Controlled Growth of Composite Nanowires Based on Coating Ni on Carbon Nanotubes by Electrochemical Deposition Method

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A novel electrochemical deposition method has been used for coating Ni onto well-aligned multiwall carbon nanotubes. Both synthesis of carbon nanotubes and deposition of Ni are processed in porous anodic aluminum oxide (AAO) templates. The design of the AAO pores allows us easily to control the size of nanotubes and the thickness of the Ni coating. Without any surface treatment to the carbon nanotubes, a continuous and smooth Ni layer is achieved.

Introduction

Since the discovery of carbon nanotubes by Iijima in 1991,[1] these one-dimensional and hollow nanomaterials are attracting increasing scientific and technological interest for their excellent properties. The morphology and size of carbon nanotubes suggest that they provide a possibility for creating nanowires or tubular structures by coating metals on their surfaces.[2] In past years the electroless plating method has been mainly used to acquire these metal−carbon nanotube composites.[2−6] But this method is limited by the wetting of carbon nanotubes. That means, if carbon nanotubes are coated with typical pure metals, it is difficult to form a continuous coating layer without any surface treatment.[7] To confine the thickness of coating layer is also a problem.

In this paper we will present a novel electrochemical deposition method to coat nanotubes with metal Ni. Both synthesis of nanotubes and deposition of Ni particles are processed in porous anodic aluminum oxide templates (AAO) as to which a continuous and thickness controlled Ni layer can be formed on the surface of well-aligned nanotubes without any surface treatment.

Experimental Section

The route of preparation is shown in Figure 1, and is described as follows. (I) Carbon nanotubes grow in the AAO pores with 60 nm in diameter by CVD.[8] After the template is placed in a tube furnace, ethylene is pyrolyzed to form CNTs by flowing a mixture of ethylene (15 sccm) and Ar (75 sccm) at 988 K for 1 h. Annealing for 15 h in Ar is done at the same temperature to graphitize CNTs further. It is emphasized that a thin barrier layer of 40 nm in AAO is necessary in our experiments. This barrier layer made the pores not through an AAO template as used, and consequently one end in the synthesized CNTs adjacent to the barrier layer is closed. (II) The pores of the template are widened by dipping into an aqueous mixture of phosphoric solution at 303 K for 20−40 min, while the barrier
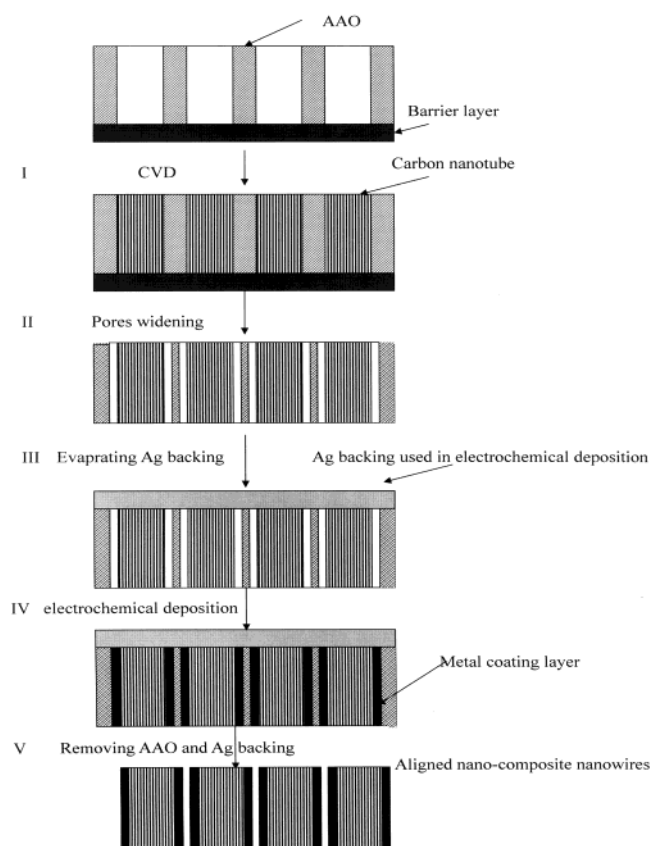

Figure 1. Scheme for the preparation of aligned and diameter-controlled composite nanowires based on coating Ni onto carbon nanotube.

layer is also dissolved out. (III) Ag backing of several hundred nanometers is evaporated on one side, and there is no barrier layer side of the surface of AAO. (IV) Ni is electrochemically deposited on nanotubes in AAO, under a constant current density of 35 mA/cm^2 for 30 min at 293−300 K. The electrolyte is 250 mL of aqueous solution dissolving 35 g of NiSO$_4$·6H2O, 2 g of NaCl, 8 g of H$_3$BO$_3$, 12 g of Na$_2$SO$_4$, and 0.02 g of laurylsodium sulfate.[9] (V) After AAO is marinated in a 10% NaOH solution for several hours, aligned nanowires are

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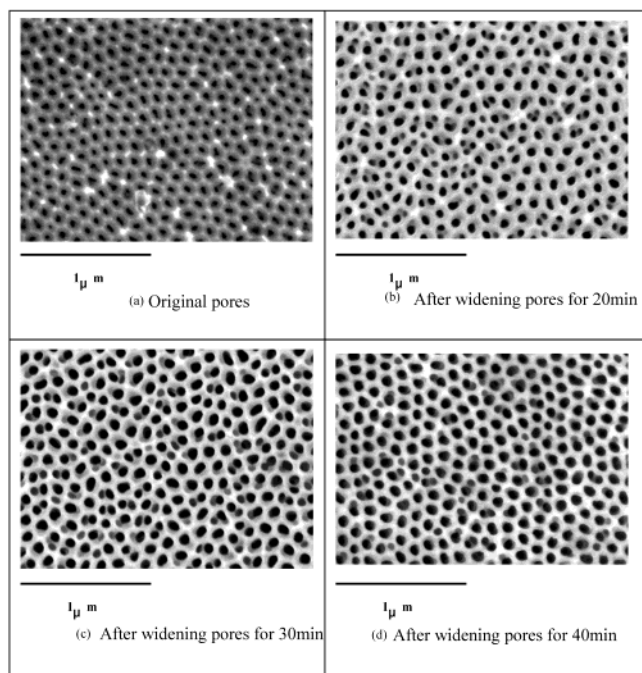† E-mail: Q.Xu@tnw.tudelft.nl.

Letters

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Figure 2. SEM images of the template after widening pores in 0.1 M H_3PO_4 at 303 K for (a) 0, (b) 20, (c) 30, and (d) 40 min, respectively.

obtained. The remaining Ag backing can be removed in the preparation of samples for observation by a transmission electron microscope (TEM). The morphology of the carbon nanotubes and composite nanowires is analyzed by a JEOL 2010F with energy dispersive spectrum (EDS). The pores of the templates are analyzed by using a scanning electron microscopy (JEOL JSM6301F).

Results and Discussion

The SEM images of templates after widening pores with different time are shown in Figure 2. The pores exhibit a hexagonal pattern and the average diameters in Figure 2a−d are respectively 60, 80, 90, and 100 nm, corresponding to the pore widening time of 0, 20, 30, and 40 min. This top view shows that pore widening rate of our templates in 0.1 M H_3PO_4 at 303 K is about 1 nm/min and it is easy to control the size of AAO pores by lengthening the time.[10]

The TEM morphology of the CNTs and composite nanowires are shown in Figure 3. The multishell CNTs and composite nanowires are both well-aligned and their diameters are about 60 and 100 nm, which equal those of the pores of AAO before and after widening, respectively. The shape of nanotubes and nanowires is close to the shape of pores. The coating layers are continuous and smooth. Most of the coating layers in our experiment are so perfect that we hardly recognize the inner carbon nanotubes until some partially covered nanotubes are found. These partially covered nanotubes, shown in Figure 3c, expose the difference between the inner and outer composite nanowires clearly. We can even find two bright lines under and along the nanowire in region A in Figure 3c, which results from the inner nannowires not being solids but tubes. The HREM analysis, shown in Figure 4, provides additional structural details of Ni deposition. The coating Ni layer on the composite nanowire fabricated by this electrochemical deposition method here is made of Ni particles with 10 nm diameters. The chemical compositions of the composite nanowire were determined by
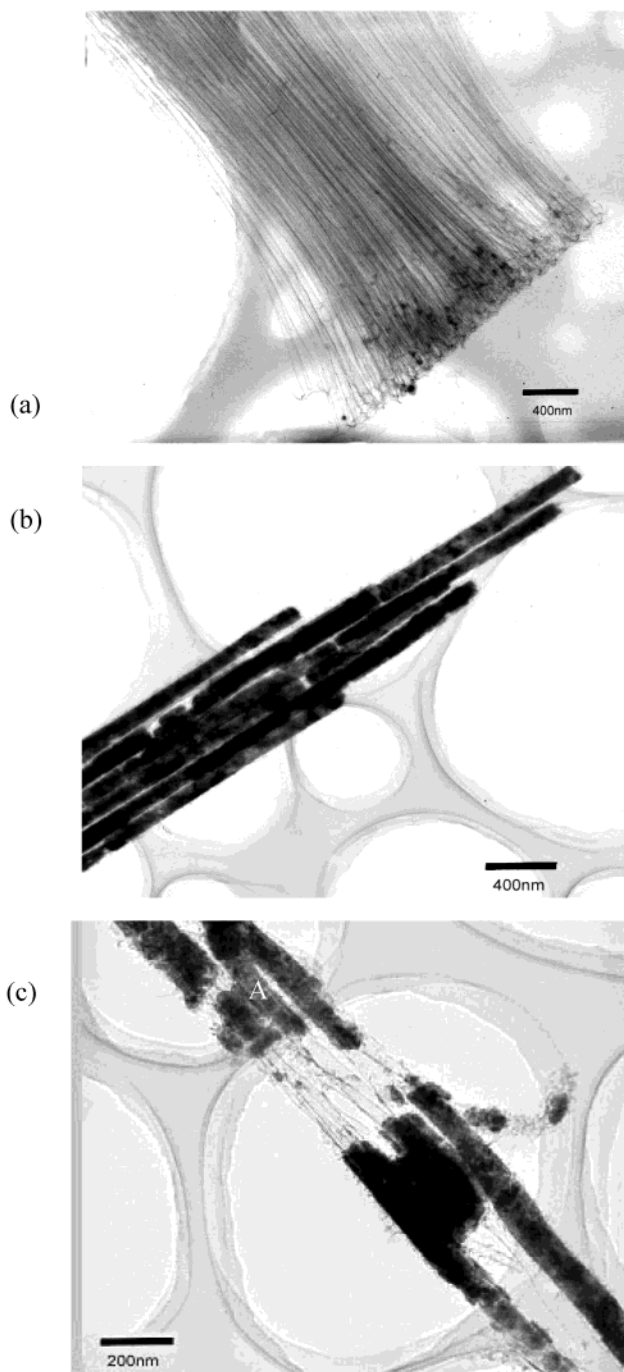

Figure 3. TEM images of (a) synsizized carbon nanotubes, (b) composite nanowires based on coating a continuous Ni layer onto carbon nanotubes, and (c) partially covered nanotubes.

using EDS in TEM. There are carbon, nickel, and copper peaks in the EDS spectrum from the composite nanowires shown in Figure 5. The Cu peak results from the Cu grid, which support the sample, and the carbon layer on the Cu grid also enhances the carbon peak higher than the Ni peak; thus the nanowires are made of carbon and nickel. Although we do not know exactly where Ni starts to deposit and nucleate, from Figure 3b we speculate every site on the surface of perfect carbon nanotubes have the same chance to electrochemically deposit Ni. Thus the continuous coating layer can be formed without any surface pretreatment of carbon nanotubes. Because the deposition is processed in the pores of the template and the diameter and length of nanowires are determined by those of the pores, the thickness of the coating layer can be controlled
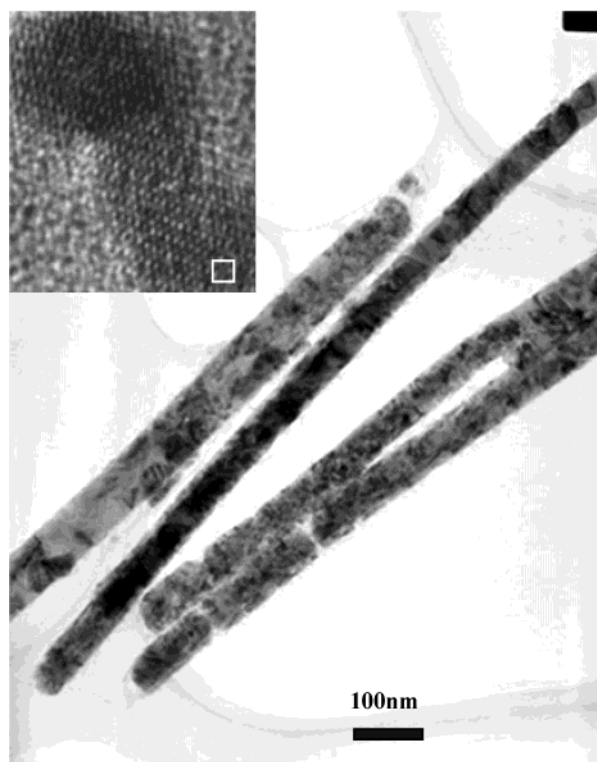
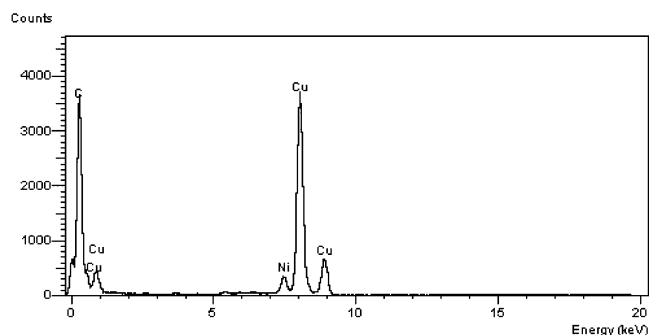**Figure 4.** HRTEM of composite nanowires.

Figure 5. EDS spectrum of composite nanowires.

effectively by changing the pore widening time. Electrochemical deposition is a common method and a lot of metals and alloys can be deposited by this method. We believe that our method may provide a new way to cover not only by Ni but also by alloys to obtain desired composite nanowires with desired size. It may be valuable to obtain some special properties for practical application.

Conclusion

A one-dimensional nanoscale composite of carbon nanotubes coated with Ni was fabricated by an electrochemical deposition method. The AAO template was used to control the size of the carbon nanotubes and composite nanowires. A continuous and smooth coating layer can be formed without any surface pretreatment. The method presented in this paper may be used to controllably synthesize a wide variety of one-dimensional composite nanowires based on coating nanotubes with metals and alloys.

References and Notes

(1) Iijima, S. *Nature* **1991**, *354*, 56.

(2) Li, Q. Q.; Fan, S. S.; Han, W. Q.; Sun, C. H.; Liang, W. J. *Jpn. J. Appl. Phys.* **1997**, *36*, L501.

(3) Ang, L. M.; Hor, T. S. A.; Xu, G. Q.; et al. *Chem. Mater.* **1999**, *11*, 2115−2118

(4) Xiaohua, Chen; Jintong, Xia; Jingcui, Peng; Wenzhu, Li; Sishen, Xie. *Composites Sci. Technol.* **2000**, *60*, 301−306.

(5) Ang, L. M.; Hor, T. S. A.; Xu, G. Q.; et al. *Carbon* **2000**, *38*, 363−372.

(6) Kong, F. Z.; Zhang, X. B.; Xiong, W. Q.; Liu, E.; Huang, W. Z.; Sun, Y. L.; Tu, J. P.; Chen, X. W. *Surf. Coating Technol.* **2002**, *155*, 33−36.

(7) Dujardin, E.; Ebbesen, T. W.; Hiura, H.; Taigaki, K. *Science* **1994**, *265*, 1850−1851.

(8) Yingjiu, Zhang; Jing, Zhu; Qi, Zhang; Yunjie, Yan; Nanlin, Wang; Xiaozhong, Zhang. *Chem. Phys. Lett.* **2000**, *317*, 504−509.

(9) Luo, J.; Zhang, L.; Zhang, Y. J.; Zhu, J. *Adv. Mater.*, in press.

(10) Gu, L.; Zhu, J. Thesis for Bachelor's degree in Tsinghua University, 2002.