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The growth of carbon nanotubes at predefined locations using whole nickel nanowires as templates

Han Gao, Jianyi Lin^{*}, Hui Pan, Guotao Wu, Yuanping Feng

Department of Physics, National University of Singapore, 10 Kent Ridge Cresent, Singapore 119260, Singapore

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Abstract

In this process carbon nanotubes were prepared by the pyrolysis of a gaseous hydrocarbon in contacting with Ni nanowires, which were typically a few microns long, electrochemically produced from an anodic aluminium oxide template. Under controlled conditions, carbon nanotubes were formed at the location of the Ni-nanowire template. They inherited the shapes of the Ni nanowires, with their inner diameter being same as the outer diameter of the Ni nanowires. A novel growth mechanism which involves the diffusion of Ni atoms and the reshape of Ni nanowires is discussed.

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1. Introduction

Since the first discovery in 1991 [1], carbon nanotubes (CNTs) have stimulated tremendous development of nanomaterials and nanotechnology. Large amount of researches have demonstrated the potential application of CNTs in many fields including nanoscaled electronic and optoelectronic devices, sensors, composite materials, and energy storage [2]. But from the viewpoint of practical applications there remain many issues to be addressed, for instance, bulk synthesis of CNTs with prescribed size and predefined structure, manipulating CNT to the desired locations, and assembling them to form special structure among others.

Among four main approaches: arc-discharge [3], laser ablation [4], chemical vapour deposition (CVD) [5–7] and high pressure carbon monoxide process (HiPco) [8], CVD is a popular method for mass and site-controllable production of CNTs. By CVD the diameter distri-

* Corresponding author. Fax: +65-6777-6126.

E-mail address: phylinjy@nus.edu.sg (J. Lin).

bution of CNTs can be controlled to some extent [5]. In particular by using porous anodic aluminium oxide (AAO) as a template, highly ordered, size-controllable CNTs array can be grown from the pyrolysis of a gaseous carbon-containing material [9–13]. Unfortunately, this kind of CNTs is normally ill-graphitized, consisting of numerous stacked carbon flakes [14] since the AAO itself can catalyze the pyrolysis of the carbon-containing gas into amorphous carbon film on the walls, blocking the formation of well-graphitized CNTs.

In this Letter, we report a novel process to grow CNTs, using whole Ni nanowires as templates. The Ni nanowires were prepared by AAO-templated electrochemical deposition. CNTs were then synthesized from the decomposition of C_2H_2 on the Ni nanowires. The outer diameter and length of CNTs were controllable, correlated with the AAO channels. More exactly, the CNTs were grown at the initial location of Ni nanowire templates. Their size and shape were tallied with the Ni nanowire. Moreover the grown CNTs were shown to be well graphitized. This novel method therefore exhibits a potential for the structure-predefined, size-controllable growth of CNTs. For instance it is possible to prepare a Ni nanostructure of designed patterns, using a routing

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lithography technology. Alternatively, with the assistance of magnetic-field [15] or electric-field techniques [16], it is possible to manipulate an individual Ni nanowire into a specific location. The subsequent CVD growth then enables to fabricate CNTs at the predefined location and with predefined shape.

As discussed later in this Letter the growth mechanism of CNTs during the above process may be different from the generally accepted vapour-liquid-solid (VLS) process [6,7,17–20]. In VLS, growth occurs via the decomposition of carbon-containing molecules on the surface of metal catalyst nanoparticles, the bulk diffusion and dissolution of carbon species in metal particles, and the precipitation of saturated dissolved carbons from the metal particle surface. This growth mechanism was recently challenged by a time-resolved, in situ highresolution TEM study of carbon nanofibre growth on supported Ni nanoparticles [21]. In the latter growth scenario Ni nanoclusters tended to transfer their initial equilibrium shape into a highly elongated shape. Ni step edges at the surface played a key role in the nucleation and growth of graphene sheet. Carbon atoms generated at the step edge sites diffused to and finally bonded to the graphene, which were developed through a reaction-induced elongation/contraction reshaping of the Ni nanocrystals. Our novel synthesis process appears to follow the new growth mechanism, since the reshape of Ni nanowires, i.e., the transfer from the elongated wire to round particles, were evidently observed by our SEM image.

2. Experimental

Ni nanowires, here serving as templates for preparing CNTs, were made by the electrochemical deposition of nickel into nanochannels of the AAO template [22]. Both-side-opened AAO were prepared following the previously reported method [9,10]. In order to improve the quality and uniformity of Ni nanowires, we first coated one side of the AAO template with a Pt film of less than 10 nm thickness by ion sputtering (JFC-1600 Coater). Then the coated side was subject to electroplating in a solution containing 300 gL^{-1} NiSO₄· $6H_2O$, 50 gL⁻¹ HBO₃ at 60 °C for 5–10 min till a thick nickel film was formed. This nickel film served as a working electrode to further electrodeposit Ni into the pores of AAO at the same solution and conditions as in the first step. The Ni-embedded AAO sample was then treated in a $3 \text{ mol } L^{-1}$ NaOH solution to fully remove the AAO template, followed by repeat rinse with distilled water till the water pH 7. They were then dispersed on a silicon wafer for the use in growing CNTs and the observation of their morphology under a scanning electron microscope (SEM, JSM-6700F). TEM (Philips-CM100)

sample is prepared by dropping the solution on a copper grid.

The silicon wafer with Ni nanowires was placed in a horizontal quartz tube reactor for growing CNTs. The sample was heated by a rate of 10 °C min⁻¹ in a 5% H_2/Ar flow of 100 mL min⁻¹. After the reactor temperature reached 700 °C, an ethylene flow of 5 mLmin⁻¹ was introduced for 10 min, and meanwhile the flow rate of the carrier gas was also increased to 300 mLmin⁻¹. Subsequently, the reactor was cooled down to room temperature in the 5% H₂/Ar gas. The as-grown CNTs were then burned in the air at 500 °C to remove amorphous carbon, and immersed in a HCl (v:v 1:1) solution for 2 h to dissolve Ni (or nickel oxide). The as-grown and post-growth-treated CNTs on the silicon wafer were directly observed under SEM. A Renishaw Raman Spectrometer 1000 with an excitation wavelength at 514 nm was employed to study the prepared CNTs. For TEM and HRTEM (Philip CM300) observation, the CNT/silicon wafer was sonicated in ethanol for a few minutes to make the CNTs dispersed in the solution and then dropped it on a copper grid.

3. Results and discussion

Fig. 1a is a SEM image of Ni nanowires dispersed on a silicon wafer, and Fig. 1b is a TEM image of an individual Ni nanowire. All the Ni nanowires in our sample are very straight, having uniform sizes with the average length and diameter around 20 µm and 40 nm, respectively. Nevertheless by varying the preparation conditions for the AAO template the diameter and length of Ni nanowires can be easily controlled [9–13]. The polycrystalline nature of the Ni nanowires was confirmed by selected-area electron diffraction (SAD). Fig. 1c is a SEM image of as-prepared CNTs on the silicon wafer. It is interesting to note that after the CVD process CNTs were grown at the place of the Ni nanowires. There were no Ni nanowires to survive, but attached many round-shaped nanoparticles, which are graphite-encapsulated nickel (see Fig. 4b). After the post-growth acid treatment, the round-shaped nanoparticles were dissolved in HCl solution, and the hollow core of the CNTs can be clearly observed in Fig. 1d. The grown CNTs inherit the shape of Ni nanowires. Unlike the conventional CNTs, they look very straight and uniform. As measured by SEM and shown in Fig. 1e most (>80%) of the CNTs have outer diameter in the range of 55-60 nm. Considering that the mean wall thickness of the CNTs is about 10 nm (see Fig. 2b,c), the inner diameter of the CNTs ranges mostly between 35 and 40 nm, basically consistent with the outer diameter of the Ni nanowire templates. (Note that the inner diameter of the CNT in Fig. 2b is almost of the same size as the outer diameter of the Ni nanowire in Fig. 1b.) To further demonstrate the diameter controllability of our CNT growth,

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Fig. 1. (a) SEM image of Ni nanowires liberated from AAO templates and dispersed on the silicon wafer for growing CNTs. (b) TEM image of a Ni nanowire with a diameter of about 40 nm. (c) SEM image of the as-prepared CNTs on the silicon wafer. (d) SEM image of the post-grown treated CNTs on the silicon wafer. (e) Outer diameter distribution of CNTS.

we have been able to prepare the CNTs with different inner diameters in the range of 20–60 nm by varying the diameter of AAO nanopores (and hence that of Ni nanowires). Adjusting the concentration of Ni nanowire/ethanol solution, we can disperse only a few pieces of Ni nanowires on a silicon wafer, and hence grow only a few pieces of CNTs on the silicon wafer (see Fig. 3a). Though the CNTs still keep the location of the Ni-nanowires template, the tube is broken at several places along the tubes, with small round particles attaching at the brokenness. In the case that the Ni nanowires are only partially liberated from the AAO template, they would be standing in vertically alignment on the AAO template base. Fig. 3b is a SEM image of the as-prepared aligned CNTs arrays from standing Ni nanowires array. This result implies that we can produce individual CNTs in the designed locations where individual Ni nanowires are placed prior to the CVD process.

Fig. 2 displaces the results of the structural characterization of the CNTs. The Raman spectrum in Fig. 2a shows two sharp peaks at 1580 (G line) and 1345 (D line) cm⁻¹ with a relative intensity of 1.44 (I_G/I_D). The strong peak at 1580 cm⁻¹ is attributed to the crystalline graphite structure while the D lines being regarding as disorder-induced features due to the finite particle size effect or lattice distortion [23–25]. The TEM images in Figs. 2b,c reveals the tubular structure of the as-prepared carbon nanotubes, with a hollow core of ~ 40 nm in diameter and a multiple-layered wall of ~ 10 nm in thickness. Only one side of the tube wall was shown in Fig. 2c, as the diameter of the CNT is large. The wall of the CNT consists of many crystalline domains with average domain size of 30 nm. It seems that our CNTs have more defects than conventional CNTs but less defects than those CNTs directly grown by the pyrolysis of C_2H_4 on AAO template [9,10,14]. The graphitized structure can also be demonstrated by a typical SAD pattern (inset in Fig. 2b), with an interlayer separation of about 3.4 Å, similar to that of graphite (d_{002} =3.35 Å).

The growth of CNTs using whole Ni nanowires as templates appears to follow different mechanism from the typical VLS process. We have carried out the following 5 tests to probe the growing mechanism. In the first test, Ni nanowires/silicon wafer was heated to 700 °C in



Fig. 2. (a) Raman spectrum of the post-grown treated CNTs. (b) TEM image of CNT with an inner diameter of 40 nm, inset is a typical electron diffraction pattern of as-prepared CNT. (c) HRTEM image of one side of CNT walls with a mean thickness of 10 nm.

a 5% H₂/Ar flow of 100 mLmin⁻¹ without introducing any hydrocarbon reactant, and we found that Ni nanowires were stable at 700 °C, without any round Ni particles appearing. In the second test, after the reactor temperature reached 700 °C, an ethylene flow of 5 mLmin⁻¹ was introduced for 2 min, which was shorter than the 10 min for producing the sample shown in Fig. 2. The SEM image of the product in the second test (see Fig. 4a) show that some Ni nanowires are wrapped by CNTs while some have been reshaped and aggregated into Ni particles, leaving a hollow core under the CNT shell (see the arrows in Fig. 4a). If the supply of ethylene was long (10 min), the Ni particles continuously grew



Fig. 3. SEM imges of (a) sparse as-prepared CNTs lying on silicon wafer and (b) aligned standing CNTs array fabricated from aligned Ni nanowires array.

and would later break out from defects of the CNT shell, as shown in Fig. 3a. In the third test, longer reaction time (20 min for example) was applied, the breaking-out Ni particles then became the centers for subsequent CNT growth. The second-generation CNTs have smaller tube diameter (commonly 20 nm) as compared to that of the CNTs grown from Ni-nanowires template (40 nm in this case). The catalytic decomposition of ethylene on Ni nanowires was found to start at as low temperature as 400 °C in our experiments. In the fourth test, the CVD was carried out on Ni nanowires/silicon wafer at 500 °C for 20 min. The SEM image in Fig. 4c show that the Ni nanowires have transferred into Ni particles and squeezed out from the carbon nanotubes. The carbon product in this figure actually is an amorphous carbon with low mechanical strength, which was easily broken into pieces when subjected to a sonicate treatment for preparing TEM sample. We can also find in the figure many small-sized CNTs (or carbon filament) grown from the squeezing-



Fig. 4. (a) SEM image of CNTs prepared by a very short time of ethylene pyrolysis. (b) TEM image of graphite-encapsulated Ni particles, inset is a HRTEM image of graphene layers; SEM images of (c) the sample prepared at 500 °C. (d) The CNTs prepared with high volume ratio of ethylene vs. carrier gas.

out Ni nanoparticles due to long reaction time. In the fifth test, after the reactor temperature reached 700 °C, an ethylene flow of 15 mL min⁻¹ (vs 5 mL min⁻¹ in the above tests) was introduced for 5 min with a 5% H₂/Ar flow of 100 mL min⁻¹ to grow CNTs on silicon wafer. The SEM image in Fig. 4d shows no Ni-nanowire-templated CNTs (which are straight and 40 nm in diameter). However, curly and randomly oriented CNTs with diameter far less than 40 nm are found along the location of Ni nanowires. These CNTs were apparently grown according to conventional VLS mechanism on the metal nanoparticles instead on the whole nanowires.

On the basis of the above five tests, we proposed a growth mechanism for the CNTs prepared by using Ni nanowires as templates. In this scenario ethylene is first pyrolyzed on the surface of Ni nanowires. The precipitation of carbon starts with the development of oversaturated Ni–C alloys on the surface of the Ni nanowires [17,18]. The growth of graphene layers takes place first on the surface of Ni nanowires while the bulk of Ni nanowires remains intact (see the first step in Fig. 5). The grown CNT covers the Ni nanowire forming CNT shells which inherit the shape of Ni nanowires, and their inner diameter is determined by the outer diameter of Ni nanowires. This growth process is driven by the energy gain when binding the grapheme sheet to the Ni surface.



Fig. 5. Schematic illustration of growth mechanism for the CNTs prepared by using whole Ni nanowires as templates.

The growth ceases when the graphene layers eventually encapsulate the Ni nanowire. In the case that the graphene sheets are not completely closured while Ni nanowires are kept in the contact with ethylene at 700 °C for longer time (such as those in Test 2), the continuous increase of dissolved carbon may result in the development of bulk Ni–C alloys. Density of functional theory (DFT) predicts that the carbon–Ni bonding energy is larger than the energy cost for Ni–carbon interface step formation [21]. Hence the diffusion of Ni atoms along interface towards the free surface is energetically favourable, and may finally cause the reshape of Ni into particles appearing at the brokenness along the carbon tube (see the second step in Fig. 5), and leaving behind the CNTs with a hollow core of the same diameter. This process is very similar to that in [21], in which Ni particles were elongated to align graphene layers into a tubular form, and then contract back towards particles when the increasing Ni surface energy during the elongation cannot be compensated by the energy gained from biding the graphitic fibre to the nickel surface. In our attempts, the low ratio of ethylene vs. carrier gas at the beginning of the growth was necessary to ensure the graphene layers occurring only on the surface of Ni nanowires. Alternatively, with a high ratio of ethylene vs. carrier gas at the beginning, the speeds of the ethylene decomposition and the liquid Ni-C alloy formation could be so fast that Ni nanowires reshaped to Ni particles immediately along the their original locations without forming nanotube shell, and curly, small-sized CNTs will be grown from these particles, as seen in the fifth test. If the growth temperature is relatively low (such as 500 °C in the fourth test), carbon atoms are either difficult to be dissolved into Ni nanowires or do not diffuse fast inside the Ni nanowires, which results in an amorphous carbon coating [26].

4. Conclusions

In summary, we have demonstrated a novel process to prepare CNTs by using whole Ni nanowires as a template. This process shows the potential of controllable growth of CNTs at predefined locations and with predefined size. High temperature and low volume ratio of ethylene vs. carrier gas are the appropriate conditions for growing higher quality CNTs. The growth of carbon nanotubes may follow a new mechanism which involves the diffusion of nickel atoms and the reshape of nickel.

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