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AFM study of gold nanowire array electrodeposited within anodic aluminum oxide template

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Abstract. Uniform gold nanowires were synthesized by electrodepositing the gold under a very low ac frequency in the pores of an anodic aluminum oxide (AAO) template. The surface of the Au/AAO composite is very even and appeared purplish red. Atomic force microscopy observation indicates that the template membranes we obtained have hexagonally close-packed nanochannels. The gold nanowire array is very orderly arranged after partially dissolving the aluminum oxide membrane. Gold nanowires were also characterized by transmission electron microscopy and the phase structure of the Au/AAO composite was proved by X-ray diffraction.

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For the synthesis of nanomaterials, template synthesis has become a very convenient and powerful process [1]. This method entails synthesizing the desired material within the pores of a membrane or other solid. The membranes used contain cylindrical pores with monodisperse diameters; and a nanoscopic fibril or tubule of the desired material is synthesized within each pore. This method has been used to make tubules and fibrils composed of polymers [2], semiconductors [3] and carbon [4] and Li^+-intercalation materials have been prepared.

The preparation of nanowires of different materials has recently attracted wide attention in view of possible future applications in areas such as photocatalysis, electrochemistry, battery research and enzyme immobilization [5]. There are different concepts of using the pores in nanoporous templates for preparing nanomaterials [6, 7]. This general template synthesis is an elegant chemical or electrochemical method for the fabrication of nanostructures, particularly in view of its flexibility to produce nanowires with different compositions. Indeed, the nanowires and their structure, mechanical and transport characteristics were studied using a variety of techniques [8], including most recently combined scanning tunneling microscopy (STM) and direct imaging with the use of high-resolution transmission electron microscopy (TEM) [9, 10].

In our previous work, we prepared the gold nanowires under a high ac frequency within the one-step anodization template [11]. As the pores in the one-step anodization template are not arranged in a more orderly way than those of the two-step anodization template, and also the metal nanoparticles deposited into the pores of the template are not very uniform under the high frequency, we adopted the two-step anodization process to fabricate the nanowires under the lower frequency. The morphologies of template membrane or nanowire array are investigated by atomic force microscopy (AFM) and TEM. And, X-ray diffraction (XRD) shows the phase structure of the Au/AAO (Anodic Aluminum Oxide) composite.

1 Experimental

1.1 Materials

$HAuCl_4 \cdot 4H_2O$ was purchased from Baiyin Chemicals. All other chemicals were used without further purification.

1.2 Fabrication of gold nanowire array within the AAO template

High-purity aluminum sheets (99.99%, 40 mm × 10 mm × 0.1 mm) were employed in our experiment. AAO membranes were fabricated by using a two-step anodization process [12, 13]. Prior to anodization, the aluminum sheets were degreased in acetone, and then annealed in vacuum at 400 °C for 4 h to remove the mechanical stresses and recrystallize them. Then the aluminum sheets were electropolished under a constant-voltage condition of 10 V for 1 min in a mixture of $HClO_4$ and C_2H_5OH at room temperature to smooth the surface morphology. In the first anodization process, the treated aluminum sheets were exposed to an oxalic acid solution under different constant voltage (40 V, 60 V) in a thermal electrochemical cell at a temperature of 20 °C for 3 h. During anodization, the electrolyte was vigorously stirred using

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a pump system. Then the produced alumina layer was removed by wet-chemical etching in a mixture of phosphoric acid (0.4 M) and chromic acid (0.2 M) at 60 °C for 3 h. The second anodization process used the same parameters as in the first step. After coating a protective layer on the surface of the porous alumina film, the remaining aluminum substrate was removed in a saturated $HgCl_2$ solution. A subsequent etching treatment was carried out in 1 M phosphoric acid at 30 °C for 70 min to remove the barrier layer on the bottom side of the AAO membrane.

A home-made ac electrochemical deposition system has been set up, which provides up to 20 W (rms, 30 V, 10 Hz to 10 kHz) output. Gold was deposited in the pores by ac electrolysis in an electrolyte containing $HAuCl_4 \cdot 4H_2O$ (0.93 g/l) and boric acid (30 g/l). The pH value of the electrolyte is maintained at 1.5. The electrolysis was conducted at 20 °C, 25 Hz, 10 V ac and using graphite counter-electrodes. During the process of ac electrochemical deposition, we found that a membrane containing gold nanowires showed the plasma-resonance band and, as a result, such a membrane can show a wide variety of colors. As we know, the diameter of a gold nanowire is determined by the pore diameter, and the length is determined by the quantity of gold deposited.

1.3 Apparatus

An atomic force microscope (SOLVER scanning probe microscope, Russia) was employed to characterize the morphology of the template membrane and the gold nanowire array (noncontact silicon cantilevers, full tip cone angle less than 20°).

Transmission electron microscopic images were recorded with a HITACHI-600 microscope. The samples were obtained as follows: Au-AAO/aluminum was exposed to a saturated $HgCl_2$ solution for 1 h in order that the aluminum oxide section was separated from the aluminum substrate as the result of amalgamation of underlying aluminum. After rinsing with distilled water, the resulting Au/AAO membrane was immersed in 2 M NaOH to dissolve the alumina, then rinsed in distilled water many times to remove the NaOH. Droplets of solution containing gold nanowires were dropped onto the copper grids. The resulting Au/AAO membrane was also investigated using X-ray diffraction (Rigaku, model D/max 2400; Cu K_α radiation, $\lambda = 1.5405$ Å).

2 Results and discussion

AAO with pores in a parallel arrangement throughout was fabricated using the two-step anodization process. The pore diameter was dependent on the anodization voltage. The depth of the AAO template is proportional to the second anodization time. A longer anodization time favored not only increasing the pore depths but also extending the uniformity of the AAO membrane. Figure 1 shows AFM top-view micrographs of as-prepared AAO with different pore diameters. Almost perfect hexagonally arranged pore domains can be seen. The pores with a narrow size distribution are surrounded by six columnar oxides, which are interconnected to form a network structure. During the period of the observation, the boundary of the domain appeared in the large scale, which perhaps resulted from the formation process of the pores.

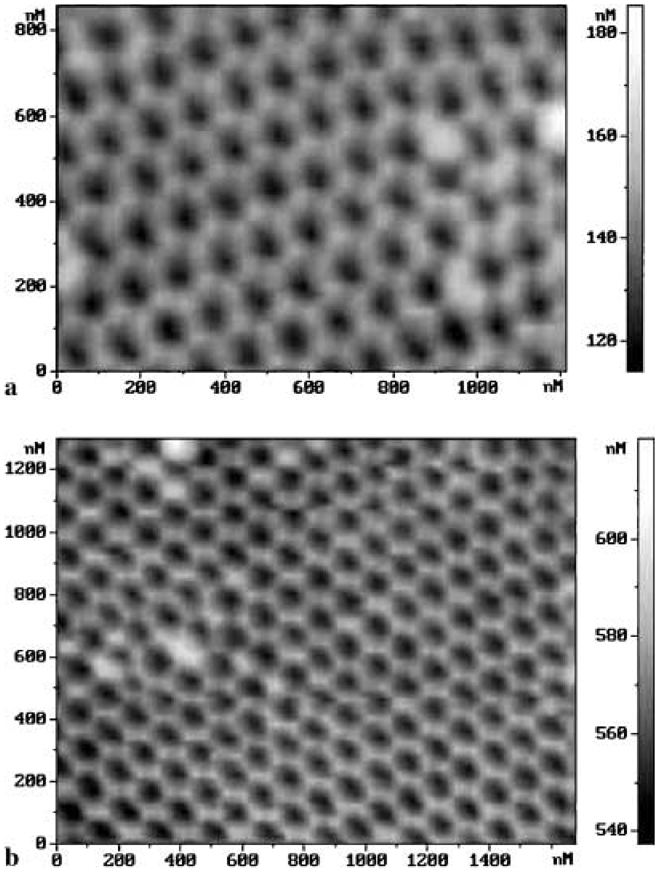

Fig. 1a,b. AFM top-view micrographs of the as-prepared AAO template with the pore diameter **a** 40 nm and **b** 60 nm

The Au/AAO membrane was investigated by the XRD measurement. From Fig. 2, the diffraction peaks of Au (111) and Au (200) correspond with $2\theta = 38.32°$ and 44.41°, respectively.

Gold nanowires that are deposited within the pores of the AAO template under the lower ac frequency are very uniform. This is in contrast to those obtained under the higher frequency (200 Hz); the surface of the Au/AAO appeared inhomogeneous because the gold nanoparticles was deposited into the pores so quickly. As the pore is not filled with

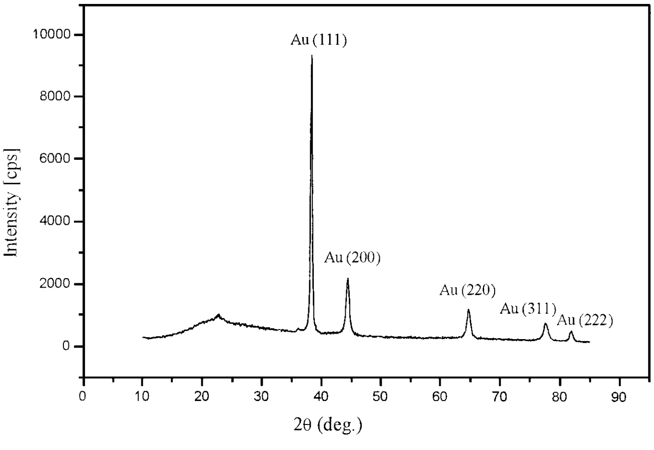

Fig. 2. X-ray-diffraction profile of the Au/AAO membrane

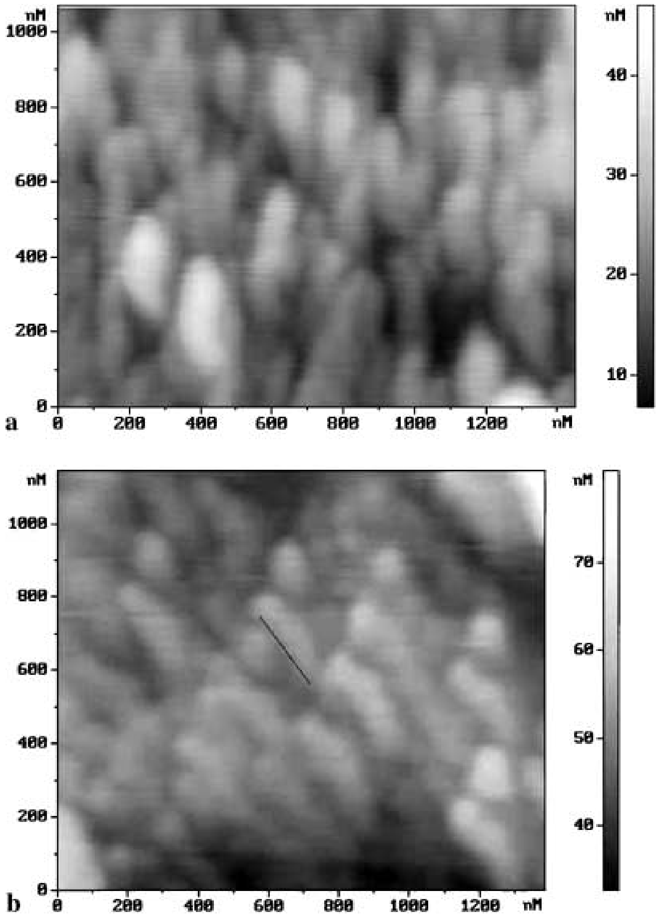

Fig. 3a,b. AFM images of the gold nanowire array after the aluminum oxide membrane was partially dissolved by 0.5 M phosphoric acid for 20 min (**a**) and 60 min (**b**)

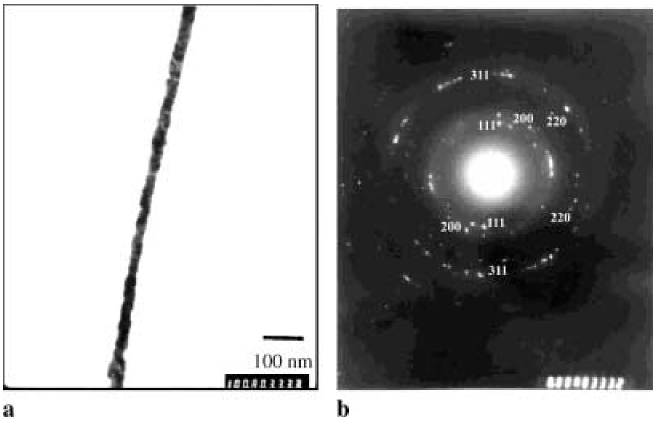

Fig. 4a,b. TEM image of the gold nanowire synthesized within the AAO/aluminum (**a**) and the corresponding selected-area electron-diffraction pattern (**b**)

gold nanowires, the morphology of the Au/AAO/Al membrane is the same as that of the blank AAO template because of using the AFM. After dissolving the AAO template in the 0.5 M phosphoric acid, the gold nanowire array could dew partly from the template. Figure 3a shows that the gold nanowire array stands straight after dissolving the aluminum oxide membrane for 20 min. With the increment of dissolving time, the length of the gold nanowires becomes longer and they presently collapse. Figure 3b shows gold nanowire array breakdown after dissolving the aluminum oxide membrane for 60 min. The diameter of the nanowire is 40 nm, which is dependent on the pores of the template membrane we selected.

The typical transmission electron micrograph of a typical gold nanowire is shown in Fig. 4a. The diameter of the gold nanowire is 40 nm, which is agreement with that obtained by AFM. Figure 4b shows the selected-area electron-diffraction pattern of the gold nanowire. According to a geometrical analysis of the electron diffractogram, the diffractive spots in the electron-diffraction pattern are marked in Fig. 4b.

3 Conclusion

We have successfully prepared a gold nanowire array in the pores of an AAO template under very low ac frequency. We used AFM, XRD and TEM techniques to characterize the morphology of the gold nanowires. AFM observation indicates that the template membranes we obtained have hexagonally close-packed nanochannels. The gold nanowire arrays are very uniformly assembled and parallel to each other in the pores of the AAO template membranes after partially dissolving the aluminum oxide membrane.

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