Chapter 7

Anodic Aluminum Oxide Template Assisted Growth of Amorphous Carbon Nanotubes from Acetylene – the Role of Sodium Metal as a Catalyst

Abstract

Growth of uniform amorphous carbon nanotubes (*a*-CNT) by chemical vapor deposition (CVD) from acetylene (C_2H_2) was carried out inside the channels of anodic aluminum oxide (AAO) membranes filled with sodium metal, which acted as an active catalyst to assist the decomposition of acetylene.

7.1 Introduction

Fabrication of various carbon materials into designed physical shapes is under intensive investigation for their potential technology applications in many areas.[1] One approach to produce well-aligned CNT arrays is based on anodic aluminum oxide (AAO) template-assisted growth. In this strategy, carbon atoms are directly deposited inside the pores of self-organized channels of AAO membranes from hydrocarbons by chemical vapor deposition (CVD) and related technologies.[2-6] The size and shape of the CNT array can be controlled effectively through this route. Drawbacks of the reported cases include the need of transition metal catalysts and high temperature reaction steps.[4,6] Improvement can be achieved by employing plasma enhanced CVD (PECVD).[5] However, in this case, the deposition step coverage was significantly sacrificed. Recently, we reported an effective method to incorporate metallic sodium into the channels of AAO. The Na filled AAO (Na@AAO) can be employed as a "reactive template" to convert chlorocarbons via a stoichiometric Wurtz type C-C coupling reaction into well-aligned amorphous CNT (*a*-CNT) arrays.[7] One

restriction of this process is that the quantity of Na inside Na@AAO limits the extent of the coupling reaction, which then limits the a-CNT formation. To overcome this, we envision that with proper reactant and reaction conditions, Na@AAO may act as an effective catalytic template to assist the growth of aligned CNT arrays. In this report, we wish to demonstrate that by employing acetylene, C_2H_2, as the carbon source, Na@AAO can indeed assist the growth of a-CNT arrays catalytically via CVD at low temperatures. The selection of acetylene is based on the observation that the acidic H atoms of acetylene can be activated by electron rich metallic Na.[8] The reaction between C_2H_2 and Na is thermodynamically favored. An estimation of the enthalpy of reaction (ΔH_r^o) for $C_2H_{2(g)} + 2\ Na_{(s)} \rightarrow NaC_2H_{(s)} + NaH_{(s)}$ gives a result of -240.2 kJ per one mole of C_2H_2 consumed.[9,10] In addition, for $C_2H_{2(g)} + 4\ Na_{(s)} \rightarrow Na_2C_{2(s)} + 2\ NaH_{(s)}$, ΔH_r^o is calculated to be -319.5 kJ per one mole of C_2H_2 reacted.[9] Since the analysis suggested the feasibility of a different pathway to activate C_2H_2, it prompted us to investigate the proposed reaction experimentally. To our knowledge, this is the first case that metallic Na is explored for such purpose.
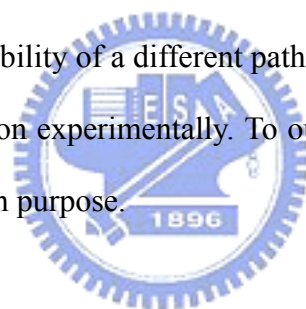
7.2 Experimental Section

a) **Growth of a-CNT in AAO.** Typically, C_2H_2 (San Fu, 99.99%; flow rate 3 sccm) was passed over an AAO (Whatman Anodisc 13, observed pore diameter of 280 - 370 nm and membrane thickness of 40 nm) substrate in a hot-wall CVD reactor at 1 atm and 773 - 1073 K. After 1 h, the AAO substrate turned black. The membrane was immersed in 48 % HF at room temperature for 10 days to remove AAO. After being washed with boiling deionized (D.I.) water and dried at 373 K, a piece of a-CNT array was isolated.

b) **Growth of a-CNT in Na@AAO.** By decomposing NaH (Aldrich, 0.1g, 4 mmol) on a piece of AAO inside a tube furnace at 1 atm and 623 K under Ar (flow rate: 30 sccm) for 0.5 h, Na filled the channels of AAO to generate a reactive template Na@AAO. In a typical reaction, Na@AAO was reacted with C_2H_2 (3 sccm) at 623 K for 3 h to produce a black membrane.

Upon exposure to air, Na metal was hydrolyzed. To remove AAO, the black product was immersed in 48 % HF at room temperature for 6 h. Then, it was washed with boiling D.I. water and dried at 373 K in air to offer a piece of *a*-CNT bundles.

7.3 Results and Discussion

For comparison, we first grew CNT arrays inside the channels of AAO membrane from acetylene by CVD. Scanning and transmission electron microscopic (SEM, JEOL JSM-6330F at 15 kV and TEM, Philips TECNAI 20 at 200 kV) images of a sample deposited at 1073 K showed an average diameter of ca. 330 nm and a wall thickness of ca. 85 nm. From an electron diffraction (ED) pattern, an intergraphene layer spacing of 0.35 nm is estimated, which is slightly larger than the spacing of graphite (002) planes, 0.335 nm.
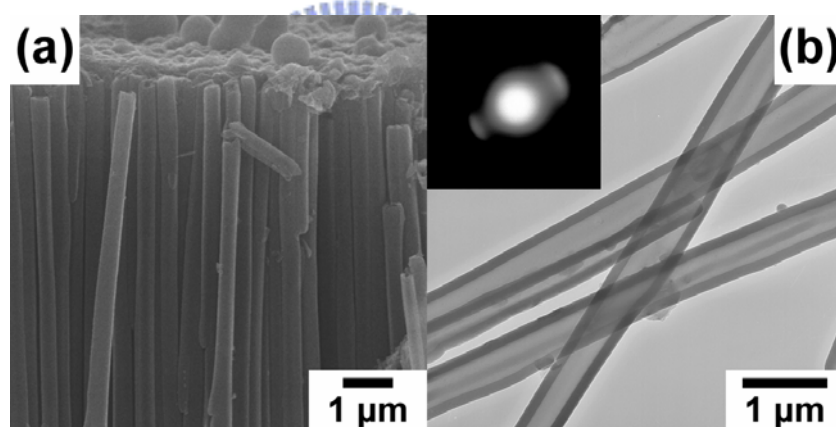

Figure 7.1 (a) SEM of a CNT array, and (b) TEM and ED of an isolated CNT grown from C_2H_2 at 1073 K. The AAO was removed.

Although C_2H_2 is thermodynamically unstable with a positive enthalpy of formation (ΔH_f^o) of 226.7 kJ mol^{-1},[9] suggesting that the decomposition of C_2H_2 into C and H_2 is exothermic, the lowest CNT growth temperature was still observed at a relatively high 773 K.[11] The decomposition of C_2H_2 in gas phase is a homogeneous process with an estimated barrier of 552 kJ mol^{-1}, which is the the C-H bond dissociation energy of acetylene, B.D.E. (HC_2-H), 552 kJ mol^{-1}.[12] With assistance of the AAO surface, the decomposition of acetylene

is estimated to be significantly lowered to 80 kJ mol^{-1}.

Table 7.1 Thermodynamic Data Related to the Study

Bond	*B.D.E. (kJ mol^{-1})*	Reference
HC_2-H	552	1
Substance	ΔH_f^o *(kJ mol^{-1})*	
C_2H_2	226.7	2
NaH	- 56.5	2
NaC_2H	98.4	3
Na_2C_2	20.1	2
Reaction	ΔH_r^o *(kJ mol^{-1})*	
$C_2H_{2(g)}$ + 2 $Na_{(s)}$ → $NaC_2H_{(s)}$ + $NaH_{(s)}$	- 240.2	2
$C_2H_{2(g)}$ + 2 $Na_{(s)}$ → $Na_2C_{2(s)}$ + $H_{2(g)}$	- 206.6	2
$C_2H_{2(g)}$ + 4 $Na_{(s)}$ → $Na_2C_{2(s)}$ + 2 $NaH_{(s)}$	- 319.5	2

B.D.E.: Bond Dissociation Energy

ΔH_f^o*: Enthalpy of Formation*

ΔH_r^o*: Enthalpy of Reaction*

Reference

1. Ervin, K. M.; Shi, Y. *Bond Dissociation Energies of the Polyynes: D$_0$(HC$_{2n}$–H) is smaller than D$_0$(HCC–H) for n > 2*, http://www.cstl.nist.gov/div838/kinetics2001/agenda/j_session/j8/j8.htm, *5th International Conference on Chemical Kinetics, 16 - 20 July 2001*, National Institute of Standards and Technology: Gaithersburg, Maryland.

2. Reaction-Web, *Facility for the Analysis of Chemical Thermodynamics*, http://www.crct.polymtl.ca/fact/, CRCT, École Polytechnique de Montréal: Montréal.

3. NIST Chemistry WebBook, *NIST Standard Reference Database Number 69 - March, 2003 Release*, http://webbook.nist.gov/chemistry/, National Institute of Standards and Technology: Gaithersburg, Maryland

Subsequently, the possibility of employing Na@AAO as a catalytic template to assist the

growth of CNT was explored. Na@AAO was prepared by filling the AAO channels with metallic Na.[7] This was achieved by decomposing powders of NaH on an AAO membrane at 623 K. The membrane turned black after C_2H_2 vapor was passed over it at 623 K. Then, the sample was washed in an aqueous solution of HF to remove the template frame. In the low magnification SEM image and the energy dispersive spectrum (EDS) in Figure 7.2 (a), formation of a well-aligned wire-shaped carbon material is observed. The wires are connected to a continuous film, which probably was formed on the topside of the template. Figure 7.2 (b) present the images from a TEM study of one of the 1D material. It has a tubular structure with a diameter of ca. 320 nm and a wall thickness of ca. 42 nm. Both the ED pattern and the high resolution TEM (HRTEM) image, shown in Figures 7.2 (b) and 7.2 (c), respectively, indicate that the sample is amorphous. In Figure 7.2 (d), the wall thickness is plotted against the growth time. It suggests that the wall thickness increased linearly from 16 to 42 nm as the growth time was increased from 1 to 3 h.
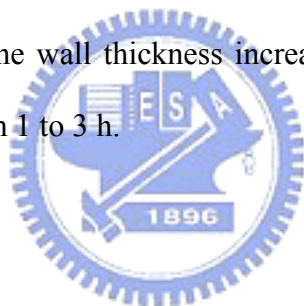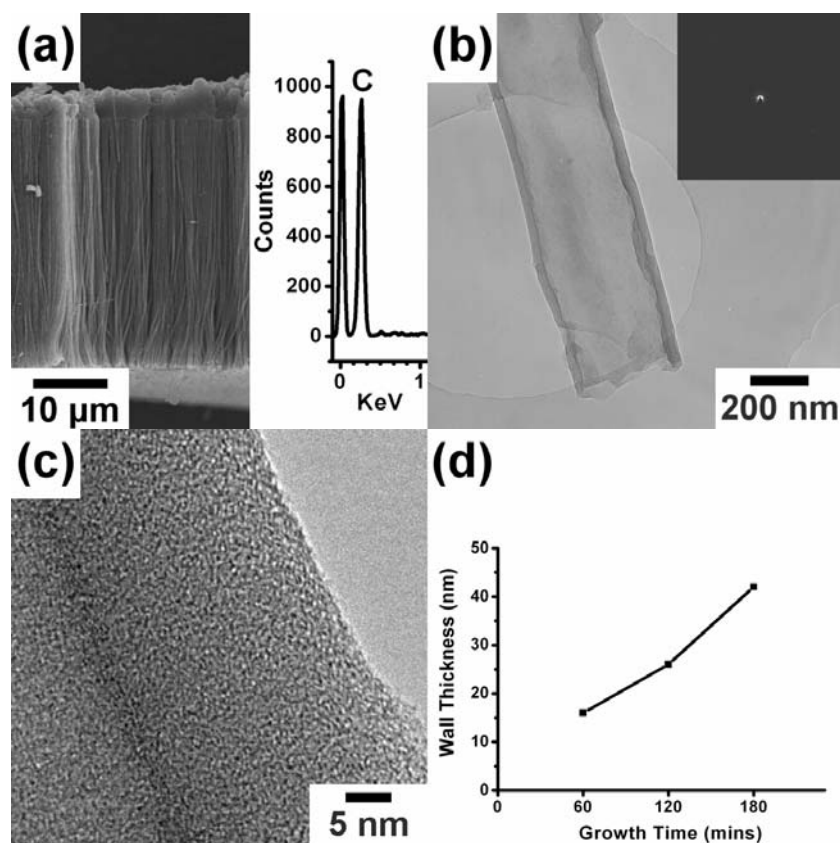
Figure 7.2 *a*-CNT deposited from C$_2$H$_2$ in Na@AAO at 623 K after the removal of AAO. (a) SEM and EDS, (b) TEM and ED of an isolated *a*-CNT, and (c) HRTEM of the wall structure; (d) wall thickness versus growth time.

Static solid-state NMR (SSNMR, Bruker DSX 400 at 100.46 MHz) studies confirmed that the CNT are composed of amorphous carbon. A typical spectrum showed two broad ^{13}C signals at chemical shift 186 and 125 ppm (chemical shift δ in ppm reference to tetramethylsilane). They are assigned to disordered and ordered graphitic carbon atoms in the solid, respectively.[13]
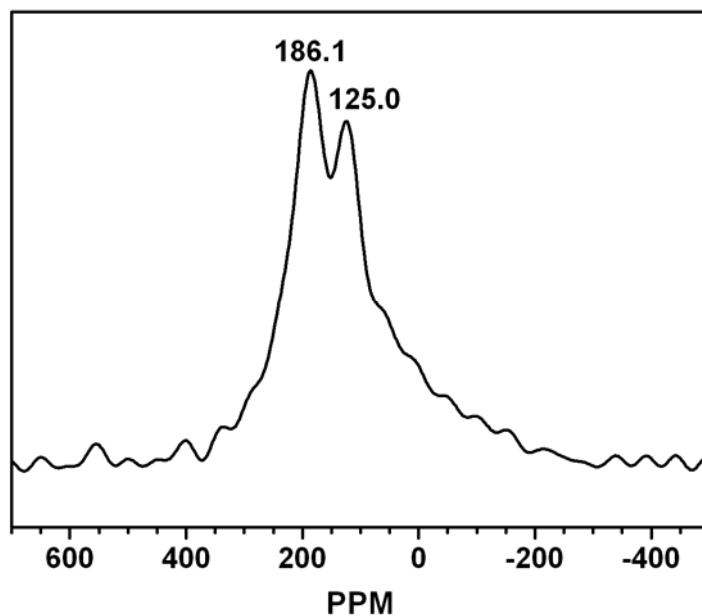
Figure 7.3 Solid state ^{13}C-NMR of *a*-CNT fabricated from C_2H_2 in Na@AAO at 623 K.

A Raman (Jabin-Yvon Raman Spectrometer T-64000, incident wavelength at 514.5 nm) scattering spectrum of the sample showed carbon G-band (1590 cm^{-1}) and D-band (1348 cm^{-1}) vibrations. The peak intensity ratio, I_D/I_G, suggests that the material is non-crystalline.[14]
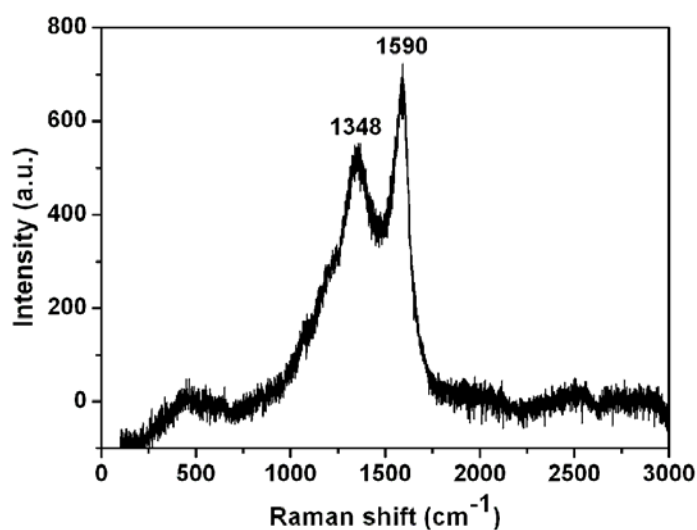

Figure 7.4 Raman spectrum of *a*-CNT fabricated from C_2H_2 in Na@AAO at 623 K.

Fourier Transform Infrared (FT-IR, Perkin-Elmer FTIR Spectrum One) spectroscopy showed broad O-H stretching at 3100 - 3650 cm^{-1}, very weak residual C-H stretching at 2880 - 2946 cm^{-1}, C=C stretching at 1612 cm^{-1} and 1573 cm^{-1}, and strong CH_2 bending at 1452 cm^{-1}.[15]
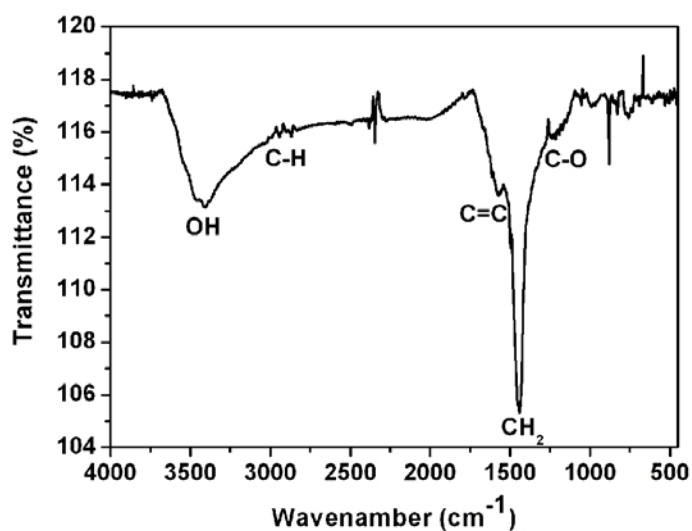

Figure 7.5 FT-IR spectrum of *a*-CNT fabricated from C_2H_2 in Na@AAO at 623 K.

A laser desorption/ionization mass spectrum (LDI-MS, Bruker Daltonics Biflex III) of the sample suggested that $(C_2)_n^+$ ions with a broad range of m/z values of several thousands were formed. This is consistent with the other spectroscopic data, supporting that the product formed in the process was an amorphous carbon material.
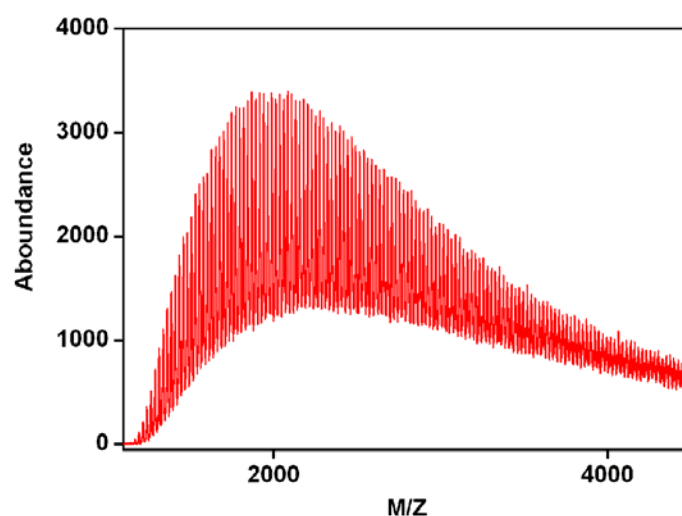
Figure 7.6 LDI-MS of a-CNT fabricated from C_2H_2 in Na@AAO at 623 K.

The experimental data above showed that the temperature of deposition of CNT from C_2H_2 in AAO has been decreased significantly after the incorporation of metallic sodium into the AAO channels. In the study, the lowest operational temperature to form a-CNT in detectable quantity was found at 323 K after Na@AAO used. The decrease in deposition temperature indicates that the activation energy of the process was lowered further. Assuming that the pre-exponential factors in the Arrhenius equation are the same for the reactions with and without the incorporation of Na in AAO, the activation energy of the former process is estimated to be 35 to 40 % lower than the later one. As mentioned above, the activation energy of the AAO assisted decomposition of C_2H_2 is estimated to be lowered to 80 kJ mol^{-1}, the activation energy of the growth of a-CNT from C_2H_2 in Na@AAO is expected to be decreased more to 48 – 52 kJ mol^{-1}. This illustrates that adding Na probably achieved the goal of finding a catalyst to assist the decomposition of C_2H_2 into a-C and H_2. A catalytic cycle is proposed in Scheme 7.1 to describe possible reaction steps. It is anticipated that C_2H_2 reacts with Na exothermically to form NaH, and sodium acetylides, NaC_2H and Na_2C_2. Then, these intermediates can decompose at elevated temperatures into a-C and H_2. This also recycles Na

back to the active metal catalyst.
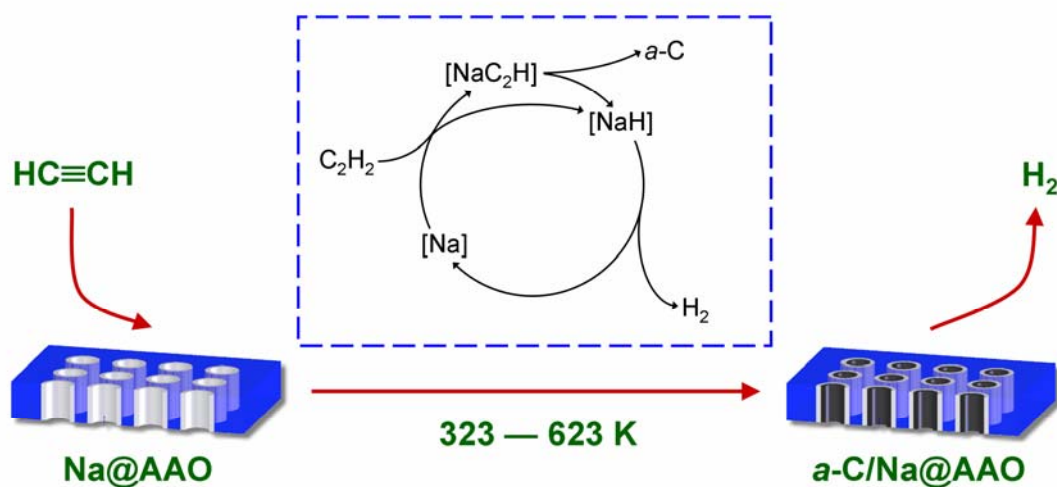
Scheme 7.1 Proposed reaction scheme and catalytic cycle.

7.4 Conclusion

In summary, by using Na@AAO as a catalytic template, we developed a novel process to deposit *a*-CNT from C_2H_2 in the channels of AAO. The overall reaction is simple, low temperature, and easy to control. Employing sodium metal into the process lowers the energy barrier of acetylene decomposition, probably by forming stable intermediates sodium hydride and sodium acetylides. At elevated temperatures, these intermediates decompose to deposit tubular shaped *a*-C, to release H_2 gas, and to regenerate the Na catalyst. The catalytic template Na@AAO not only assisted the growth of *a*-C but also guided the tubular shape development. Other alkali metals may be utilized to perform the similar task. Research is still in progress.

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