Individual alumina nanotubes coaxially wrapping carbon nanotubes and nanowires

T. Qiu\textsuperscript{a}, X.L. Wu\textsuperscript{a,\!*}, G.S. Huang\textsuperscript{a}, G.G. Siu\textsuperscript{b}, Y.F. Mei\textsuperscript{b}, F. Kong\textsuperscript{a}, M. Jiang\textsuperscript{c}

\textsuperscript{a}National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Han Kou Road 22, Nanjing 210093, People’s Republic of China
\textsuperscript{b}Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, People’s Republic of China
\textsuperscript{c}Process Developing Department, Hangzhou Silan Integrated Circuit Co. Ltd., HangZhou 310018, Zhejiang Province, People’s Republic of China

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Abstract

Al-based anodic porous alumina membranes with ordered nanopore arrays are fabricated for exploring the template synthesis of carbon nanotubes and nanowires. Via the polymerization of acrylonitrile in the ordered nanopores of the membranes and subsequent heating, the polymer structure was converted into a quasi-graphitic structure. Atomic force microscopy observations revealed that the quasi-graphitic nanostructures are located in the pores of the porous alumina membrane, displaying a hexagonal symmetry. Raman scattering investigation confirmed the formation of carbon nanotubes in the nanopores. With further mild, controlled treatment in aqueous alkali and acidic solution, individual alumina nanotubes (ANTSs) coaxially wrapping the carbon nanotubes and nanowires are obtained, as evidenced by transmission electron microscopy observations.

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1. Introduction

In recent years, fabrications of nanometer-sized materials have gained considerable attention because of their potential uses in mesoscopic researches and development of nanodevices. Of all the fabrication methods, anodic porous alumina (APA) membranes have been widely used as templates or masks to fabricate orderly nanostructured materials [1–5]. Some important parameters in fabricating APA membrane, such as nanopore sizes, densities, and barrier layer thickness, have also been explored in detail [6]. The applied voltage during the anodization of Al sheet has been revealed to be a key experimental parameter for the fabrication of the nanopore-size-controllable APA membrane [7]. More recently, we reported individual alumina nanotubes (ANTSs) fabricated in a controlled way by stepwise anodization of silicon-based Al membrane [8], instead of the route of uncontrollable ultrasonic agitation that may introduce defects into the nanotubes [9]. This investigation is expected to open fascinating possibilities for further chemical and physical explorations of nanostructures, such as individual carbon nanotubes, nanowires, cylindrical capacitors, and nanocables, which are useful in future nanodevices. So far, there are a few reports on the fabrications and formation mechanism of the ANTs from Si-based APA membranes [8,10], while research activities concerning nanotube- or nanowire-embedded ANTs are still absent. Therefore, more work is needed to fabricate this kind of coaxial composite nanotube structure and then seek applications in future nanodevices.

In this article, we report successful fabrications of the ANTs coaxially wrapping carbon nanotubes and nanowires,
using the APA membrane as a template. With the help of simply controlled electrochemical etching of aluminum sheet, we first obtain Al-based APA membrane with ordered nanopore array. Via the polymerization of acrylonitrile in the nanopores and subsequent thermal treatment, we convert the polymer structure into a quasi-graphitic structure. With further mild controlled treatment in aqueous alkali and acidic solution, we obtain carbon nanotube- and nanowire-embedded individual ANTs. Spectral analysis and microstructural observations confirm the formation of this kind of composite nanostructure. The obtained nanostructures can be expected to have important applications in future nanoelectronics.

2. Experimental details

We used a sheet of Al (2×2 cm) with a thickness of 0.1 mm and a purity of 99.99% to fabricate the APA template. The Al sheet was first cleaned by acetone to degrease the Al surface and then polished via electrochemical methods in a solution of 20% perchloric acid and 80% ethanol under a constant DC voltage of 18 V for 2 min. Anodization with a platinum plate as a cathode and the Al sheet as anode was carried out in oxalic acid of 0.5 M under a constant DC voltage of 40 V [5]. By monitoring the anodic $I–t$ curve, the anodization of the Al sheet can be controlled easily. Two hours later, the current was turned off, and thus, an APA template was obtained. A schematic diagram of the anodization device is shown in Scheme 1. The as-made APA membrane was then immersed into a 50-ml aqueous saturated solution of CuCl$_2$. This aqueous polymerization process is necessary because Al would be melted when heated over 550 °C in a tube furnace. In addition, the Al/ alumina interfacial layer (barrier layer) was also removed by immersing the resultant APA membrane into a phosphoric acid of 5 wt.%. Hence, the morphology of the membrane can be characterized from two surfaces by transmission electron microscopy (TEM) observations. Afterwards, the polyacrylonitrile/alumina composite membrane was heated at 250 °C in air for 1 h for the cyclization of the polymer chain in a tube furnace, followed by further heating at 800 °C in N$_2$ for 1 h for partial graphitization of the polymer.

In our experiments, atomic force microscopy (AFM) images (512×512) were obtained on a Nanoscope IIIa of the Digital Instruments Veeco Metrology Group, working in contact mode using commercial Si$_3$N$_4$ cantilever (Type NP-S20) with a spring constant of 0.58 Nm$^{-1}$. The scan rate was 549 Hz. The Raman spectral measurements were carried out on a T64000 triple Raman system of Jobin Yvon company. The structures of the samples were observed on a JEOL JEM-2000 TEM equipment at an operating voltage of 10 kV. In the process of preparation of the TEM samples, the APA membrane with embedded carbon nanostructures was treated in a 2 M NaOH solution at 40 °C for 5 min for removing the base Al oxide at the surface to form individual ANTs in which carbon nanotube and nanowire are embedded. To confirm the presence of carbon nanotubes and nanowires, a 5 M HCl solution was further added into the concentrated suspension at 40 °C for 10 min to dissolve the ANTs, followed by TEM observations.

3. Results and discussions

Scheme 2a shows the structural model of the APA template. Each cell consists of an oxide (Al$_2$O$_3$) layer on the surface, a barrier layer between the oxide layer and Al base, and a porous layer under the oxide deposition layer. The barrier layer is composed of compact amorphous alumina which has an interface with the Al base. Mei et al. [10] have previously suggested that, during the formation of the ANTs, the voids begin to grow at the triple points between cell grains and then gradually fill whole grain boundaries. The voids with the largest sizes are located at the triple points between cell grains. The voids with small sizes appear in the inner wall of the cell grain. This model gives the possibility of interlaced cleavages of the cells [11]. Based on the model, we draw a structural model of the APA template with deposited polymers in the pores in Scheme 2b, considering that polymers are easy to deposit on the wall of the pores to form tubes [12]. After removal of the barrier layer and subsequent thermal treatment, we obtain the APA membrane containing quasi-graphitic structure in the pores. The quasi-graphitic structure occupies whole pore channel and partially covers the surface of the cell boundary. This
situation can clearly be seen in Fig. 1b, which shows an AFM image of the surface of the APA template with graphitic structure. As a comparison, we also give an AFM image of the surface of the as-prepared APA template in Fig. 1a. We can find that the surface of the template has been greatly changed from before the polymerization of acrylonitrile to after thermal treatment, but all the apexes (quasi-graphitic structures) are well organized. Each apex is hexagonal in shape and has an average diameter of ~100 nm. This size is greater than that of the pore in the alumina host (about 80 nm).

With treatment in a 2 M NaOH solution at 40 °C, bare oxide on the surface of the membrane is first dissolved, and then dilute alkali solution gradually leaks into the voids to split the junctions between the voids.

Scheme 2. (a) Structural model of Al-based APA template. (b) Structural model of the APA template with quasi-graphitic structure, which spills over the pore and covers partial surface of the cell boundaries. With the treatment of a 2 M NaOH solution at 40 °C for 5 min, dilute alkali solution gradually leaks into the voids to split the junctions between the voids.

solution splits the junctions between the voids and thus causes the interlaced cleavages of the cell boundaries. This process may be expected to separate the cell grains and therefore lead to the formation of individual ANTs.

Fig. 2 shows a TEM image of the membrane with graphitic structure after the treatment of mild alkali solution. We can clearly see that individual composite nanotube structures have been separated with each other. The average diameter of the nanotubes is ~100 nm, approximately equal to those of the hexagonal-shaped apexes in Fig. 1b.

Fig. 1. AFM images of the surfaces of (a) the as-prepared APA template and (b) the APA template after filling the nanopores with polyacrylonitrile.

Fig. 2. TEM image of the APA membrane with graphitic structure after the treatment of mild alkali solution.
Raman scattering has been proved to be a useful tool to identify the existence of carbon nanotubes [13–15]. To confirm the formation of carbon nanotubes in the template with graphitization treatment, we measured the Raman spectra of this kind of composite nanotube structure and present a typical result in Fig. 3. This spectrum clearly shows two Raman vibration bands at 1351 and 1600 cm$^{-1}$. Because no noticeable Raman bands exist in the APA film and corresponding ANTs, the two bands should correspond to the D- and G-band of the typically first-order Raman spectrum of carbon nanotubes, respectively. The G-band at 1600 cm$^{-1}$ is noteworthy because its peak position is higher than that reported previously (1581 cm$^{-1}$; [16]). Because the position of the G-band is slightly dependent on the domain sizes of the graphite planes formed, the upshift of the peak position of the G-band may be due to different crystalline sizes of the carbon nanotubes in our samples. The appearance of the D- and G-bands in the Raman spectrum implies the formation of carbon nanotubes in our APA template.  

Shown in Fig. 4 is a TEM image of singly coaxial quasi-graphitic structure embedded in ANT. The corresponding sample was obtained after dilute alkali treatment. Attached to the APA mother skeleton, it is tube-like in shape and has a length of ~1.2 μm. This ANT is filled with graphitic structure. Its outer and inner diameters are 80 and 55 nm, respectively. The outer diameter is approximately equal to that of the ANT from the APA template (see Fig. 2), whereas the inner diameter is smaller than that of the nanopore in the APA template. The outer wall of the ANT is not smooth, displaying local surface damage. However, we can see that the thickness of the tube wall is almost the same, which implies that the permeation of the NaOH solution into the boundaries of the nanotube structure is mild and directional.  

To further demonstrate the structure of the wrapped graphitic material in the ANTs, we use a 5 M HCl solution to treat the remnant aqueous solution at 40 °C for 10 min to remove the alumina content. Fig. 5 shows the corresponding TEM results. In Fig. 5a, we can see a single carbon nanotube from the dissolved composite ANT structure with a diameter of ~55 nm. A number of TEM observations indicate that the diameters of the carbon nanotubes are 50±6 nm (mean±standard deviation), indicating that they are indeed localized in the nanopores of the APA membrane.
and formed during the polymerization of acrylonitrile. In addition, we can further note that the orifice of this carbon nanotube is larger in diameter. This can be explained according to our structural model presented in Scheme 2b: The quasi-graphitic structure spills over the nanopore of the APA template and covers partial surface of the cell boundary. Fig. 5b shows a cluster of carbon nanotubes. Partial walls of these carbon nanotubes have been damaged due to tensile strain during the pyrolytic cracking of polyacrylonitrile. The lattice image of the wall of the carbon nanotube is shown in the inset of Fig. 5a. The wall consists of several stacks of chips of carbon atomic layers with thickness ranging from 3 to 5 nm. Such wall has been observed previously [17]. The above result further indicates that the isolated carbon nanotubes indeed exist in the ANTs separated from the APA matrix.

Carbon nanowires are also found to exist in the sample solution used for the HCl treatment. Fig. 6a shows a single nanowire 55 nm in diameter and 3 μm in length. Fig. 6b shows several individual carbon nanowires. This result indicates that there exist two kinds of graphitization structures in the ANTs, one being carbon nanotubes and the other carbon nanowires. In comparison with other fabrication methods such as carbon evaporation at high gas pressure [18], our fabrication route in liquid solutions is intrinsically unstable, which might lead to nonhomogeneous polymerization in polyreaction. As a result, after a series of thermal treatment, carbon nanotubes and nanowires are formed and coexist in an APA template.

4. Conclusions

With mild controllable electrochemical route, individual carbon nanotube- and nanowire-embedded ANTs have been obtained from the APA template via the polymerization of the acrylonitrile in the nanopores, a series of thermal treatments, and final separation in NaOH solution. The ANT structure with a length of 1–3 μm has outer and inner diameters of 80 and 55 nm, respectively. The embedded carbon nanotubes or nanowires have a diameter of 40–55 nm. Because the ANT is a kind of insulative packing material [19,20], and the embedded carbon nanotubes or nanowires may be a kind of conductive materials [21], this kind of composite nanotube or nanowire structures may be expected to have important applications in modern nanodevices such as nanocables.

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