Synthesis of carbon nanotubes on graphene quantum dot surface by catalyst free chemical vapor deposition

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ARTICLE INFO

Article history:
Received 5 September 2013
Accepted 6 November 2013
Available online 15 November 2013

ABSTRACT

The growth of carbon nanotubes (CNTs) on graphene quantum dot surface has been explored using acetylene as the carbon source in a catalyst free chemical vapor deposition process. Dynamic studies were conducted to observe the CNT growth. The obtained nanotubes have a diameter distribution of 10–30 nm and show medium graphitic quality. Transmission electron microscopy observations and dynamic studies indicate that the formation of CNTs follows a different mechanism from traditional growth models, in which a wire-to-tube process and self-assembling of CNTs are involved. On the basis of these observations, a tentative continuous growth model is proposed for the CNT growth.

1. Introduction

Carbon nanotubes (CNTs), with unique mechanical and electrical properties, have attracted much attention in fundamental scientific studies and in a wide range of applications, including high strength composites, sensors, field emission displays, nanometer-sized semiconductor devices, and hydrogen storage media [1]. Various synthesis methods including arc discharge [2], laser evaporation [3] and chemical vapor deposition (CVD) [4,5] have been developed for the production of CNTs. Therein, CVD has received considerable attention because it has inherent advantages such as higher scalability, better control of process parameters and product purity [6].

In traditional CVD methods, carbon is produced from the decomposition of carbon sources such as hydrocarbons, carbon monoxide, alcohols, and so on, over a metal catalyst [7]. However, the unavoidable metal species remaining in CNTs would lead to obvious disadvantages for property characterization and application exploration [8,9]. Despite sustained efforts, it is still an intractable problem to remove metal catalysts completely from CNT samples without introducing defects and contaminations. Recently, very few reports reported the observations to fabricate CNTs by catalyst-free solid-state transformation [10–12], but the synthesis temperatures were above 1300 °C, which are not attractive for scaling up to mass production. Furthermore, it has been confirmed that multi-walled carbon nanotubes (MWCNTs) can grow directly on carbon black [13] and defective graphite surfaces [14]. In addition, C60 fullerenes [15] can be also used as nucleation precursors for the fabrication of double-walled CNTs. These findings challenge the traditional opinions about the indispensable role of the metal catalysts in the growth process of CNTs. The pore structures, nano-scale curvatures and defect-rich structures may play important roles in the formation of CNTs during catalyst-free CVD (CFCVD).

Graphene quantum dots (GQDs), single- or few-layer graphene with a tiny size of only several nanometers, stand for a new type of QDs with the unique properties associated...
with both graphene and QDs [16]. They have attracted tremendous research interest due to their large surface area, high carrier transport mobility and some other intriguing properties. Besides, their large surface area and the physical and/or chemical defects along the graphene nanosheets provide a myriad of active sites and high specific surface energy. The fabrication of MWCNTs on defect-rich graphite surfaces by CFCVD, as mentioned above, shows that the defective sites play key role in the formation of CNTs. Thus, similar to defective graphite, it is suggested that GQDs may have potential for CNT growth by CFCVD. However, no relevant work has been reported as far as we know.

In this work, the fabrication of MWCNTs on the surface of GQDs by CFCVD at mild temperature has been demonstrated for the first time. This work has explored the potential use of GQDs as substrates for the formation and growth of CNTs, which can be considered as a green and cheap way to synthesize CNTs in a large scale, and holds a great potential for the realistic industrial production of CNTs.

2. Experimental section

2.1. Preparation of MWCNTs

The detailed experimental procedure for the preparation of GQD solution is as described in our previous work [17]. Carbon fibers (0.6 g) were dispersed in the mixture of concentrated H$_2$SO$_4$ (120 mL) and concentrated HNO$_3$ (40 mL) for 5 h under continuous ultrasonic treatments. The dispersed suspension was refluxed at 100 °C while keeping magnetic stirring for 24 h. After cooling down the temperature, the suspension was diluted with double distilled water (1500 mL). The pH of the solution was adjusted to 8 with addition of Na$_2$CO$_3$ aqueous solution. The resulting suspension was filtered through a 0.22 μm microporous membrane and further dialyzed in a dialysis bag (molecular weight cut off: 2000 Da) for 3 days. Prior to CNT growth experiment, silicon wafer (with a sample size of 5 × 5 mm) was successively ultrasonically cleaned in acetone solution and ethanol solution, followed by air drying at room temperature. The aqueous solution of GQDs was dropped on the silicon wafer and kept for natural drying.

In CNT growth experiment, the sample was placed in a quartz boat, which was located in the heating center of the CVD furnace. Argon gas was firstly introduced to flush out remnant air and moisture from the CVD furnace. Subsequently, the furnace was heated up to 700 °C. Next, a 17:3 Ar:C$_2$H$_2$ gas mixture was introduced at a combined flow rate of 200 standard cubic centimeters per minute for 2 h. During this period, the pressure value of the furnace was kept at the range of 4000–6000 Pa (see Fig. S1). Finally the tube was cooled down in a mixed gas atmosphere of argon and hydrogen. A schematic illustration of synthesis experiment device configuration is shown in Fig. 1.

2.2. Characterization

The morphological and microstructural investigations of the resulting CNTs have been carried out by employing field emission scanning electron microscopy (FE-SEM, Ultra55, Carl Zeiss, Germany) and transmission electron microscopy (TEM, JEM-2100, JEOL, Japan). To prepare sample for high-resolution TEM analysis, the synthesized CNTs were scraped off the silicon wafer using a razor blade and dispersed into deionized water. A drop of the resultant solution was then placed onto 300 mesh carbon-coated Cu grids. The qualitative measurement of CNTs have been carried out by analyzing Raman spectrum which was characterized using Bruker Senterra dispersive Raman microscopy (R200-L, Bruker Optics, Germany) with laser excitation wavelengths of 532 nm (20 mW) at room temperature. The elemental composition and purity of CNTs were investigated employing energy dispersive X-ray spectroscopy (EDS, Oxford Instruments INCA PentaFET x3, Model: 7426) analysis, where random selection of several areas of CNTs have been done to eliminate causal factors.

3. Results and discussion

3.1. Analysis results of GQDs

The GQDs have a narrow height distribution ranging from 0.3 to 0.9 nm, suggesting that the GQDs consist of 1–2 graphene layers. The mean size of the GQDs is about 40 nm. These data are shown in Fig. 3 in Ref. [17] in our previous work.

3.2. Quality and purity of CNTs

Fig. 2a and b represent SEM images of CNTs under different magnifications. It has been clearly observed that the wafer is fully covered by roughly uniform CNTs with diameters ranging from 10 to 30 nm. The morphologies of CNTs (see Fig. 2b) show their curly shapes. The EDS analysis (see Fig. 2c) suggests that the as-grown CNTs are free from contaminated catalyst particles. No sign of non-carbon element is observed in the present investigation. Raman spectroscopy was used to evaluate the purity and degree of graphitization.

![Fig. 1 – The schematic illustration of the device configuration for the growth of CNTs. (A color version of this figure can be viewed online.)](image-url)
of the obtained CNTs. As shown in Fig. 2d, the absence of discernible radial breathing mode peaks typically observed in the range of 150–300 cm$^{-1}$ in single-walled carbon nanotubes (SWCNTs) corroborates that the synthesized CNTs are multi-walled, which has been confirmed by the TEM observation in Fig. 3e. Raman spectrum reveals three prominent characteristic bands of CNTs as well. D and G bands are observed at around 1334 and 1590 cm$^{-1}$, respectively. The former is usually associated with the impurities that destroy the graphitic symmetry, while the latter represents the splitting of the E$_{2g}$ stretching mode for the graphite [18,19]. The 2D band is observed at about 2820 cm$^{-1}$, which is usually correlated with the degree of disorder and breaking of symmetry [20]. The relative intensity ratio of D-band to G-band is known as an index for the crystalline order of CNTs [21]. The obtained value of $I_D/I_G$ is around 0.9, indicating an intermediate degree of graphitization/crystallinity even without the aid of any catalyst.

### 3.3. Microstructure of CNTs

Fig. 3 presents a series of TEM micrographs of samples with special structures coexisting in one product. Sometimes, these samples and CNTs with similar diameters stay together. We believe that some of them are intermediate products which have not completely evolved into CNTs. Their structures may provide critical evidences for the formation of CNTs. Fig. 3a and b show several carbon nanowires which are almost solid despite few small hollow areas in the center sections. Fig. 3b clearly shows the closed tip without any catalyst particles and the graphitic layers whose curvatures are directed toward the tip. The curvature characteristic and the layer-by-layer structure reveal that the nanowires are the results of gradual stack-up of graphitic layers. As nanowires grew continuously, the graphitic layers deformed at the same time. Some neighboring layers departed from each other and formed compartments (Fig. 3c) whose sizes changed from small to large, owing to the axial pulling force caused by further growth of the nanowire (Fig. 3d). Interestingly, the sample in Fig. 3d is composed of morphologically different sections. Some sections still exhibit the solid structures (indicated by arrow 1) while other sections have been already developed into tubular-similar structures with continuous hollow channels (indicated by arrow 2), although the tube walls are not well-developed. It suggests that the nanotube formation possibly abides by a stepwise evolution process and the samples in Fig. 3a–d are likely to be the intermediate stage of CNT evolution. Most CNTs shown in Fig. 3f are made up of several empty compartments, which represent typical bamboo-like
structure. The diameter of the bamboo-shaped CNT is about 10–30 nm, which agrees with the SEM observation. The inset of Fig. 3e reveals the closed tip without any catalyst particles and the compartment layers whose curvature is directed toward the tip. Fig. 3e presents the high-resolution TEM (HRTEM) image of a bamboo-like CNT showing the multi-walled structure and compartmentalized graphitic layers. It is comprised of an outer diameter of around 22 nm and an inner diameter of about 8–10 nm. It can be seen from the micrograph that the crystalline graphitic layers of wall are not arranged in parallel to the axis of the tube. The distance of two neighboring graphitic layers is around 0.34 nm, which is almost like that in ordinary CNTs [22,23]. There is a joint between the wall and the compartment layers. We notice that the presence of the joint has a significant influence on the number of the wall layers. If one follows the downward direction, the wall thickness reduces from 6.7 to 4.7 nm at the joint, and then increases to 7.9 nm after the joint, subsequently returning to a thickness of 6.7 nm. Despite the change in wall thickness, the outer diameter remains almost same. Two arches almost broken (marked by 1 and 2) and the diffusion indicated by 3 provide evidence for further transformation of compartments.

Fig. 3 – TEM images of samples with special structures coexisting in one product.
The compartment layers are supposed to serve as a carbon complements to the neighboring walls by diffusion, which is proved by the walls indicated by arrow 4. Crystalline graphitic sheets of wall combine with those of compartment layers, resulting in an increase of wall thickness.

3.4. Dynamic studies and mechanism analysis

For a better understanding of formation and growth of CNTs, a set of experiments with different reaction time have been performed. After each experiment the sample was cooled down to room temperature under argon atmosphere. Note that the time point \( t = 0 \) min corresponds to the time wherein the reactor system pressure was pumped down to the corresponding reaction pressure (Fig. 4a). It is noticed that a few ultra-short tubes and caps with closed tip formed within 3 min of initiation of the reaction (Fig. 4b). It has been firmly established that nanoscale active catalytic sites are required for the growth of CNTs [24,25]. We believed that scores of defects along GQD edges and their large surface area provide active sites and high energy for the formation of these structures. GQDs play catalyst role during the deposition process, which is similar to the function of defect-rich graphite in previous work [14]. In Fig. 4d, the CNTs exhibit closed tips (indicated by arrows), which is in accordance with TEM results in Fig. 3b and the inset in Fig. 3e. Then, longer growth durations of up to 10 min give rise to a thin layer of CNTs with uniform distribution. The gradual increase of growth time

![Fig. 4 – (a–f) SEM images of CNTs grown at different time intervals (t = 0, 3, 5, 10, 30 and 120 min, respectively). The arrows in Fig. 4d indicate the closed tips of CNTs.](image-url)
leads to an augment in both length and quantity of the grown CNTs (Fig. 4b–f). After deposition for 2 h, the entire surface is covered by dense CNTs (Fig. 4f). Although the CNT growth rate in our work is slower than those catalyzed by metal catalysts [26–28], it is still comparable to some of those catalyzed by metal-free catalyst [29,30]. This shows that GQDs is a good candidate to produce CNTs in a large scale.

Basing on the analysis of CNTs above, we proposed that the formation of CNTs in our experiment follows the wire-to-tube model, as depicted in Fig. 5, which is different from previous models [31–33]. When acetylene decomposes into carbon atoms and hydrogen on GQD film, deposited carbon atoms form as solid caps (or ultra-short carbon wires) layer by layer. The formation of the solid caps may be influenced by the surface structure or curvature of GQDs. The generating of defects, such as sp³ carbons, non-hexagonal rings or disconnected bonds, make carbon atoms come into the one with anisotropy structure, then the following carbon atoms will sequentially deposit onto the most stable position, and keep on growing in one direction for one-dimensional assembly of carbon nanowire [34]. Besides, nanoscale curvatures were supposed to provide a platform for the formation of carbon caps and the subsequent growth of CNTs [29,35]. As the carbon layers stack up layer by layer, nanowires form and grow longer. The self-assembled nanowires, viewed as the intermediates, will undergo a slow and complex process, and then transform to bamboo-shaped CNTs by self-assembly. Some compartments layers of the tube may deform and break, serving as carbon complements to the neighboring outer walls [36]. This process may complete through carbon diffusion. However, we emphasize that we cannot here give more direct evidence for this possible mechanism due to the limitation of our present experimental setups. Further studies are still required to understand the mechanism, especially the formation of the solid caps and the carbon diffusion during the wire-to-tube transformation.

4. Conclusions

We have described a route to produce uniform MWCNTs on GQD surface through CFCVD at mild temperature. The as-grown bamboo-shaped CNTs have a diameter in the range from 10 to 30 nm. Raman spectrum indicates their intermediate degree of graphitization/crystallinity. A wire-to-tube model for the formation and growth mechanism of CNTs is subsequently proposed. This model is based on microscopic observations and dynamic growth studies, which involves the formation of short cylindrical networks, deformation and transformation of compartments inside the tubes. This will provide an insight into understanding the complicated growth process of CNTs in CFCVD.

Acknowledgments

This work was supported by the National High-Tech R & D Program of China (863 program, 2011AA050504), National Natural Science Foundation of China (51102164), Program for New Century Excellent Talents in University (NCET-12-0356), Shanghai Science and Technology Grant (12JC1405700 and 12nm0503800), Shanghai Natural Science Foundation (13ZR1456600), Shanghai Pujiang Program (11PJ011), and the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning. We also acknowledge the analysis support from the Instrumental Analysis Center of Shanghai Jiao Tong University.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2013.11.016.

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