

Content

	page
English abstract	II
Chinese abstract	V
Acknowledgements	VIII
Contents of tables and schemes	XII
List of figures	XIII
Chapter 1 Introduction	1
Chapter 2 New Nanotube Synthesis Strategy – Application of Sodium Nanotubes Formed Inside Anodic Aluminum Oxide as a Reactive Template	9
Chapter 3 Elongation of Arrays of Amorphous Carbon Nanotubes	18
Chapter 4 Fabrication of Coaxial Double-Shelled SiO ₂ /C Nanotubes	25
Chapter 5 Graphitization of Carbon Nanotubes Fabricated from Na@AAO Template Method	35
Chapter 6 Anodic Aluminum Oxide Template Assisted Chemical Vapor Deposition of Carbon Nanotubes from Acetylene	45
Chapter 7 Anodic Aluminum Oxide Template Assisted Growth of Amorphous Carbon Nanotubes from Acetylene - the Role of Sodium Metal as a Catalyst	56
Chapter 8 Summary	68
Chapter 9 Synthesis and Properties of Silver Filled Carbon Nano-cables	71

Novel Synthesis of One Dimensional Tubular Carbon Materials from Reactive Template Na@AAO

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Abstract

In this thesis, I present several methods to synthesize the one dimensional materials by employing bottom-up concept relied on the chemical reduction of the reagents.

In Chapter 2, we have demonstrated a novel synthesis methodology for nanostructured materials. The reactive template strategy is exemplified by the preparation of Na@AAO and the use of it to generate high-density ordered arrays of carbon nanotube (CNT). Applications of the template structure and the halide source are discussed in the content.

In Chapter 3, we conclude that amorphous carbon tubes were prepared via a template-assisted synthesis route. First, using AAO as the substrate, short *a*-CNT arrays are grown from $\text{SiCl}_3\text{CCl}_3$ at 1073 K by low pressure chemical vapor deposition. 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 . The fabrication of heterojunctions structure of CNT arrays is discussed.

In Chapter 4, we conclude that the double-shelled amorphous SiO_2/C nanotubes were prepared via the designed synthesis route. First, using AAO as the substrate, Na nanotubes are grown by decomposing NaH at 623 K to form the Na@AAO reactive template. For the formation of the outer amorphous carbon shell, hexachlorobenzene (C_6Cl_6) is used as the C source to react with Na@AAO. Following the above Wurtz type reaction, we employed an

analogous route which deposits the Si layer in the pre-grown *a*-CNT by reacting chlorosilanes with Na@*a*-C/AAO at 623 K. After the removal of AAO by HCl, we generated well-aligned coaxial double-shelled SiO₂/C nanotubes successfully. These noble fabrications of the coaxial multi-shelled nanotubes in a controlled manner may facilitate probable building of a variety of nanodevices.

In Chapter 5, graphitization of the *a*-CNT and the porous CNT generated both tubular and fibrous products but with different yields. A possible explanation for the phenomenon is routed in the original structure of the tubes. Apparently, the CNT with a porous structure is structurally stronger and more resistant to the collapsing of the tube walls than the CNT with a hollow tubular structure. The later does not have the internal support and probably collapse more easily to form CF at high temperature. The study shows the importance of the micromorphology to the structural transformation in a high temperature process.

In Chapter 6, we have synthesized highly-ordered CNT arrays over a large area on AAO from acetylene by CVD. The growth property of carbon tubes were closely related to the structure of the deposition temperature and time. We found that the pyrolysis temperature of acetylene to deposit carbon atom starts above 773 K. Increasing the temperature of deposition to 1073 K, CNT with more ordered graphite structure can be obtained. The study provides a simple low cost, low temperature, and controllable technique to grow CNT. The highly-oriented and isolated CNT array membranes could be very useful in a variety of applications.

In Chapter 7, by using Na@AAO as a catalytic template, we developed a novel process to deposit *a*-CNT from C₂H₂ in the channels of AAO. 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 H₂ gas, and to regenerate

the Na catalyst. The catalytic template Na@AAO not only assisted the growth of α -C but also guided the tubular shape development.



利用活性模板Na@AAO製備一維管狀碳材料

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摘 要

本研究提供多樣性之化學合成法，成功地製備出各式一維奈米材料。

在第二章節中，我們研發出一種合成奈米結構材料的新穎方法。製備Na@AAO的反應性模板並用來合成出高密度且整齊陣列的奈米碳管。同時，並討論結合模板與鹵化物前驅物的相關應用。

第三章中，我們利用模板合成法成功地合成出非晶質奈米碳管。首先，利用SiCl₃CCl₃當作前驅物在1073 K下以低壓化學氣相沉積法先在陽極處理氧化鋁模板上形成短的非晶質奈米碳管，接著在氧化鋁模板的孔洞中先製備出反應性模板，並在通過C₆Cl₆後成功的得到增長型奈米碳管陣列。碳管陣列的異接合結構製備亦在文中探討。

第四章中，我們藉由經過設計的反應途徑成功地得到雙層結構的非晶質SiO₂/C奈米管。首先使用陽極處理氧化鋁當作模板，在623 K下將氫化鈉裂解形成Na@AAO的反應性模板並與六氯苯反應後先得到外層的非晶質碳管。接著沿用伍茲反應，我們利用相似的過程將矽氯烷與Na@a-C/AAO在

623 K下反應並在先前製備出的非晶質碳管上沉積矽層。在利用氫氟酸移除陽極處理氧化鋁後，我們成功地得到筆直排列的共軸型雙層SiO₂/C奈米管。在高度精控所得到的共軸型多層SiO₂/C奈米管，將能在奈米元件上有多樣性的應用。

在第五章中，非晶質奈米碳管與孔洞型奈米碳管經過石墨化後會得到不同比例的管狀與纖維狀產物。合理的去解釋此現象乃是由於原先奈米管的結構變化而來。顯然的，多孔洞型結構的奈米碳管比空心的奈米碳管具有較強的結構特性去阻抗管壁的崩潰。後者沒有內部結構的支撐，在高溫下更容易崩潰形成碳纖維結構。此研究顯示了微米形貌在高溫過程下結構轉變的重要性。



在第六章中，我們使用乙炔氣體當作反應氣體，以化學氣相沉積法在陽極處理氧化鋁中形成大面積且排列整齊的奈米碳管。奈米碳管的結構成長特性與沉積溫度和時間息息相關，我們發現到溫度到達773 K時乙炔會開始裂解並沉積碳。當溫度升高至1073 K時，我們可以發現更加石墨排列的奈米碳管。此研究中，我們提供了一種簡易、低廉、低溫並且容易控制的技術成長奈米碳管，此高度整齊排列的奈米碳管陣列薄膜能具有多樣性的應用。

在第七章中，利用Na@AAO當作催化性模板，我們研發出一種經由乙炔氣體在陽極處理氧化鋁模板的孔道中形成非晶質奈米碳管。使用金屬鈉

可以降低乙炔的沉積能障，並形成穩定的中間產物氫化鈉與乙炔鈉，當提升溫度後，這些中間產物會進行裂解以形成管狀形貌的非晶質碳，同時間釋出氫氣並獲得鈉催化劑。使用催化性模板Na@AAO不僅可以幫助形成非晶質碳並且可以引領形成一維管狀材料。



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Content of Tables and Schemes

		Page
Chapter 1		
Table 1.1	Summary of fabrication methods of CNT and coaxial structure.	5
Chapter 2		
Scheme 2.1	Reaction steps of forming Na@AAO and <i>a</i> -C/AAO.	12
Chapter 3		
Scheme 3.1	Scheme of elongating <i>a</i> -CNT.	23
Chapter 4		
Scheme 4.1	Summary of reaction steps.	32
Chapter 6		
Table 6.1	Summary of AAO assisted CVD of CNT.	45
Scheme 6.1	CNT formation process.	46
Chapter 7		
Table 7.1	Thermodynamic Data Related to the Study	59
Scheme 7.1	Proposed reaction scheme and catalytic cycle.	65
Chapter 9		
Scheme 9.1	Proposed pathway to form Ag@C nanocables.	85

List of Figures

		Page
Chapter 1		
Figure 1.1	The variety of carbon.	3
Chapter 2		
Figure 2.1	Cross-sectional SEM image of Na@AAO after brief exposure to air. The inset shows EDS of elemental distribution inside a channel.	11
Figure 2.2	(a) Cross-sectional view of <i>a</i> -CNT arrays inside AAO channels.(b) Bundles of <i>a</i> -CNT after removal of AAO by 48 % HF.	13
Figure 2.3	(a) TEM image of an <i>a</i> -CNT prepared at 623 K and annealed at 1073 K. (b) HRTEM image of the wall of the open end.	14
Figure 2.4	TEM image of an <i>a</i> -CNT prepared at 623 K.	14
Figure 2.5	TEM image of an <i>a</i> -CNT prepared at 623 K and annealed at 1073 K.	15
Figure 2.6	HRTEM image of the wall of an <i>a</i> -CNT prepared at 623 K and annealed at 1073 K.	15
Figure 2.7	HRTEM image of the wall of the open end of an <i>a</i> -CNT prepared at 623 K and annealed at 1073 K.	16
Chapter 3		
Figure 3.1	SEM images of (a) top and (b) side view of short <i>a</i> -CNT arrays grown from SiCl ₃ CCl ₃ at 1073 K by LPCVD after AAO is removed.	20
Figure 3.2	SEM images of an elongated <i>a</i> -CNT. (a) Side view and (b) enlarged view of the region marked by arrow in (a).	20
Figure 3.3	TEM and ED images of elongated <i>a</i> -CNT. (a) Arrow 1 marks <i>a</i> -CNT formed by LPCVD and Arrow 2 shows the section formed by the reactive template method. (b) A well-aligned <i>a</i> -CNT bundle, (c) Magnified view of area marked by Arrow 3. (d) Magnified view of area marked by Arrow 4.	22

Figure 3.4	Raman spectrum of elongated <i>a</i> -CNT.	23
Chapter 4		
Figure 4.1	SEM of a bundle of SiO ₂ /C nanotubes, and (b) TEM and ED of an isolated SiO ₂ /C nanotubes grown from SiCl ₄ in Na@AAO at 623 K. The AAO was removed. (c) SEM of SiO ₂ /C nanotubes, and (d) TEM and ED of an isolated SiO ₂ /C nanotubes deposited from Si ₂ Cl ₆ in Na@AAO at 623 K. The AAO was removed.	28
Figure 4.2	Representative EELS shown the existence of (a) C K-edge (284.0 eV), O K-edge (533.3 eV) and (b) Si K-edge (1841.4 eV) within the aligned double-shelled SiO ₂ /C nanotubes generated by reacting SiCl ₄ (lower curve) and Si ₂ Cl ₆ (upper curve) with Na@AAO at 623 K.	29
Figure 4.3	(a) TEM zero-loss image of an isolated SiO ₂ /C nanotubes grown from SiCl ₄ at 623 K, (b) elemental C mapping of the image shown in (a), and (c) elemental Si mapping of the image shown in (a); (d) TEM zero-loss image of aligned double-shelled SiO ₂ /C nanotubes obtained from Si ₂ Cl ₆ at 623 K, (e) elemental C mapping of the image shown in (d), and (f) elemental Si mapping of the image shown in (d).	30
Figure 4.4	An isolated SiO ₂ /C nanotubes TEM image. The double-shelled nanotubes consists an outer C layer and an inner SiO ₂ layer.	31
Chapter 5		
Figure 5.1	Images of a CNT array grown from C ₆ Cl ₆ (a) SEM, (b) TEM and ED (inset); and from C ₆ F ₆ (c) SEM, (d) TEM and ED (inset) after AAO is removed	37
Figure 5.2	Morphology of the materials grown from C ₆ Cl ₆ after annealed at 3073 K. SEM images of (a) CNT and (b) CF; (c) TEM image of a section of a CNT; and (d) TEM, HRTEM and ED (insets) of a CF.	38

Figure 5.3	Morphology of the materials grown from C_6F_6 after annealed at 3073 K. SEM images of (a) CNT and (b) CF; (c) TEM and ED (inset) of a section of a CNT; (d) and (e) HRTEM images of areas selected from (c); and (f) TEM and ED (inset) of a CF.	40
Figure 5.4	XRD of samples prepared from C_6Cl_6 and C_6F_6 after graphitization at 3073 K.	41
Figure 5.5	Raman spectra of samples grown from (a) C_6Cl_6 and (b) C_6F_6 before and after heat treatment at 3073 K.	42
Chapter 6		
Figure 6.1	Photographs of CNT containing AAO membranes. Deposited at (a) 773, (b) 873, and (c) 1073 K. SEM images of CNT containing AAO membranes. Grown at (d) 773, (e) 873, and (f) 1073 K.	48
Figure 6.2	Electron micrographs of AAO-free CNT. Grown at 773 K, (a) SEM image of a bundle of CNT, (b) TEM image of some CNT, and (c) HRTEM image of wall structure of CNT shown in (b). Grown at 1073 K, (d) SEM image of a bundle of CNT, (e) TEM image of some CNT, and (f) HRTEM image of wall structure of CNT shown in (e).	49
Figure 6.3	Montage of TEM images of an individual CNT grown at 873 K.	50
Figure 6.4	Arrhenius plot of CNT growth inside AAO channels from C_2H_2 .	51
Figure 6.5	FT-IR spectrum of CNT fabricated at 773 K.	52
Figure 6.6	LDI-MS spectra of CNT grown at 773 – 1073 K.	53
Chapter 7		
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.	58
Figure 7.2	<i>a</i> -CNT deposited from C_2H_2 in Na@AAO at 623 K after the removal of AAO. (a) SEM and EDS, (b) TEM and ED of an isolated <i>a</i> -CNT, and (c) HRTEM of the wall structure; (d) wall thickness versus growth time.	61

Figure 7.3	Solid state ^{13}C -NMR of <i>a</i> -CNT fabricated from C_2H_2 in Na@AAO at 623 K.	62
Figure 7.4	Raman spectrum of <i>a</i> -CNT fabricated from C_2H_2 in Na@AAO at 623 K.	62
Figure 7.5	FT-IR spectrum of <i>a</i> -CNT fabricated from C_2H_2 in Na@AAO at 623 K.	63
Figure 7.6	LDI-MS of <i>a</i> -CNT fabricated from C_2H_2 in Na@AAO at 623 K.	64
Chapter 8		
Figure 8.1	Chemical reactions involved in the process of preparing CNT from AAO template.	69
Figure 8.2	Further fabrications of complex CNT based structures.	70
Chapter 9		
Figure 9.1	(a) SEM image of Ag@C nanocable bundles synthesized by 10 % Ag powder with carbon black using arc discharge method. (b) Enlarge image of nanocable tip. (c) Ag@C nanocables synthesized by pure Ag powder. (d) Ag@C nanocables synthesized by pure Ag rod.	75
Figure 9.2	Low magnification TEM image of (a) an individual Ag@C nanocable with Ag@C ball and (b) Ag@C nanocable bundle. (c) TEM image of an individual purity single crystalline nanocable. HRTEM images of (d) a Ag@C nanocable with about 6 nm graphite sheets and (e) the core lattice image from (c). (f) The correspondind SAED pattern indicates [100] growth direction.	77
Figure 9.3	(a) A typical TEM image of the Ag@C nanocable with a graphite shell. (b) EDXS indicates the composite of nanocable by C and Ag. (c) The HADF z-contract image made from (a), showing the bright region is Ag and (d) the elemental profile taking across a nanocable.	79

Figure 9.4	The raw materials formed in 100 torr of hydrogen and with 30 V dc (100 A) supply. (a) SEM image of carbon nanotubes unfilled with Ag and the insert EDXS indicates it is made of carbon. Low magnification TEM images of (b) insular CNTs after using supersonic, (c) a CNT bundle and (d) Ag nanoparticles.	80
Figure 9.5	Typical EELS spectra were taken from part of a nanocable with a diameter about 100 nm. (a) zero-loss and (b) core-loss spectrum.	81
Figure 9.6	EELS plasmon spectra obtained on a part of (a) a pure Ag@C nanocable and (b) a CNT unfilled with Ag.	82
Figure 9.7	The position of the Ag plasmon peaks were plotted against the diameters of the Ag@C nanocables.	83
Figure 9.8	The <i>I-V</i> property of a Ag@C nanocable. The insert shows a SEM image of an individual nanocable across two parallel gold electrodes.	83

