by (ii) the CO_2 neutralization method and the SEM image of the Ni-P microfibers, respectively. The outer diameter of the fibrous template material was about 500 nm, which was identical to that of the fibrous material prepared by (i) the air neutralization method. However, the outer diameter of the hollow Ni-P microfibers was in the range of 70 – 130 nm and was significantly smaller than the outer diameter of the fibrous template material.

When the fibrous template material was not used for electroless plating, Ni-P aggregated spheres were only obtained. Taking account of the fact, it was no wonder that the fibrous template material was useful for the formation of the Ni-P nanotubes.

In our previous report,[7] XRD measurements revealed that the fibrous template material prepared by (ii) the CO_2 neutralization method was amorphous, while the fibrous template material prepared by (i) the air neutralization method was crystalline. Rapid growth of the fibrous molecular assemblage by neutralization under a CO_2 atmosphere probably causes the fibrous material composed of hydrogen-bonded supramolecular polymers to become amorphous. X-ray photoelectron spectral analyses indicate that Pd^{2+} species in a $PdCl_2$ aqueous solution is adsorbed through coordination to the surface pyridyl group of the fibrous material in the catalyzation process.[6] Taking the facts into consideration, it was anticipated that the Pd^{2+} species might penetrate into the amorphous fibrous material and dissolve its surfaces more than the crystalline fibrous material. As a result, the outer diameter of the template core would be reduced and the Ni-P microfibers having an outer diameter of 70 – 130 nm would be formed. Consequently, it was found that the fibrous template material prepared by (ii) the CO_2 neutralization method was not useful for the template-directed synthesis of hollow Ni-P microfibers, but useful for preparation of Ni-P nanotubes.

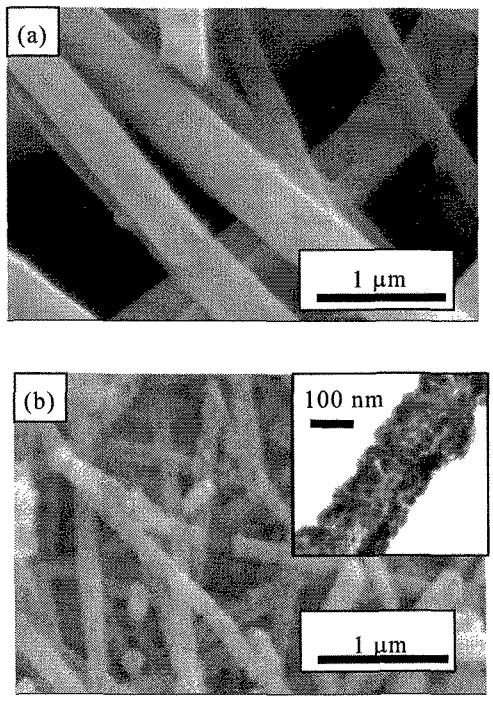

Figure 2. (a) SEM image of a fibrous template material prepared by (ii) the CO_2 neutralization method. (b) SEM image of Ni-P microfibers fabricated by the fibrous template material. The inset of Fig 2(b) is the TEM image of a Ni-P nanotube.

3-3. Hollow Ni-P microfibers having an inner diameter of 1 – 2 μm prepared by (iii) the crystal growth method

It is well known that a large organic single crystal suitable for X-ray crystallography is obtainable by partial dissolution and subsequent growth of small single crystals. In a similar manner, the outer diameter of the fibrous template material can be enlarged step-by-step. An original fibrous template material prepared by (i) the air neutralization method has an average diameter of 500 nm. Once the crystal growth method is applied to the fibrous material, the fibrous molecular assemblage of Pr-APC with an outer diameter of 1 - 3 μm is obtained.[7] We attempted to fabricate hollow Ni-P microfibers with a micron pore by using the large fibrous molecular assemblage as a template.

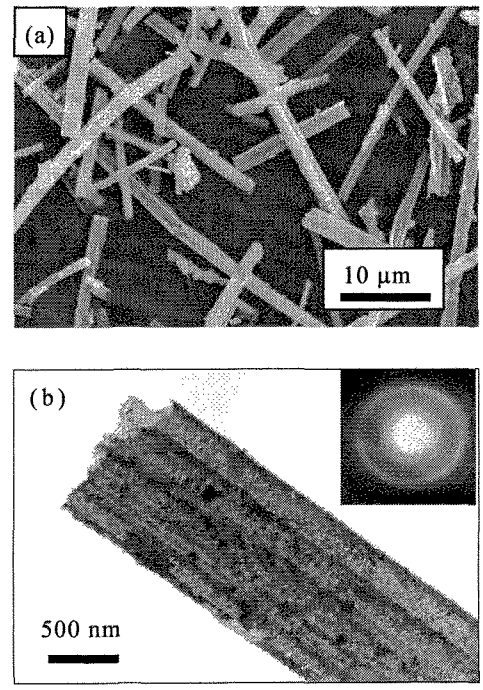

Figure 3. (a) SEM image and (b) TEM image of hollow Ni-P microfibers obtained from fibrous template material prepared by (iii) the crystal growth method. The inset of Fig. 3(b) indicates the electron diffraction pattern of the hollow Ni-P microfibers.

Figure 3(a) indicates the SEM image of Ni-P hollow microfibers obtained from the fibrous template material prepared by (iii) the crystal growth method. The width of the hollow Ni-P microfibers was 1 – 3 μm, which was almost consistent with the outer diameter of the fibrous template material. As seen in Fig. 3(b) indicating the TEM image, the hollow Ni-P microfibers were composed of Ni-P nanoparticles having a diameter of 10 - 20 nm. The thickness of the Ni-P wall was found to be 40 – 60 nm. The Ni-P nanoparticles were amorphous as shown in the inset of Fig. 3(b) indicating the electron diffraction pattern. It was found that the fibrous template material prepared by (iii) the crystal growth method was suitable for the template-directed synthesis of hollow Ni-P microfibers with a large pore.

3-4. Hollow Ni-P microfibers having an outer diameter of 100 – 300 nm prepared by (iv) the SDS-containing air neutralization method

Fine fibrous molecular assemblage with an outer diameter of 100 – 300 nm is obtained by neutralization under an air atmosphere from an aqueous alkaline solution of Pr-APC and sodium dodecyl sulfate (SDS).[7] Up to date, this SDS-containing air neutralization method is an only method for preparing the finest fibrous molecular assemblage from the amphoteric compound Pr-APC. We attempted to fabricate hollow Ni-P microfibers with a small pore below 500 nm using the Pr-APC fibers as templates.

Figure 4(a) shows the SEM image of Ni-P microfibers made from the fibrous template material prepared by (iv) the SDS-containing air neutralization method. The outer diameter of the hollow Ni-P microfibers was in the range of 100 – 300 nm, which was almost identical to the outer diameter of the fibrous template material. A notable morphology was observed for the hollow Ni-P microfibers. The microfibers were composed of fibrils with a width of about 4 nm as show in Fig. 4(b).

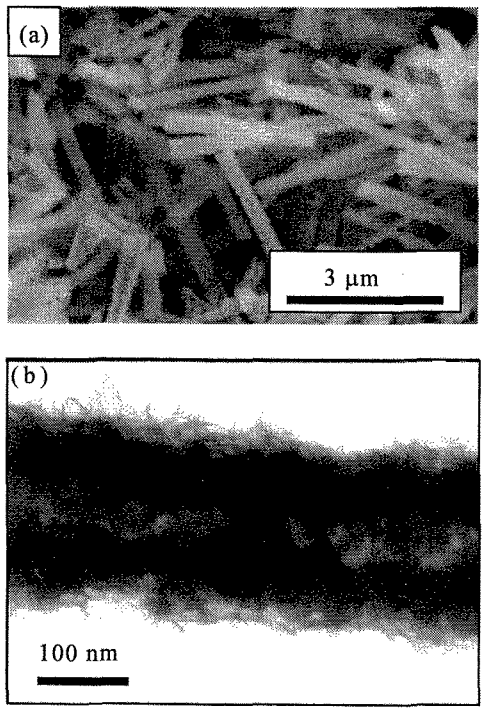

Figure 4. (a) SEM image of Ni-P microfibers prepared by (iv) the SDS-containing air neutralization method and (b) TEM image of a Ni-P microfiber composed of 4 nm nanofibrils.

Kijima et al. have reported that silver nanotubes with inner diameter of 4 nm can be fabricated by a template-directed synthesis using rod-like micelles formed from SDS as templates.[9] Their result indicates that the outer diameter of the SDS rod-like micelles is about 4 nm. Taking account of the fact, it was anticipated that the Ni-P microfibers composed of nanofibrils would be formed in the following mechanism. The fibrous template material prepared by (iv) the SDS-containing air neutralization method might contain partially SDS rod-like micelles. The assumption was supported by the fact that it was difficult to remove SDS from the fibrous template material by multiple rinses with a copious amount of deionized water. By washing the fibrous material with deionized water, SDS molecules are removed from the SDS/Pr-APC hybrid template fibers. As a result, the template fibers become porous at a nanometer scale. In the catalyzation process using a $PdCl_2$ aqueous solution, Pd^{2+} species is adsorbed in the nanoporous structure. Ni-P nanofibrils might be formed by electroless plating. The plausible formation mechanism of the Ni-P nanofibrils will be confirmed by atomic force microscope (AFM) observation of the fibrous template material after multiple rinses with deionized water. The formation of the nanoporous structure is under investigation in detail. Consequently, nanofibril-coated Ni-P tubes were could be prepared with the fibrous template material prepared by (iv) SDS-containing air neutralization method.

4. CONCLUSION

In this study, we demonstrated that hollow Ni-P microfibers with different morphologies could be obtained through electroless plating of morphology-tunable hydrogen-bonded fibrous molecular aggregates formed from one amphoteric compound. It was found that template-directed syntheses of the hollow Ni-P microfibers were successfully performed using the fibrous template materials prepared by (i) the air neutralization method and (iii) the crystal growth method. The inner diameter of Ni-P tubes was almost consistent with the outer diameter of the fibrous template materials. Because the Ni-P microfibers contain magnetic metal of nickel, the magnetic property will be interesting.

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