Entrapping of Inclusions Within Carbon Nanotubes During Catalytic Decomposition of C$_2$H$_4$ on a “Thick” Nickel Film

Feng Ji Li$^1$, Sam Zhang$^1$,* Geng Zhi Sun$^1$, Jun Hua Kong$^2$, R. S. Rawat$^3$, Usman Ilyas$^3$, and Bo Li$^4$

$^1$School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
$^2$School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
$^3$NSSE, NIE, Nanyang Technological University, 1 Nanyang Walk 637616, Singapore
$^4$Central Iron and Steel Research Institute, 76 South Xueyuanlu Road, Haidan District, Beijing, 100081, China

To understand the formation mechanism of catalyst inclusions in carbon nanotubes, multi-walled carbon nanotubes were grown via catalytic decomposition of C$_2$H$_4$ on a 50-nm-thick nickel film at 725 °C. Atomic force microscopy, glancing incidence X-ray diffraction, field emission scanning electron microscopy, and high resolution transmission electron microscopy were employed to examine the evolution of the nickel film and the structure of the nanotubes. It was found that pretreating of the nickel film resulted in lots of small nanoparticles extruding on the surface, among big ones, serving as seeds for the growth of tubes. The inner walls of a few tubes were sealed internally by multiple elongated “beads-like,” “bullet-shaped” or “needle-shaped” nickel inclusions. The inclusions retained the face-centered-cubic crystalline structure of the as-sputtered nickel film. The entrapping of nickel inclusions is explained by a continuous tip growth model. A conservative upper limit of the nickel layer thickness (50 nm) was estimated for growing high purity carbon nanotubes.

**Key Words:** Catalytic Decomposition, Multi-Walled Carbon Nanotube, Nickel Nanoparticle, Tip Growth Model.

1. INTRODUCTION

Carbon nanotubes (CNTs) are well known as the strongest among the known materials,$^{1,2}$ of unique biocompatibility,$^3,4$ large field emission area,$^5,6$ excellent electronic transport,$^7,8$ and good electrochemical properties,$^9,10$ thus making them promising in a wide range of applications. Nanotubes with near-perfect microstructure yield composite materials with compressive-to-tensile strengths approaching unity,$^{11,12}$ whereas nanotubes containing a small fraction of the metal inclusions in the tubes or tending to have defects along the tube walls would reduce both their electrical and structural properties. Defects within the nanotube degrade the effective band overlap and therefore carrier density, leading to an increase in the material’s electrical resistivity. Therefore, growth of high purity CNTs with the lowest amount of catalyst inclusions and defects plays an important role in providing better electrical and structural properties, thus helps the introduction of these materials into practical application.$^{12,13}$ CNTs could be of a single-walled or multi-walled, synthesized via arc-discharge,$^{12,13,15}$ laser ablation,$^{16,17}$ plasma enhanced chemical vapor deposition,$^{19,20}$ or hot filament chemical vapor deposition (HFCVD).$^{21,22}$ As a non-plasma technique, HFCVD allows CNTs to be grown in predefined locations such as those on silicon (Si) substrate for electronic applications, in turn providing a certain control of the nanotube types, rendering the highest chance of commercial success. However, lots of materials and processing variables lead to the intricacy of the nanotube synthesis and the incomplete understanding of the growth of carbon nanotubes.$^{23}$ On one hand, the size of the catalyst particle controls the final structure of CNTs. The critical size of nickel (Ni) catalyst for growing single-walled, multi-walled CNTs and bamboo-like CNTs is reported...
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...were shut off and the reactor chamber was naturally cooled down.


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2. EXPERIMENTAL DETAILS

2.1. Deposition of the Nickel Film

A layer of Ni (as catalyst) was sputtered on Si (100) wafer (of roughness 0.5 nm) in an E303A magnetron sputtering system (Penta Vacuum, Singapore) from a Ni target (101.6 mm in diameter, and 99.999 at.% in purity). The Si wafer was ultrasonically cleaned for 20 min with acetone followed by 10 min in ethanol before loading into the chamber, followed by a 20 min pre-deposition plasma etching at a radio frequency induced bias voltage of −300 V to remove possible surface oxides and contaminants. A direct current power density of 1.85 W/cm\textsuperscript{2} was applied for 60 min at the Ni target for a Ni film of approximately 50 nm in thickness. Details of the deposition parameters are tabulated in Table I.

2.2. Growth of Carbon Nanotubes

After the deposition, the Ni-coated Si wafers were placed in a hot filament chemical vapor deposition chamber and ramped up to 725 °C in a H\textsubscript{2}/Ar gas mixture respectively flowing at 25 and 100 standard cubic centimeters per minute (sccm) within 12 min. At the temperature, the flow of the H\textsubscript{2}/Ar gas mixture was held for 5 min to prevent oxidation of the Ni. During this time, the Ni catalyst nanoparticles/spikes form on the surface. Then the reaction gas flow of C\textsubscript{2}H\textsubscript{2}/H\textsubscript{2}/Ar gas mixture was introduced into the chamber at 25/25/100 sccm to start the CNT growth. The temperature was maintained at 725 °C during the growth. 20 min later, the C\textsubscript{2}H\textsubscript{2}/H\textsubscript{2} gas supplies were shut off and the reactor chamber was naturally cooled down.
to 250 °C in an Ar (100 sccm) atmosphere for 10 min. Table I presents the details of the growth process.

### 2.3. Characterization

The cross section of the as-sputtered Ni catalyst film was observed by field emission scanning electron microscopy (JEOL JBM-6340F, JEOL Ltd., Japan). Atomic force microscopy (Simadzu SPM-9500J2, Simadzu Pte., Ltd., Asia Pacific) was employed to observe the surface morphologies of the before and after pretreatment. The crystalline structure of the as-sputtered Ni film was examined by glancing incidence X-ray diffraction (PANalytical B.V., Almelo, Netherlands) with monochromatic copper Kα radiation (40 kV and 40 mA) at wavelength of 0.15406 nm using an incidence angle of 1°. The scanning range is conducted from 40° to 120° at step size 0.02° and 1 second per step. The structure of the as-grown CNT and the inclusions was examined by high resolution transmission electron microscopy (TEM, JEOL 2010, JEOL Ltd., Japan), and the equipped selected area electron diffraction (SAED). HRTEM samples were prepared by using a sharp stainless tweezers to scratch the as-grown CNTs off the substrate surface into a small plastic container of acetone, and subsequently followed by 1 min ultrasonic agitation for dispersion. The sample was then picked up with a copper grid for HRTEM observation. The SAED patterns and the electron dispersive X-ray (EDX) spectroscopy were carried out to examine the structure and the chemical composition of the inclusions.

### 3. RESULTS AND DISCUSSION

#### 3.1. Structure of the Nickel Film and As-Grown Nanotubes

The as-sputtered Ni film has a root mean square roughness of $R_q = 1.2$ nm, and a thickness of around 50 nm (cf., Figs. 1(a), (b)). The surface root mean square roughness of the annealed film dramatically increased to $R_q = 4.5$ nm as shown in Figure 1(d), with many small spikes/particles of around 13.0 ± 2.4 nm in diameter uniformly inlaying among the bigger ones (100.2 ± 5.3 nm in diameter). Figure 1(c) shows the X-ray diffraction patterns of the as-sputtered Ni film, where five characteristic peaks: (111) centered at 44.51°, (200) centered at 51.85°, (220) centered at 76.37°, (311) centered at 92.94°, and (222) centered at 98.45° are detected, exhibiting the typical face-centered-cubic (FCC) crystalline structure of Ni. Figure 1(f) shows the TEM image of the as-grown tubes. The tubes have uniformly distributed diameters ranging from 20 to 40 nm, and lengths up to several microns. Ni inclusions are not observed in the tubes, indicating the high purity of the tubes. The as-grown nanotube is multiple-walled with more than twenty layers (cf., Fig. 1(g)). The innermost tube has a fluctuating diameter ranging from 4.8 to 9.8 nm. The outer diameter fluctuates from 35.5 to 40.1 nm. The spacing between adjacent walls is approximately 0.34 nm, revealing that the tube is a multi-walled carbon nanotube. In summary, Ni nanoparticles were formed serving as the launching pad for the tube nucleation after the pretreatment. The 50-nm-thick as-sputtered Ni film has a typical FCC crystalline structure. The as-grown tubes have a uniform distribution of diameters and high purity without entrapping any inclusions.

#### 3.2. Entrapping of Nickel Inclusions

As shown in Figure 1(f), most of the tubes are empty without entrapping any multiple particles, however, a few ones are occasionally found entrapping multiple “bullet-shaped,” “beads-like,” and “needle-shaped” Ni particles in the middle, at the bend or at the tip (cf., Fig. 2). Figure 2(a) shows a huge Ni particle of around 100 nm in diameter is located at the bend of the tube as indicated by a small white dotted circle. The corresponding SAED patterns shown in one of the insets demonstrate a typical Ni FCC crystalline structure, where five characteristic rings correspond well to the (111), (200), (220), (311) and (222) crystalline planes of the FCC structure of Ni. Also in Figure 2(a), two elongated particles were respectively encapsulated in the middle and at the end of the tube (10.0 nm in diameter, and 42.1 nm or 123.2 nm in length). The “needle-like” inclusion at the tip is enlarged in the upper-right inset exhibiting a shrinkage process. The diameter of the needle narrows 17.6 from to 7.0 nm during the enveloping of the carbon nanotube. The EDX elemental analysis (cf., Fig. 2(a), bottom inset) confirms that the “needle” is Ni. The EDX elements are carbon (84.39 at.%), nickel (3.55 at.%), silicon (2.19 at.%), oxygen (1.53 at.%), and copper (5.35 at.%). Nickel originates from the supporting copper grid, silicon is from Si substrate in TEM sample preparation using stainless tweezers, and oxygen comes from the oxidation in air. Figure 2(b) shows five elongated Ni particles as indicated by white arrows are sequentially entrapped in a single multi-walled CNT. The tip particle is magnified...
in the inset showing a “bullet-shaped” Ni particle located at the tip of the tube, revealing the tip growth of the tube. Figure 2(c) shows a “bullet-shaped” Ni inclusion (around 14.4 nm in diameter, 31.2 nm in length) in the middle of the nanotube. The tube is not totally hollow as discerned in the below inset, where one end of the “bullet” is covered with graphene layers indicated by the white dotted circle, whereas the other end of the “bullet” is at the hollow tubeing that is smaller than the diameter of the “bullet” itself as indicated by a white dotted arrow. The shape of the entrapped particle is reminiscent of a drop of mercury left inside a glass capillary.35 However, the contact angle between the Ni particle and the inner wall of graphene is larger than 90° (the measured angle is ranging from 140° to 150°), indicating that the Ni particle poorly wets the tube walls. The strong capillary action anticipated in nanometer-sized cavities, does not seem to be enough to suck the metal into the tubes, again conflicting with the fluid movement argument.21 Even the free end of the Ni “bullet” is partially covered with a few layers of graphitic carbon layers parallel to the tube axis (cf., Fig. 2(c), the white dotted arrows in the inset). These carbon layers covering the free end of the “needle” are suggested to be formed through the interfacial diffusion at the graphene/bullet junction.

Figure 2(d) shows four elongated Ni particles as indicated by white dotted arrows are continuously encapsulated in a multi-walled CNT. The inclusions are located at the tip and middle of the tube. The inner diameter of the tube is fluctuating due to the incorporation of the Ni

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**Fig. 2.** TEM images of as-grown multi-walled carbon nanotubes encapsulated with multiple “bullet-shaped,” “beads-like,” and “needle-like” nanoparticles, where the inset shows the EDX or SAED of as-grown carbon nanotubes and Ni inclusions.

Inclusions. The inset at the upper-left shows the SAED patterns of the big “beads-like” Ni inclusion at the tip (cf., Fig. 2(d), as indicated by a white dotted circle, around 42.2 nm in length), where four characteristic rings correspond well to the (200), (220), (311) and (222) crystalline planes of the FCC crystalline structure of Ni. This patterns are obviously different from that of the single crystalline diffraction patterns generated by the Ni inclusion through the vapor–liquid–solid growth of CNTs, where arc discharge in 7.3 × 10$^{-4}$ Pa helium gas between graphite electrodes is used as the carbon vapor source, and a silica substrate supporting Ni catalytic particles is positioned at a short distance from the arc and held in the temperature range 800–950 °C. The Ni inclusion in the growth is formed from liquid Ni. The reservation of the same FCC crystalline structure of Ni in the present growth indicates...
that the inclusions maintain the solid crystalline structure during the whole growth. Additionally, the big “beads-like” particle located at the tip gradually shrinks the diameter (around 33.8 nm at the end) down to the inner diameter of the tube (around 6.4 nm at the right end), implying the contraction process of the solid Ni particle during the growth of CNT.

Figure 2(e) shows five elongated Ni particles as pointed by white arrows are sequentially entrapped in a circle-shaped multi-walled carbon nanotube exhibiting a bamboo-like structure. The tube consists of a circular chain of hollow compartments. The tip of the tube is capping a “needle-shaped” Ni particle with a length of up to around 307.6 nm and a diameter of around 33.0 nm at the middle length place. Note that it is gradually shrunken to a diameter of around 12.1 nm at the top end, also exhibiting the shrinking process. The inset in the center shows the SAED patterns of the “needle-shaped” inclusion indicated by a white dotted circle, where four characteristic rings correspond well to the (200), (220), (311) and (222) crystalline planes of the FCC structure of Ni, again supporting the solid state of Ni particles during the growth. Other four Ni particles are sequentially located in other compartments, i.e., in the middle or at the bend of the bamboo-shaped tube. The shape of each compartment in the tube is quite similar to the shape of the entrapped Ni particles, suggesting that the Ni particles were once at the cavities. One end of the “needle” (202.2 nm in length, 15.1 nm in diameter, as highlighted by a white dotted ellipse) capped with graphene layers has the similar structure in Figure 2(c).

These features are characteristics of the “Tip Growth” of carbon nanotubes. To summarize, the followings are confirmed: (a) formation of small Ni spikes/nanoparticles (around 13.0 ± 2.4 nm in diameter) takes place during the pretreatment, (b) the as-grown one dimensional nanostructures are multi-walled carbon nanotubes, (c) the multiple “bullets,” “beads” and “needles” entrapped in the tube are Ni nanoparticles, (d) Ni inclusions reserve the same FCC crystalline structure of as-sputtered Ni film during the pretreatment and the growth of the tube, (e) the narrowing of the inclusion diameter indicates the shrinkage process during the growth of the carbon nanotube.

3.3. Formation Mechanism

A continuous tip growth model responsible for the formation process of multi-walled CNTs and the entrapment mechanism of the multiple Ni inclusions is developed in Figure 3, where Ni particles stay in a solid crystalline state throughout the whole nanotube growth process.

3.3.1. Extruding of Crystalline Ni Nanoparticles

The Ni particle remains in a solid crystalline state with the same FCC structure of the as-sputtered Ni film throughout the pretreatment and growth process, though the liquid Ni at around 700 °C is estimated by molecular dynamic simulation. However, the direct observation of the de-wetting of 1-nm-thick Ni catalyst film into around 5-nm Ni nanoparticles during surface-bound catalytic chemical vapor deposition of single-walled carbon nanotubes at 615 °C, also reveals the crystalline state of Ni catalysts during the growth. An in-situ experimental observation of bamboo-like multi-walled carbon nanotube growth also shows that Ni particles of about 10 nm remain metallic and solid crystalline although the shape of the particle changes constantly at 650 °C. The in-situ growth dynamics of an individual single-walled carbon nanotube during Ni-catalyzed (<6 nm in diameter) decomposition of C2H2 at 650 °C in a TEM chamber provides the direct evidence that the catalyst particles remain as metallic Ni, instead of forming the intermediate Ni3C phase or liquid nickel-carbon phase during growth. It is also reported that the nanotube growth is conducted through solid tip Ni catalyst particles at 700 °C, whereas, it grows via liquid catalyst particles by extrusion mode at 800 °C. Moreover, a semi empirical equation, estimates the melting temperature of Ni at the particle size of 10 nm is over 1100 °C. The phase diagram of carbon–nickel alloy shows the eutectic temperature of around 1326.5 °C, again supports the solid state of Ni particles during the growth of CNTs. Therefore, from the view of experiment and theory, under the present experiment condition (725 °C, around 13.0 ± 2.4 nm in Ni particle diameter), Ni particle is de-wetted and remains in a crystalline metallic solid state. Moreover, the SAED patterns of Ni inclusions in Figure 2, where the elongated Ni particles maintain the characteristic FCC crystalline rings of the as-sputtered Ni film, again reveal that liquid carbon–nickel droplets can never be formed.

Upon pretreating at 725 °C in H2/Ar atmosphere, therefore, the as-sputtered Ni film is transformed by de-wetting from the Si substrate into small solid spikes or particles of 13.0 ± 2.4 nm in diameter (cf., Fig. 1(d)). The Ni film underwent restructuring, further sintering, and formation of the crystal shape to reach a surface and interface energy minimization. The dewetting of Ni particles initiates at grain boundaries and edges through surface diffusion. The Ni particle denotes in a fast self-diffusivity and long-range crystalline order, in contrast to liquids, thus remains in a crystalline state. The chemical state and the shape of the Ni particles are influenced by the H2/Ar flow via adsorbate-induced changes of surface energies and changes of the interfacial-induced energy.

3.3.2. Initiation of the Tip Growth

The essential mechanism for the growth of CNTs in early studies describes that abundant carbon decomposed from the hydrocarbon feedstock precipitates on the surface of transitional metal catalysts, diffuses into the catalysts, and...
nucleates the carbon nanotube at the edges of the catalyst. If the adherence between the catalyst and the substrate surface is strong and the mass of the catalyst is heavy, carbon would precipitate from the top surface of the particle anchored to the substrate. Thus the nanotube grows away and extends from the particle in a “Root Growth” (where the catalyst remains “rooted” on the substrate surface while the tube grows “away”). If the adhesion between the catalyst particle and the substrate is weak and the particle is light in mass, the precipitation of carbon occurs at the bottom surface of the particle, and as the tube forms and grows, it lifts the particle up, thus the “Tip Growth.”

In the present growth, since the Ni remains in solid crystalline state during the growth, the mechanism for the nanotube growth is not through carbon precipitation from carbon supersaturated Ni3C droplet, but rather through the diffusion of carbon adatoms followed by nucleation and growth. Therefore, once the H2/Ar/C2H4 gas mixture is introduced into the reaction chamber, carbon adatoms are decomposed from the C2H4 molecules and diffuse to form carbon network on the crystalline Ni particle, and then the nucleation of the nanotube takes place (cf., Fig. 3(I)). The surface diffusion of carbon adatoms to the boundary of the nickel-graphene interface is responsible for the growth of the outer graphene layer. For growth of inner graphene layers, the interfacial diffusion of carbon adatom through the nickel-graphene edges/interface is suggested to be the dominating route. The growth is driven by minimizing the nucleation energy of the graphene layer when it is constrained to grow and form a tube, meanwhile, by the interaction between the surface energy and strain energy per unit volume on a small metallic Ni particle. Due to the smaller torsional stress of the carbon–carbon bond on the spherical end of the particle 1, very low strain energy is needed to envelope graphene layers on the spherical end. This explains why the Ni particle at the end of the tube is covered with graphene sheets (cf., Figs. 2(b) and (e)), which is different from the conventional “Tip Growth” with no covering graphene sheets on the end of the catalyst. In this process, the decreasing of the inner diameter of the tube gives rise to the elastic elongation of the particle 1 and increases the strain energy. The increase in the graphene-nickel interfacial energy and the strain energy during the graphene layer formation is consumed to form graphene layers from an aggregate of isolated carbon adatoms on the surface of the particle 1 while constraining the nanotube to grow. To summarize, the built-up strain energy is relaxed by directing the tubular growth with a hemispherical graphene cap. The tangential extrusion of graphene sheets results in the formation of the present multi-walled nanotube structure.

### 3.3.3. Entrapping of Nickel Inclusions

The entrapping of the Ni inclusion in carbon nanotubes is explained through a continuous tip growth process. Once the tip growth of the nanotube has been initiated, the carbon network forces its shape onto the “bullet-shaped” particle 1 (cf., Fig. 3(II)). Meanwhile, the enveloped Ni particle 1 is constrained by the nanotube to a more cylindrical shape with more spherical ends. At a critical point,
the Ni particle 1 transforms from its initial equilibrium shape into a highly elongated shape and breaks off from the Ni film. Then the particle 1 overcomes the substrate anchorage and lifts up from the Ni film through a “Tip-Growth” manner. The contraction time has been attributed to the point when the increase in Ni surface energy is unable to be compensated by the energy for binding the nanotube wall to the Ni film surface.38 The adhesion between the Ni particle 1 and the tube wall moves particle 1 with the tube toward the region of higher hydrocarbon feedstock concentration. The base of the tube anchoring to the Ni film with weak force contact continues to anchor on newly formed particle 2 until it breaks off from the Ni film in the same way. Herein, the new particle 2 is formed as a result of the de-wetting of Ni film at the grain boundaries and edges through surface diffusion during heating at 725 °C in H2/Ar atmosphere via the same mechanism of the particle 1. Because of the continuous deformation, contraction, lift-up of Ni particles and the increasing weight of the nanotube, and then, multiple particle inclusions and the bending of the nanotube take place (cf., Figs. 2 and 3(III)). In summary, the Ni inclusions are formed by sustaining contraction of Ni particles at the root of the as-grown CNT on the “thick” Ni film, where relatively large amount of catalysts are provided.

3.3.4. Thickening of the Tube Wall and Capping of the Nickel Inclusion

As a result of the continuous contraction and shrinkage of the Ni inclusions, cylindrical “bullet-shaped” particles with spherical ends are formed (cf., Fig. 2(c), white dotted arrow). As more carbon adatoms are added into the graphene layers, new graphene layers initiate at the spherical edge of the nickel-graphene junction by interfacial diffusion (cf., Figs. 2(c), and 3(II), arrow B). Similar to the phase boundary between two material systems, the interface provides a low energy diffusion pathway for surface carbon adatoms to diffuse through and incorporate into the growing inner graphene layers at the spherical edge. As a result, graphene layers parallel to the as-grown nanotube walls are nucleated on the left, and others are nucleated on the right (cf., Figs. 3(II) and (III)). The continuous interfacial diffusion of carbon adatoms results in a hemispherical graphene cap enveloping the upper end of the “bullet-shaped” particle 2, sealing the tube internally (cf., Figs. 2(c) and (e), and 3(IV), arrow C). This results in the formation of the knot in the nanotube, fully encapsulating the upper part of the Ni inclusion. The absence of graphene fragments on the upper end suggests that the bigger curvature particle edge site is the preferred growth front for nucleating the graphene sheets during interfacial diffusion of the carbon adatoms through the nickel-graphene edges/interface.25

In formation of the new parallel graphene sheets and inclusion cap, both the effective diameter of the inclusion and the nanotube shrink, thus resulting in the elongation or reshaping of the inclusions along the growth direction of the tube. This increases the effective surface and interface area of the Ni inclusions. The elastic elongation also increases the strain energy of the inclusion which results in the contraction and ejection of the Ni particle. The contraction time is suggested to be determined by the adhesive attraction from the tube and the substrate anchorage, the new graphene sheets in conjunction with the capping of Ni inclusion give rise to different inclusion length and inner diameters of the tube along the tube length (cf., Fig. 2). The whole growth process repeats to yield a multi-walled carbon nanotube embedded with multiple elongated Ni inclusions and graphene knots sealing internally along the tube length.

4. CONCLUSION

Nickel (Ni) catalyst layer thickness plays an important role in growing high purity multi-walled carbon nanotubes (CNTs) with the lowest Ni inclusions. This work grew large quantities of high purity CNTs using a 50-nm-thick Ni film as the catalyst supply. Multiple ‘bullet-shaped’ Ni particles were occasionally found wrapping in the middle, at the bend and at the tip of a few nanotubes. The entrapment of Ni inclusions was explained by a continuous tip growth model. As nanosized crystalline solid Ni particles form during annealing at 725 °C, chemisorption and catalytic decomposition of C2H4 molecules on the surface of the Ni nanoparticles take place to nucleate a carbon layer, this layer of carbon is then covered by a new layer of carbon newly deposited and diffused over. As this process takes place, multi-walled CNT forms encapsulating the Ni particle inside. Meanwhile, the length of the tube increases and the particle breaks off under its surface tension and becomes totally entrapped in and is lifted up by the growing tube. As the tube continues to grow, a second Ni particle is raised and the process repeats. As a result, the tube entraps multiple Ni particles within, Ni layer thickness of 50 nm is thus suggested to be the conservative upper limit for the purpose of growing high purity carbon nanotubes in hot filament chemical vapor deposition.

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References and Notes
