Preparation of Free-standing Bamboo-like Ni Nanowire Arrays

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(Received January 5, 2009; CL-090026; E-mail: gtfei@issp.ac.cn)

Free-standing bamboo-like Ni nanowire arrays with periodic branches have been produced by electrochemical deposition in the pores of layer-by-layer anodic alumina membrane. This method could provide a possible approach to prepare free-standing nanostructures of various functional materials with great self-support ability and large surface area in practical applications.

It is well-known that Ni, generally prepared by electrodeposition and chemical liquor phase preparation, exhibits attractive abilities in a variety of applications including hydrogen storage, solid oxide fuel cells, and electrochemical oxidation of organic molecules like methanol, ethanol, cyclohexanol, and glucose.[1–8] Compared with Ni in bulk and film traditionally used with low specific surface area, 1-D nanostructure arrays, which have attracted enormous research interest recently, possess much higher specific surface area.[9–14] Among various approaches, the fabrication of large-area and well-ordered Ni nanowire arrays in anodic alumina membrane (AAM) is outstanding.[15–18] Usually, the AAM needs to be removed for achieving as large a surface area exposure as possible. However, without the support of AAM the neighboring nanowires would assemble when their aspect ratio (the length to width ratio) reaches a certain limit. This could make the surface area of nanowires lower and the liquid harder to flow into the interspaces of the structure especially for the electrochemical oxidation, which may probably hinder the nanowire arrays from practical application to some extent. Therefore, to make a well-standing nanowire array with great self-support ability, adequate separation and without agglomeration becomes very important in either experiment or practical application, and it is still a challenge to achieve this.

In this paper, we prepared free-standing bamboo-like Ni nanowire arrays of periodic branches using layer-by-layer AAM by electrochemical deposition.[19] Even if there is a relatively high aspect ratio that the branches of each nanowire lean against the neighboring one would still make the whole array stand well with AAM being removed. Furthermore, the well-aligned array could give rise to much more exposure of nanowire surface area, which plays an important role especially in the electrochemical oxidation for liquid which can easily and sufficiently contact the surface of almost each nanowire. It is anticipated that our method will motivate the study of preparing promising free-standing nanomaterials network with great self-support ability and large surface area.

At first, high-purity aluminum foils (99.999%) were annealed and electrochemically polished. The layer-by-layer branched AAM was prepared by adjusting the anodizing voltage periodically during electrochemical anodization. A cell voltage period procedes as follows: the voltage first increases sinusoidally from 23 to 53 V over 30 s, and then it decreases linearly from 53 to 23 V over 3 min.[19] After the remaining aluminum and alumina barrier was removed, a layer of Au film was sputtered onto one side of the AAM to serve as the working electrode.

In our experiment, the electrolyte for Ni nanowire preparation was a mixture of 105 g/L $NiSO_4 \cdot 6H_2O$, 5.8 g/L NaCl, 6.2 g/L H_3BO_4, and 125 g/L $C_6H_5Na_3O_7 \cdot 2H_2O$. The electrodeposition was then performed for 4 h with a constant current of 0.5 mA. To testify the self-support ability of the nanowire arrays, the AAM was totally removed by 1 M NaOH solution. The morphologies of the AAM and nanowire arrays were observed by field-emission scanning electron microscopy (FE-SEM, Sirion 200).

Figure 1a shows the profile of layer-by-layer branched AAM, anodized for about 12 h in the second oxidation, with main channels and branched pores growing in a fixed spatial order in the direction perpendicular to the surface of AAM. Figure 1b is the side view of Ni nanowire arrays with AAM completely removed. We can observe that the nanowires have successfully replicated the structure of the AAM. Along the main channel, each nanowire has periodic branches that are perfectly natural brackets separating one nanowire from the neighboring ones, which guarantees enough room between these nanowires, and plentiful surface area exposed to air. The periodic appearance of branches on nanowires corresponds to the periodic occurrence of branched pores of the channels in our unique AAM. Figures 1c and 1d are large-scale SEM images of nanowire array in side view and top view, respectively. It can be seen that the whole array stands upright very well even without the support of AAM, in sharp contrast to straight nanowire prepared using ordinary AAM with cylindrical pores. The length of the nanowires can be adjusted by varying the electrodeposition time. Even when the aspect ratio reaches about 60:1 seen from Figure 1c, the array still possesses great self-support ability as

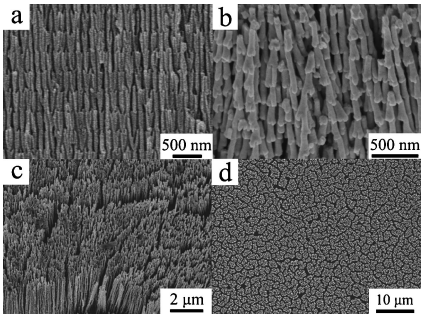

Figure 1. The SEM images of layer-by-layer AAM (a), and free-standing bamboo-like nanowire array in side view (b), (c) and top view (d).

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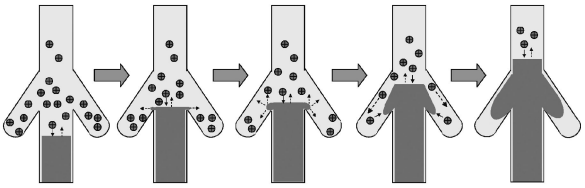

Figure 2. The schematic illustration of the growth process of bamboo-like nanowires.

a whole. This high aspect ratio could possibly enhance the electroactivity of Ni nanowire arrays as a catalyst in electrocatalytic oxidation.

Figure 2 schematically illustrates the growth process of nanowires. Initially, by receiving electrons, Ni^{2+} ions become Ni atoms being deposited into the main channels, and the stem of nanowires grows as ordinary straight wires do (Figure 2a). When the top of a nanowire reaches the branching position of the AAM, the branches of nanowires begin to stretch out forward into the branched pores and meanwhile the stem continues to grow upward (Figure 2b). At the preliminary stage, the tips of these neonatal branches heading to the branched pores develop dimensionally in all directions owing to the loss of confinement from the walls of pores (Figure 2c). The deposition of Ni atoms at the top of nanowires and at the brim of branched pores occurs simultaneously. In this case, the Ni grows into the branched pores gradually (Figure 2d). Meanwhile, Ni^{2+} ions in main channels of AAM diffuse into branched pores to balance the difference in concentration. Since the supplement could not satisfy the exhaustion of Ni^{2+} ions in branched pores in time, the growth speed of stem is higher than that of branches. With the entrance to the branched pores closed down by the stem and the left Ni^{2+} ions exhausted, the branches will finally stop growing. Subsequently, the nanowires will still develop along the main channels (Figure 2e). With several deposition periods being repeated, the nanowires successfully replicate the geometry of channels in our layer-by-layer AAM.

During this process, the growth rate is pivotal, which can be controlled by varying the deposition electric current. At the step shown in Figure 2d, when the branches grow larger, the exhaustion of Ni^{2+} ions in the branched pores probably could not be supplemented as sufficiently as that in main channels since the entrances into pores are getting narrower. To obtain comparatively sound branches, a relatively low electric current is needed in this case to make sure that the cations in solution have enough time to diffuse into branched pores and build up the branches of nanowires. To prove this we also prepared another sample with layer-by-layer AAM under a comparatively high electric current shown in Figure 3. It can be clearly observed that owing to the excessively rapid growth rate the branches of nanowires do not appear obviously as the cations could not diffuse into lacuna of branched pores in time.

In summary, we have successfully generated free-standing bamboo-like metallic nanowire arrays of periodic branches with layer-by-layer AAM under a relatively low electric current by electrochemical deposition. Because the branches of different nanowires lean against each other, the nanowire array stands very well even with a high aspect ratio while AAM is totally removed. The controllable preparation in our experiment could

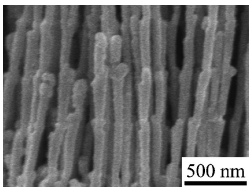

Figure 3. The SEM image of bamboo-like nanowire array prepared under a comparatively high electric current.

open another possibility in the fabrication of free-standing nanostructure with great self-support ability and large surface area exposure out of a variety of materials, even metallic oxide by using sol–gel methods. We believe this could bring benefits in many applications, such as electrocatalytic oxidation, surface-enhanced Raman scattering, surface plasmon resonance, and photocatalysis. It is expected that our solution will develop the large-area nanostructures of functional materials in practical applications.

This work was supported by the National Natural Science Foundation of China (Nos. 50671099, 50172048, 10374090, and 10274085), Ministry of Science and Technology of China (No. 2005CB623603), and Hundred Talent Program of Chinese Academy of Sciences.

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Published on the web (Advance View) March 28, 2009; doi:10.1246/cl.2009.394