

Chapter 3

Elongation of Arrays of Amorphous Carbon Nanotubes

Abstract

Amorphous carbon nanotube arrays (*a*-CNT, diameter = 340 nm, length = 800 nm) were grown inside anodic aluminum oxide (AAO) membranes from $\text{SiCl}_3\text{CCl}_3$ at 1073 K by low-pressure chemical vapor deposition (LPCVD). The as-prepared *a*-CNT arrays were elongated up to 60 μm , after the channels of the membrane were filled with Na and reacted with C_6Cl_6 at 623 K.

3.1 Introduction

Due to its special properties, amorphous carbon (*a*-C) materials have been reported to display novel functions for many potential optical,¹⁻² frictional³ and electronic^{2,4} applications. These include protective coating, ultra durable anti-reflection coatings,¹⁻² mechanical devices,²⁻³ and electron emitters.⁴ The ability to fabricate *a*-C into desired physical shapes has attracted much attention. For example, anodic aluminum oxide (AAO) has been used as templates to shape *a*-C into tubular shapes by pyrolyzing propylene inside the AAO channels.⁵ In our study herein we report on a process to grow *a*-C nanotubes (*a*-CNT) by coupling two fabrication methods we recently developed.⁶⁻⁷ First, a layer of short aligned *a*-CNT was deposited by LPCVD from $\text{SiCl}_3\text{CCl}_3$ on an AAO substrate.⁶ Then, by employing the Na-filled AAO (Na@AAO) reactive template method, we were able to significantly elongate the *a*-CNT.⁷

3.2 Experimental Section

Using a hot-wall LPCVD reactor with a base pressure of 10^{-1} Pa, $\text{SiCl}_3\text{CCl}_3$ (Aldrich,

97%) was evaporated at 273 K without carrier gas. The precursor was decomposed at 1273 K and 10 Pa to deposit a layer of carbon on AAO substrates (Whatman Anodisc 13, observed pore diameter: 280 nm, thickness: 60 μm). After 3 h, the AAO substrates turned black and the product *a*-C film on AAO (*a*-C/AAO) was obtained. By decomposing NaH (Aldrich, 0.2 g, 8 mmol) on *a*-C/AAO inside a tube furnace at 623 K under 1 atm of Ar (flow rate: 30 sccm) for 0.5 h, Na filled the channels of AAO to generate Na@*a*-C/AAO. Further reaction of Na@*a*-C/AAO with C₆Cl₆ (*Toxicity*: LD₅₀ oral, mouse = 4 g kg⁻¹; Aldrich, vaporized at 393 K) at 623 K for 20 h produced a brittle black product which broke easily into small pieces. The product was immersed in 48% HF at room temperature for 9 h to remove the AAO template. It was then washed with boiling D.I. water and dried at 373 K in air to offer elongated arrays of *a*-CNT.

3.3 Results and discussion

As shown by the scanning electron microscope (SEM, JEOL JSM-6330F at 15 kV) images in Figure 3.1, the average diameter of the open-ended *a*-CNT, 330 ~ 340 nm, is close to the channel diameter in the AAO. The average thickness of the *a*-CNT wall was 30 nm. In Figure 3.1 (b), the average thickness of the array layer was estimated to be 800 nm, much thinner than the AAO thickness of 60 μm . We speculate that the activated species generated from SiCl₃CCl₃, :CCl₂, cannot diffuse effectively into the AAO channels to form a thick carbon layer. Figure 3.1 (b) also shows that the *a*-CNT array is connected as a layer of film on top of the AAO. Using energy dispersive spectroscopy (EDS), the composition of the isolated tube array layer was confirmed to be carbon. Thus, the data support the conclusion that we have successfully deposited *a*-C on AAO (*a*-C/AAO) in the form of short *a*-CNT array. We also attempted to perform this process on a home-made AAO with a channel diameter of 30 nm. However, :CCl₂ apparently could not diffuse into the narrow AAO channels to grow into an *a*-CNT layer.

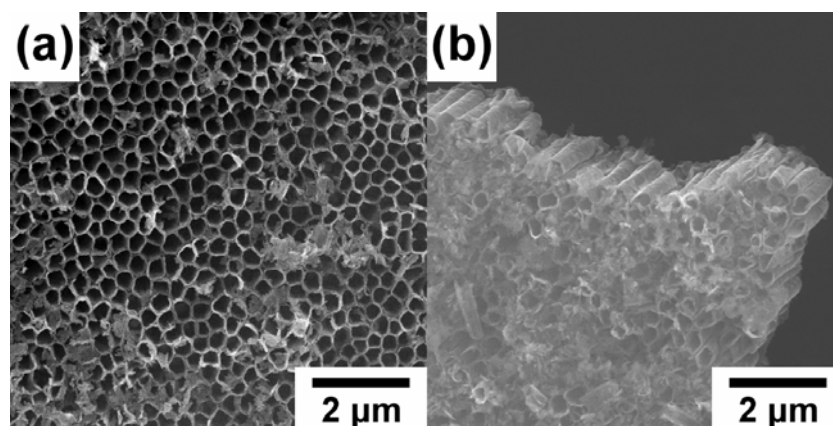


Figure 3.1 SEM images of (a) top and (b) side view of short α -CNT arrays grown from $\text{SiCl}_3\text{CCl}_3$ at 1073 K by LPCVD after AAO is removed.

After the short α -C/AAO layer was fabricated by LPCVD, we explored the possibility of extending the tube length by the sodium reactive template method that had been previously developed.⁶ Figure 3.2 shows that this sample is composed of bundles of elongated α -CNT. Due to some breakage of the solid product, the observed α -CNT lengths, 20 μm , are shorter than the original AAO thickness. One side of the tube array is connected with a continuous film, probably formed in the previous LPCVD process, while the individual carbon tubes generated in the reactive template step are straight and well-aligned. The diameter of the α -CNT, 340 nm, is close to the AAO channel diameter.

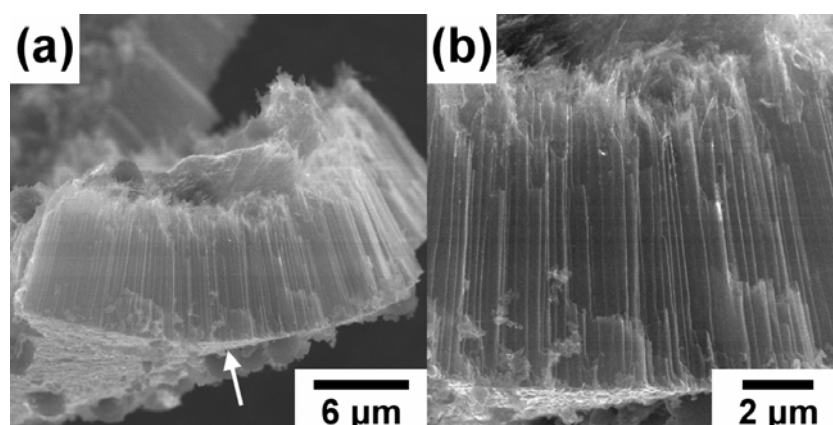


Figure 3.2 SEM images of an elongated α -CNT. (a) Side view and (b) enlarged view of the region marked by arrow in (a).

Figure 3.3 presents bright field transmission electron microscope (TEM, Philips TECNAI 20 at 200 kV) images and the corresponding selected area diffraction (SAD) patterns of dispersed *a*-CNT samples. The observed morphology, shown in Figure 3.3 (a), suggests that the two long tubes attached to one end of the two linked short tubes is the consequence of the processes employed in this study. Arrow 1 points to an end section layer with a thickness of ca. 800 nm. The layer is a bundle of *a*-CNT with increased wall thickness. We attribute the first formation of this section to the LPCVD process. On the other hand, the elongated portion of the tubes, as indicated by Arrow 2, has an average diameter of 300 nm, a wall thickness of 30 nm and a length of 2.5 μm . The long segments appeared to be produced solely by the reactive template process. The ED pattern and the wall structure shown in Figures 3.3 (a) and 3.3 (b), respectively, indicate that the tubes are amorphous.



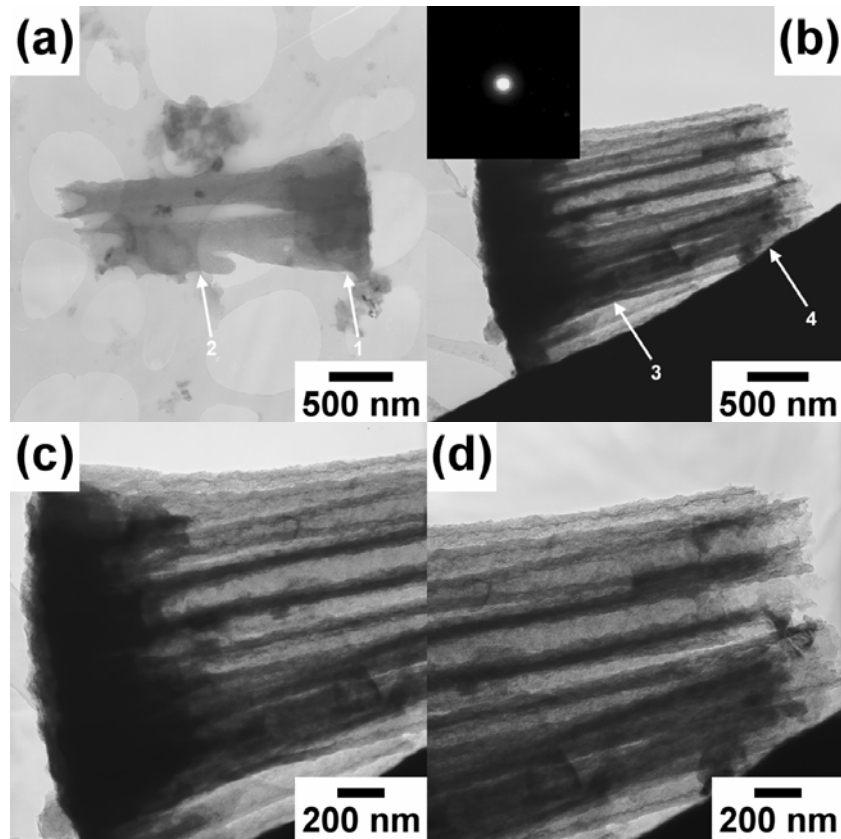


Figure 3.3 TEM and ED images of elongated *a*-CNT. (a) Arrow 1 marks *a*-CNT formed by LPCVD and Arrow 2 shows the section formed by the reactive template method. (b) A well-aligned *a*-CNT bundle, (c) Magnified view of area marked by Arrow 3. (d) Magnified view of area marked by Arrow 4.

A Raman (Jabin-Yvon Raman Spectrometer T-64000 with the incident wavelength at 514.5 nm) scattering spectrum of the elongated *a*-CNT array is displayed in Figure 3.4. The vibrations are assigned to G-band (1587 cm^{-1}) and D-band (1350 cm^{-1}) of a carbon material. The peak intensity ratio, I_D/I_G , strongly suggests that this carbon material is non-crystalline.

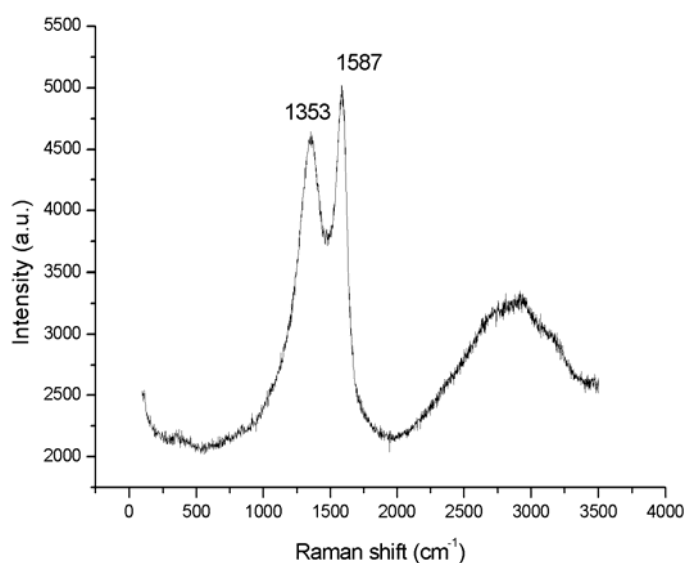
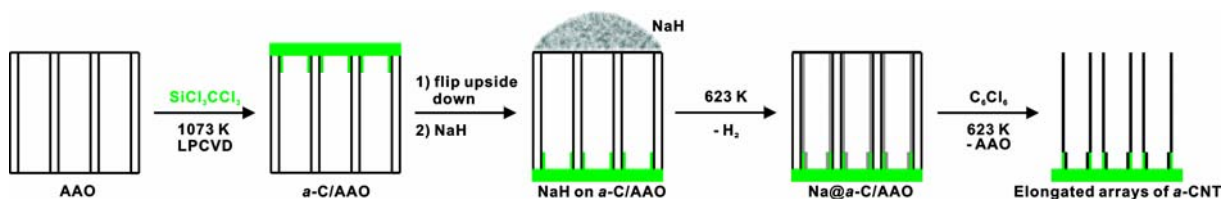


Figure 3.4 Raman spectrum of elongated *a*-CNT.

3.4 Conclusion

To summarize, we conclude that amorphous carbon tubes were prepared via a template-assisted synthesis route as shown in Scheme 3.1 (not to scale). First, using AAO as the substrate, short *a*-CNT arrays are grown from $\text{SiCl}_3\text{CCl}_3$ at 1073 K by LPCVD. Elongation of the tubes into bundles joined at one end is achieved by filling the AAO channels with Na to generate the reactive template, followed by the reaction with C_6Cl_6 . Because sections of the tubular structure were fabricated independently, we postulate that this process can be extended to form tubular structures containing heterojunctions between carbon and other elements such as silicon. For example, replacing C_6Cl_6 with silicon chlorides as the sources may achieve this goal. This research is still in progress.



Scheme 3.1 Scheme of elongating *a*-CNT.

References

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