Growth and Application of Ultra-long Multi-walled Carbon Nanotube

Sayaka Shimizu, Morihiro Okada,Yoku Inoue, Youitirou Neo, Hiroshi Kume, Toru Aoki, Hidenori Mimura

Abstract:

We found the easy and efficient synthesis method of the vertically aligned ultralong multi-walled nanotubes using iron chloride powder. The 2.1-mm-long bulk nanotubes can be grown by conventional thermal chemical vapor deposition on bare quartz surface with the single gas flow of acetylene for 20 min. In addition to the high growth rate, the bulk of carbon nanotubes is easily spun into the yarn by pulling it out, and the present method also provides the coating ability with nanotubes as a new functionality of this nanomaterial. © 2008 American Institute of Physics.

Keywords: CNT, CVD, yarn, FeCl$_2$.

1. Introduction

Since their discovery in 1991 [1], carbon nanotubes (CNTs) have been regarded as a key nanomaterial for a wide range of applications [2]. Their small tubular structure is responsible for diverse features, such as high mechanical strength [3], strong electric properties [4], good heat conductance [5], and high electron emission [6], which are of interest for academic researchers and industries [7]. However, despite several efforts [8]-[10], a suitable mass-synthesis method for CNTs that promotes widespread practical applications is not yet to be established.

Here, we present a simple and easy way for mass synthesis that yields ultra-long, vertically aligned multi-walled CNTs (MWCNTs).This method requires no additional process for catalyst preparation predeposition and only requires iron chloride powder and acetylene gas used. We found that high dehydrogenation activity of iron chloride on acetylene increases the growth rate of CNTs compared to conventional predeposited metal catalysts. The lengths of obtained MWCNTs ranged up to the millimeter scale, and they can easily be spun into yarn by hand with the naked eyes. In addition, this method can be used to coat the entire surface of a target with MWCNT using iron chloride in vapor phase as a growth initiator. The most attractive feature of the proposed method is that it is extremely simple, and therefore, could be used in any laboratory for bulk production of MWCNTs.

Vertically aligned CNTs (VACNTs) were synthesized using a conventional thermal chemical vapor deposition (CVD) system.

A smooth quartz substrate was placed at a center of horizontal quartz tube furnace (40 mm in diameter and 30 cm in length) with iron chloride (FeCl$_2$) powder (99.9%, Kojundokagaku Laboratory) using a quartz boat.

As a pretreatment, the quartz substrate was cleaned using ethanol. Typically, a thin metallic film deposited on a substrate is widely used as a catalyst; however, in the proposed method, such a film need not be predeposited. During heating, the sample was maintained at vacuum of 5×10^{-2} Torr, and once the optimal growth temperature was reached, it was purged with acetylene (98%, Japan Air Gases) gas using a mass flow controller. CVD growths were carried out at a furnace temperature of 820 °C at 5 Torr. Hereafter, we refer to the proposed method as "chloride mediated CVD" (CM-CVD). Features such as using a pure gas flow and not using a metallic film on the substrate are peculiar to CM-CVD and could lead to significant reduction in the mass-production costs of CNTs.

2. Result and discussion

A VACNT sample is shown in Fig. 1(a). Densely grown CNTs are vertically aligned on a quartz substrate(10×10 mm^2). The top (grown) surface is macroscopically flat, i.e. the CNT length is uniform throughout the substrate (Fig. 1(a)).] Figure 1(b) compares the samples. From Figs. 1(a) and 1(b), one can observe the vertically aligned growth throughout the surface, including the side and back surfaces.
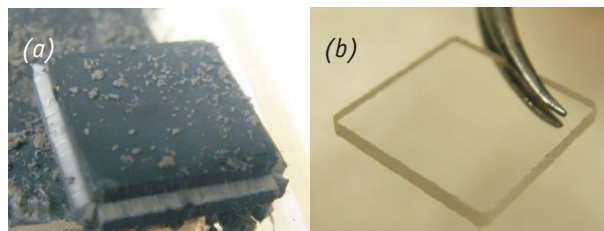

Fig. 1. (a) VACNT samplel (b) SiO$_2$ substrate.

In CM-CVD, the stability of the VACNTs grown on a substrate depends on the growth conditions, such as the growth time and pressure. It is found that the 1.5 mm-long CNTs adhere strongly to the substrate, while the VACNTs grown under 4 Torr detached easily, leaving a very clean surface.
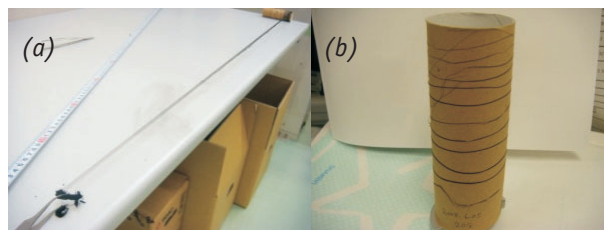

Fig. 2. (a) Pinching and pulling out 50cm CNTl, (b) extended CNT.

For this type of VACNTs, one can easily spin a CNT yarn using tweezers or an adhesive tape [11]. As seen in Fig. 2(a), we obtained a 50 cm CNT yarn by pinching and pulling out CNTs [12]. Figure 2(b) shows that during the pulling, a tensioned yarn extended up to 1 m 50 cm in length.

In this study, we propose the CNT growth model in CM-CVD. To understand the reaction process, the transition of the partial pressure of released gases was measured using a quadrupole mass analyzer (MKS instruments, PPT-C200-F2T), as shown in Fig. 3. In the mass analysis, a part of the released gas was sampled, and the operating pressure was reduced to 1×10^{-6} Torr. After the beginning of the growth process with the acetylene (C_2H_2, 26 amu) feed, HCl (36 amu) was generated for a very short time as a trigger signal. After some time, hydrogen (2 amu) increased for 15 min, and then decreased gradually. We believe that the generation of the two gases (HCl and H_2) relate to "bud beak" and "CNT growth", respectively.

HCl generation can be expressed as

$$FeCl_2 + C_2H_2 \rightarrow FeC_2 + 2HCl \tag{1}$$

Since $FeCl_2$ is completely vaporized at 820 °C [13], therefore, FeC_2 molecules or related carbon-rich iron carbide species are considered to nucleate into nanoparticles as a result of multiple collisions, and to be deposited on the surfaces in the heated zone. Then, the FeC_2 nanoparticles segregate into graphene layers as follows [14].

$$FeC_2 \rightarrow FeC_{2-x} + xC \tag{2}$$

We believe that CNT growth in CM-CVD is initiated during the segregation of the graphene layers from carbon-rich iron carbide (FeC_2) as predicted by Jourdain *et al.* [15]. Once budlike CNT structures are formed, the growth is triggered.

The subsequent hydrogen generation reflects the carbon supply for the growth of CNTs because hydrogen generation is the result of only the decomposition of acetylene. There are two possible reactions that result in the decomposition into hydrogen. One is a Fe-catalyzed dehydrogenation reaction, and the other is the reaction mediated by iron chloride. However, from our conventional CVD experiments, we found that small amounts of hydrogen are generated during the growth on a Fe predeposited quartz substrate, and the hydrogen generation is terminated within 3 min. In addition, the length of the CNTs grown using this simple thermal CVD method was less than 300 μm. Therefore, these results indicate that the observed high-speed growth is mediated by iron chloride. At first, iron chloride surfaces may appear on the catalyst nanoparticles at the root of CNTs due to the adsorption of the remaining $FeCl_2$ and/or chlorination of surface. Fe atoms with the remaining HCl, according to the following well-known reaction:

$$Fe + 2HCl \rightarrow FeCl_2 + H_2 \tag{3}$$

Then, acetylene is highly decomposed at the root of CNTs due to the high dehydrogenation activity of iron

chloride [16]. Reactions of acetylene at the iron chloride surfaces are expressed as follows:

$$FeCl_2 + C_2H_2 \rightarrow FeC_2 + 2HCl \tag{4}$$

In the reaction, acetylene is decomposed, and FeC_2 phase is again considered to form. Since FeC_2 highly exceeds a solubility limit of carbon in iron, carbon is expected to rapidly segregate as follows:

$$FeC_2 \rightarrow FeC_{2-x} + xC \tag{5}$$

By this process, the CNTs grow because of this carbon segregation. Here, Eq. (5) is the same with Eq. (2). This reaction cycle is expected to repeat rapidly, which means the ultra-long VACNTs are grown in a short amount of time. This reaction cycle, where iron chloride acts as catalyst, is one of the most important discoveries of this study.

For the CNT coating, a vapor phase reaction of iron chloride with acetylene is essential. By observing the heating process through a viewing port, we found that $FeCl_2$ started to vaporize at 550 °C, and completely vaporized over 800 °C, when the local vapor pressure reached 70 Torr. During this heating process, $FeCl_2$ vapor spreads across the entire heated space. Since acetylene flow causes the sublimation of FeC_2 nanoparticles on the entire surfaces, CNTs can be grown everywhere, even on micron-spaced quartz wool. This growth initiation *via* vapor phase $FeCl_2$ is another important finding of this study.
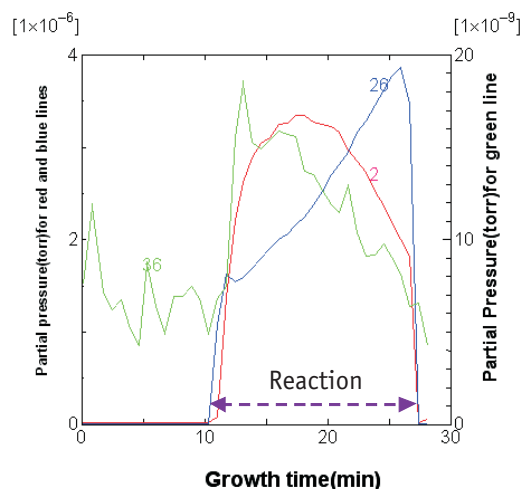
Fig. 3. Sampled partial pressure of released gases as a function of growth time. Numbers denote the mass unit, where 2, 26 are left axis and 36 is right axis.

3. Conclusion

In summary, we established a simple one-step growth method of aligned bulk CNTs mediated by iron chloride. The CM-CVD offers a potentially viable VACNT mass production method. In the present system, we can grow 1 g of VACNT for 2 h process time including 15 min of growth time, and material cost performance is as low as US $ 0.5/g. If a large number of flat plates are arranged in a growth chamber, then a significant amount of VACNTs can be easily obtained from the entire surface by high-speed coating growth. Although our VACNTs length has not exceeded the world record [17] (18 mm: reported by

University of Cincinnati researchers), the rate of "production per process time and cost [g/h-$]" might be significantly high. We believe that this very simple one-step growth technology, based on bifunctionality of $FeCl_2$, will contribute to the development of new CNT applications.

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