Effects of ferrite catalyst concentration and water vapor on growth of vertically aligned carbon nanotube

Thi Thanh Cao¹, Van Chuc Nguyen¹, Thi Thanh Tam Ngo¹, Trong Lu Le², Thai Loc Nguyen¹, Dai Lam Tran¹, Elena D Obraztsova³ and Ngoc Minh Phan¹

¹Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Road, Cau Giay District, Hanoi, Vietnam
²Institute of Tropical Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam
³A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, 38, Vavilova Street, Moscow, 117942, Russia

E-mail: chucnv@ims.vast.ac.vn

Received 2 October 2014
Accepted for publication 9 October 2014
Published 4 November 2014

Abstract
In this study Fe₃O₄ nanoparticles were used as catalysts for the growth of vertically aligned carbon nanotubes (VA-CNTs) by chemical vapor deposition (CVD). The effect of catalyst concentration and water vapor during the CVD process on the properties of the VA-CNTs was investigated. Monodisperse Fe₃O₄ nanoparticles (4.5–9.0 nm diameter) prepared by thermal decomposition of iron acetylacetonate compounds were spin-coated on clean silicon substrates which served as a platform for VA-CNTs growth. The results indicated that the length, density and growth rate of CNTs were strongly affected by the catalyst concentration. CNTs grown at 0.026 g ml⁻¹ Fe₃O₄ catalyst had greater length, density and growth rates than those obtained at 0.01 and 0.033 g ml⁻¹ Fe₃O₄ catalyst. Addition of water during the CVD process had drastically improved CNTs growth. The length and growth rate of obtained CNTs were 40 μm and 1.33 μm min⁻¹, respectively. The results provided insights into the role of Fe₃O₄ catalyst and water vapor during VA-CNTs growth process by CVD method and the obtained information might serve as a starting point for further optimization of VA-CNTs synthesis.

Keywords: aligned CNTs, CVD, ferrite nanocatalysts, water vapor
Mathematics Subject Classification: 5.00, 5.14

1. Introduction
The discovery of carbon nanotubes (CNTs) in 1991 by Iijima [1] has prompted extensive investigations of the unique physical, chemical, mechanical and electronic properties of this new material [2, 3]. Vertically aligned CNTs (VA-CNTs) are carbon cylinders which orient perpendicularly to a substrate [4]. VA-CNTs have advantages of large aspect ratio, good orientation and high purity. CNTs arrays have attractive potential applications in field emission devices, anisotropic conductive materials, filaments, membrane, super springs, and electrochemical and bioelectrochemical sensors [5–7]. The growth of VA-CNTs has been studied on various materials such as mesoporous silica, planar silicon substrates, quartz plate using Fe, Co, or Ni catalyst [5]. Fe₃O₄ nanoparticles have been applied in diverse fields such as biomedicine [8], ferrofluid technology [9], information storage [10] and environmental engineering [11]. Recently, monodispersed Fe₃O₄ nanoparticles have been investigated as a catalyst for CVD synthesis of boron nanowires [12] and carbon nanotubes [13, 14]. Nevertheless, few researches utilize Fe₃O₄ nanoparticles as a catalyst for synthesis of VA-CNTs via the CVD process [15, 16]. The influence of Fe₃O₄ concentration on CNTs morphology and other properties has
not been reported yet. The control of diameter, number of walls, structural defect, length and density of CNTs is very critical [17]. Addition of water is found to be conducive to CNTs growth enhancement, evidenced by increased CNTs length and density [18]. Previous studies demonstrate that water vapor is related to the surface hydroxylation and etching of amorphous carbon during CNTs growth [18, 19]. The water vapor helps protect the catalyst from ripening and/or carbide formation which would usually result in early termination of CNT growth. However, the effects of water on CNTs quality apparently differ with different catalysts and substrates [20, 21]. So far, scarce information has been available with respect to the effects of water on CNTs growth using Fe3O4 nanoparticles as catalyst.

In this study VA-CNTs growth by the CVD process using Fe3O4 nanoparticle catalyst and water vapor was investigated. The effects of catalyst concentrations and water vapor on CNTs properties were thoroughly investigated.

2. Experiment method

2.1. Materials

Iron acetylacetonate, oleic acid, oleylamine, 1,2-hexadecanediol, 1-octadecene (Sigma Aldrich) were of analytical grade and used without further purification. Silicon wafer with 100 nm thick SiO2 was used as substrate for VA-CNTs growth.

2.2. Preparation of the sample

In this work Fe3O4 nanoparticle catalyst was prepared by thermal decomposition of iron acetylacetonates (Fe(acac)3). Briefly, Fe(acac)3 (0.69 g, 0.63 mM), oleic acid (OA) (3.6 mL, 372 mM), oleylamine (OLA) (3.6 mL, 372 mM), 1,2-hexadecanediol (0.58 g, 75 mM) and 30 mL of 1-octadecene were added to 100 mL three-neck round-bottom flask. The mixture was magnetically stirred under nitrogen atmosphere for 30 min and heated to 295 °C at a rate of 20 °C min−1. In the next stage of the reaction, the mixture was maintained at 200 °C for 30 min and then cooled to room temperature. Raman spectra were recorded in the range of 500–2000 cm−1 on a JobinYvon Lab RAM-1B (France), using He-Ne laser source of 632.8 nm as the incident light.

2.3. Synthesis of vertically-aligned carbon nanotubes

Synthesis of the VA-CNTs was carried out at atmospheric pressure via catalytic decomposition acetylene (C2H2). The samples were placed in the furnace and calcined at 600 °C in the air for 30 min to remove the residual polymers. The furnace was heated to 750 °C at ramping rate of 20 °C min−1 under an Ar flow of 800 sccm. The samples were incubated at 750 °C under flow of Ar/H2 (300/100 sccm) for 30 min to deoxidize the catalysts. Then C2H2 (30 sccm) was added for 30 min. After that, the furnace was cooled down to room temperature in Ar gas to prevent oxidation of the CNTs. In this work the effects of Fe3O4 catalyst concentrations (0.01, 0.026 and 0.033 g ml−1) on the properties of VA-CNTs were studied. The optimal concentration of catalyst was then used to evaluate the effect of water vapor on the growth of VA-CNTs. Water vapor was introduced during the CVD process by bubbling partly argon gas supply (60 sccm) through water prior to entering the furnace.

2.4. Characterization of Fe3O4 catalyst and VA-CNTs

The morphology of Fe3O4 nanoparticle catalysts was observed by a transmission electron microscope (TEM) (JEM 1010 JEOL, Japan) at 80 kV and an atomic force microscope (AFM) (N9451A, USA). Sizes of Fe3O4 nanoparticle catalysts were analyzed by ImageJ sofware. The morphology of VA-CNTs was characterized by field emission-scanning electron microscopy (FE-SEM) (Hitachi S-4800) operating at an acceleration voltage of 10 kV. Diameter and length of the CNTs were estimated by analyzing SEM images using ImageJ software. Growth rate of the CNTs was calculated by the following equation:

\[ \nu = \frac{l}{t}, \]

where \( \nu \) is growth rate, \( l \) is the length of the tubes and \( t \) is CVD time (30 min).

Raman spectra were recorded in the range of 500–2000 cm−1 on a JobinYvon Lab RAM-1B (France), using He-Ne laser source of 632.8 nm as the incident light.

3. Results and discussion

3.1. Effects of catalyst concentration on growth of VA-CNTs

Figures 1(a) and (b) illustrate morphology and size distribution of Fe3O4 nanoparticles, respectively. Under given synthesis conditions, Fe3O4 nanoparticles are relatively well dispersed. The average diameter of the particles was estimated to be about 8 ± 1 nm. The distribution of as-synthesized Fe3O4 nanocatalyst on Si/SiO2 substrate after spin-coating was examined by AFM and the smooth coating of catalyst particles was clearly observed (figure 1(c)).

Figure 2 shows the SEM images of the VA-CNTs synthesized by CVD method using different concentrations (0.01, 0.026 and 0.033 g ml−1) of Fe3O4 catalyst. It is clear that Fe3O4 concentrations strongly affect density, length and
Figure 1. (a) TEM image, (b) size distribution, and (c) AFM image of Fe₃O₄ nanoparticle catalyst.

Figure 2. SEM images of VA-CNTs grown using various concentrations of Fe₃O₄ nanocatalyst: (a), (d) 0.01 g ml⁻¹; (b), (e) 0.026 g ml⁻¹; (c), (f) 0.033 g ml⁻¹.
growth rates of CNTs (figure 2 and table 1). For the given catalyst concentrations, diameters of CNTs are virtually similar and range from 8 to 10 nm (figures 2(d), (e), and (f)).

When Fe$_3$O$_4$ concentration is 0.026 g ml$^{-1}$, obtained VA-CNTs have the most uniform length and highest density (figure 2(b)). In addition, the length of CNTs produced at this catalyst concentration is highest among three concentrations studied. At 0.033 g ml$^{-1}$ Fe$_3$O$_4$, CNTs are shorter than those synthesized with 0.026 g ml$^{-1}$ Fe$_3$O$_4$ and amorphous carbon can be observed on the surface of the CNTs (figures 2(c) and (f)). This is possibly due to the formation of multilayers of catalyst particles on substrate surface at high Fe$_3$O$_4$ concentrations. The stacking of particles might lead to incomplete removal of residual polymer shell during initial heating stage. Eventually, amorphous carbon formed from the polymer shell would hinder the growth of VA-CNTs during CVD process. At 0.026 g ml$^{-1}$ FeSO$_4$, growth rate of CNTs is also highest among three concentrations used (table 1).

### 3.2. Effect of water vapor during CVD on VA-CNTs

Significant changes in properties of VA-CNTs are observed with the addition of water vapor in the CVD process (figure 3). Water-assisted CVD produces CNTs with greater length (40 μm) (figure 3(b)) than the ones grown without water (6 μm) (figure 3(a), table 1). Some studies previously evidenced the effects of water on CNTs growth using various catalysts such as Fe$_2$O$_3$, cobalt [17, 18, 21]. The role of water in purifying amorphous carbon is well documented [17, 19, 20]. Water is considered as a weak oxidant which removes the deposited amorphous carbon on the active sites of the catalyst [21]. Another function of water is to inhibit Oswalt ripening by surface hydroxylation [17]. As a result, the introduction of water during CVD helps extend catalyst lifetime and promote growth rate, which are conducive to notably increased length of CNTs. However, exceeding a certain level, H$_2$O showed an overall negative effect on the growth of CNTs. In this case, it was difficult to keep the balance between the carbon supply and the solid carbon precipitation [22]. It was more and more difficult for the acetylene molecules to reach the catalysts. So, an amount of amorphous carbon was increased and the length of CNTs was reduced.

![SEM images and size distribution of VA-CNTs synthesized at 0.026 g ml$^{-1}$ Fe$_3$O$_4$. Synthesis conditions: 750 °C, Ar/H$_2$/C$_2$H$_2$ = 300/100/30 sccm, 30 min respectively. (a), (d) without water addition and (b), (c), (e) with water addition.](image)

![Table 1. The effect of catalyst concentrations and assisted gas on VA-CNTs synthesis.](table)

| Catalyst concentration (g ml$^{-1}$) | Feeding gas | Length of CNTs (μm) | Growth rate of CNTs (nm min$^{-1}$) |
|-------------------------------------|-------------|---------------------|-------------------------------------|
| **No water addition**               |             |                     |                                      |
| 0.010                               | Ar, H$_2$, C$_2$H$_2$ | 3.0             | 100                                 |
| 0.026                               | Ar, H$_2$, C$_2$H$_2$ | 6.0             | 200                                 |
| 0.033                               | Ar, H$_2$, C$_2$H$_2$ | 4.2             | 140                                 |
| **Water addition**                  |             |                     |                                      |
| 0.026                               | Ar, H$_2$, C$_2$H$_2$, H$_2$O | 40.0             | 1333                                |
spectroscopy. The TEM images can clearly distinguish amorphous carbon and structural defects of carbon nanotubes. As seen in figure 4(a), the rough surfaces of the CNTs are probably attributed to the formation of amorphous carbon and structural defects.

During CNTs growth, under certain conditions, side walls can form cap-like structures and stack in the same direction to produce bamboo-like wall [23] morphology which are considered undesirable structural defects. The graphite layers consisting of one side of tubes are broken and are no longer continuous graphite sheets (figure 4(a)). The addition of water not only reduces the formation of amorphous carbons but also promotes the growth of VA-CNTs into well-defined vertically standing and organized structures. Unlike the CNTs grown without H2O, the CNTs have a hollow structure without a bamboo-like wall (figure 4(b)). It is known that the diameters of CNTs depend on the size of catalyst particle, amount of amorphous carbon formed on the CNTs walls and structural defects. Collected data point out that diameters and diameter distribution of CNTs grown with H2O are smaller and more homogeneous than those synthesized without H2O (figures 3(d), (e) and figures 4(a), (b)). Results in previous works show that the presence of reactive gases like H2 or NH3 can improve the homogeneity of nanoparticles which help narrow the size distribution of CNTs [21]. Hence, enhancement in uniformity of CNTs diameter may suggest a similar effect with respect to the presence of H2O in the feed gas.

In this research Raman spectroscopy was used to detect the presence of amorphous and crystalline phases in CNTs samples. The Raman spectra (figure 5) of the CNTs samples grown with and without water vapor show the peaks at 1354 cm\(^{-1}\) (D-line) and at 1594 cm\(^{-1}\) (G-line), which are ascribed to amorphous carbon and to graphitized CNTs, respectively.

The integrated intensity ratio of the G band over the D band can express the graphitization of the CNTs samples. Results from figure 5 show that values of I_G/I_D are 1.6 and 0.88 for the CNTs samples with and without water vapor. The analysis of Raman spectra evidences increased graphitization of CNTs samples with addition of water vapor during CVD process. These results are consistent with the SEM and TEM images which demonstrate the improvement in VA-CNTs structures in the presence of water vapor.

4. Conclusion

The vertically-aligned CNTs were successfully synthesized using Fe_3O_4 nanoparticle catalyst. The length, density, diameter and quality of the VA-CNTs were strongly affected by catalyst concentration as well as by the presence of water vapor during the CVD process. Within the ranges of studied catalyst concentrations, CNTs obtained at 0.026 g ml\(^{-1}\) Fe_3O_4 had the highest uniformity, density and length. Addition of water vapour drastically reduced formation of amorphous carbon, structural defects which led to significantly enhanced VA-CNTs quality.
Acknowledgments

The authors are grateful for the support for this work by the VAST projects (VAST.HTQT.Nga.10/12-13; VAST03.06/14-15; VAST.DLT.04/12-13). This work was also supported in part by the National Foundation for Science and Technology Development (grant 103.99-2012.15) and Nippon Sheet Glass Foundation for Materials Science and Engineering. Facilities was done with the help of IMS key lab. We are in debt to MSc Thanh Nga Nguyen and MSc Van Tu Nguyen for their kind help and fruitful discussions.

References

[1] Iijima S 1991 *Nature* **354** 56
[2] Javey A, Shim M and Dai H 2002 *Appl. Phys. Lett.* **80** 1064
[3] Lee N S et al 2001 *Diamond Relat. Mater.* **10** 265
[4] Feng W, Bai X D, Lian Y Q, Liang J, Wang X G and Yoshino K 2003 *Carbon* **41** 1551
[5] Zhang Q, Zhao M Q, Huang J Q, Liu Y, Wang Y, Qian W Z and Wei F 2009 *Carbon* **47** 2600
[6] Kim S N, Rusling J F and Papadimitrakopoulos F 2007 *Adv. Mater.* **19** 3214
[7] Zhang Q D, Piro B, Noël V, Reisberg S and Pham M-C 2010 *Adv. Nat. Sci.: Nanosci. Nanotechnol.* **1** 045011
[8] Feng B, Hong R Y, Wu Y J, Liu G H, Zhong L H, Zheng Y, Ding J M and Wei D G 2009 *J. Alloys Compd.* **473** 356
[9] Raj K and Moskovitz R 1990 *J. Magn. Magn. Mater.* **85** 233
[10] Liu Z, Wang J, Xie D H and Chen G 2008 *Small* **4** 462
[11] Dong K Y, Su S L and Jackie Y Y 2006 *Chem. Mater.* **18** 2459
[12] Xu Z, Shen C, Hou Y, Gao H and Sun S 2009 *Chem. Mater.* **21** 1778
[13] Dupuis A C 2005 *Prog. Mater. Sci.* **50** 929
[14] Minh P N, Chuc N V, Hong P N, Tam N T T and Khoi P H 2008 *J. Korean Phys. Soc.* **53** 2725
[15] Chuc N V, Tam N T T, Tu N V, Hong P N, Tinh T X, Dat T T and Minh P N 2011 *Int. J. Nanotechnol.* **8** 188
[16] Zhao W, Basnet B, Kim S and Kim I J 2014 *J. Nanomater.* **2014** 327398
[17] Pint C L, Pheasant S T, Parra-Vasquez A N G, Horton C, Xu Y Q and Hauge R H 2009 *J. Phys. Chem. C* **113** 4125
[18] Amama P B, Pint C L, McJilton L, Kim S M, Stach E A, Murray P T, Hauge R H and Maruyama B 2009 *Nano Lett.* **9** 44
[19] Hata K, Futaba D N, Mizuno K, Namai T, Yumura M and Iijima S 2004 *Science* **306** 1362
[20] Saengmee-anupharb S, Thongpang S, Bertheir E S P and Singjai P 2011 *ISRN Nanotechnol.* **2011** 684748
[21] Xie K, Muhler M and Xia W 2013 *Ind. Eng. Chem. Res.* **52** 14081
[22] Liu H, Zhang Y, Li R, Sun X, Wang F, Ding Z, Me’rel P and Desilets S 2010 *Appl. Surf. Sci.* **256** 4692
[23] Jung M, Eun K Y, Lee J K, Baik Y J, Lee K R and Park J W 2001 *Diam. Relat. Mater.* **10** 1235