Large area growth of aligned CNT arrays on spheres: Cost performance and product control

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ABSTRACT

We present a systematic optimization of the ferrocene chemical vapor deposition process for the low cost mass production of millimeter aligned carbon nanotubes (CNT), and also a successful control on the structure of the CNT product in this process. An overall carbon efficiency of 50%, almost 50 times higher than the conventional procedure, was achieved. The length and average diameter of the CNTs can be controlled in a wide range. CNTs with narrow diameter distribution were also obtained from nickelocene based catalyst.

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Aligned carbon nanotube (CNT) arrays grown vertically on flat substrate possess superior properties, such as similar length, identical orientation, high purity and easy incorporation to macroscopic fibers.[1–3] The as-grown products can be introduced, without complex pretreatments, into many potential applications.[4–8] Owing to these advantages, various chemical vapor deposition (CVD) methods[4,9–14] have been proposed to produce aligned multi-walled and single-walled CNTs with controlled structures.[4,15,16] Among all these processes, ferrocene-based CVD[10,11] (called ferrocene CVD hereafter), where catalyst is *in situ* formed and continuously provided, is considered as the most promising way for the large scale production of aligned CNTs, since complex catalyst preparation is avoided. Previously, we have demonstrated that, on large amounts of spherical particles, bulk synthesis of aligned MWNT arrays up to millimeter, with the productivity of 200 g/h, was achieved by this ferrocene CVD process.[17] In that work, spherical substrates held keys to the successful mass production, since large growth area and easy fluidity of spheres had never been achieved before when conventional flat substrates were used. In this letter, we present our recent results on the further improvement of this process, which contain mainly the following three aspects: (1) the optimization of growth conditions, such as growth temperature and growth area, to reach highest growth rate and feedstock efficiency; (2) the coupling of current process with the production of CNT aggregates[18] to further lower the process cost; (3) the control on CNT length, average diameter, as well as diameter distribution. The

current work leads us to the large scale production of long MWNT arrays in a more controllable and cost-effective way.

Aligned CNT arrays were synthesized by CVD using ferrocene as the catalyst precursor and cyclohexane as the solvent and carbon source in 1 inch alumina or quartz tube, similar to our previous work.[19,20] Quartz wafer ($25 \times 25 \times 0.8$ mm) or ZrO_2 spheres (0.8 mm in average diameter) were kept in the center of the tube as growth substrates for CNT arrays while $Fe/Mo/Al_2O_3$ catalysts[18] (in a quartz boat) were placed at the downstream region. The temperature at the center of the furnace was controlled to be around 800 °C, while the catalyst at the downstream was usually around 700 °C. Feedstock solution was injected into the reactor by a syringe pump, along with Ar/H_2 as a carrier gas (the different growth parameters are listed in Table 1). After the CVD, aligned CNT arrays on quartz (or spheres) and random CNT aggregates in the quartz boat were collected and weighted separately. All the products were characterized by SEM (JEOL 7401F, excited at 3.0 kV), TEM (JEOL 2010, excited at 200.0 kV), the Raman Spectroscopy (RM2000, Renishaw, excited at 633 nm).

Fig. 1 presents the morphologies of aligned CNTs grown on the quartz wafer and ZrO_2 spheres. Vertically aligned multi-walled CNT arrays can always form perpendicular to the growth surface. In the case of spherical particles, continuous and dense CNT film forms uniformly at all directions (Fig. 1c and d). This uniformity is attributed to the high driven force of CNT growth. Aligned CNT film can grow upwards without the influence of applied pressure, as demonstrated before.[21] As spheres offer significantly larger growth area than conventional quartz slices in the same reactor space (usually 2 orders of magnitude higher), more CNT arrays can be obtained in one CVD. The products are of the same purity and defect degree as those from quartz wafers, confirmed by TGA and Raman. The details can be found in our previous report[17].

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Table 1
Influence of operation parameters on the CNT yield in 1 h growth

Experiment no.	Substrate[a]	Growth area(dm²)	Feeding rate(ml/h)	Carrier gas (sccm)	CNT yield(g)	Carbon efficiency (%)
1	Q	0.125	4.8	600	0.044	1.2
2	Z	3	4.8	600	0.60	16.1
3	Z	20	4.8	600	0.61	16.3
4	Z	3	2.4	300	0.30	16.1
5	Z	3	1.6	200	0.18	14.5
6	Z	3	2.4	600	0.18	9.6
7	Z	3	7.2	600	0.95	17.0
8	Z	3	9.6	600	1.53	20.5
9	Z+C	3	4.8	600	0.60+0.74	35.8
10	Z+C	3	1.6	200	0.18+0.49	53.8

[a] Q stands for quartz wafer, Z stands for ZrO_2 spheres and C stands for $Fe/Mo/Al_2O_3$ catalyst.

First, we conducted experiments under different temperatures. The average growth rate reached the maximum around 800–820 °C, where almost 2 mm arrays were synthesized within 1 h. However, even at this highest growth rate, 4.8 ml cyclohexane yielded only around 0.044 g of aligned CNTs when only one quartz wafer (1 in.) was used as the growth substrate. The carbon efficiency, which is defined as percentage of carbon in feedstock converted into the final CNT product, was as low as 1.2% (the carbon efficiency in our previous fluidized process can be over 90% [18]). This low conversion rate of cyclohexane not only resulted in a high cost for CNT product, but also caused a high liquid content in the exhaust, making the operation and maintenance of this process more difficult. We therefore systematically studied the influences of growth parameters such as growth area, residual time, feeding rate (partial pressure of catalyst precursor and carbon source) on the carbon efficiency and listed the some typical results in Table 1.

As can be seen in the comparison of experiment No.1 and No.2, when spheres were involved, the CNT yield was significantly improved by 13 times and feedstock efficiency reached 16%, due to the larger available growth surface provided. However, the CNT yield does not always increase proportionally to the growth surface, as shown in experiment No. 3, where more spheres were used but CNT yield remained almost the same. When we decreased flow rate of carrier gas and feeding rate of cyclohexane/ferrocene solution at the same time, as shown in No.4 and 5, the carbon efficiency still remained around 16%. The above two results consist with each other since larger growth and longer residual time should work similarly. Both of them just provide more chance/time for further reaction (larger volume space velocity in chemical engineering).

One possible reason why the feedstock could not be further converted to CNT is presented here. We examined the iron content in our CNT products and found that, the amount of ferrocene in the precursor solution used in a typical CVD (mostly resulted in encapsulations inside of produced CNTs), was around 50%, much higher than the percentage of carbon deposition, 16%. It is thereby suspected that the gradual consumption of catalyst precursor may be one reason for the lower reactivity. Therefore, higher catalyst concentration should be helpful for the further carbon deposition. However, although we did find that faster catalyst feeding really increased the carbon efficiency slightly, as shown in experiment No.6, 7, and No.8 (up to 20%), it gave larger diameter, more metal contamination and worse crystallization for the final product, as confirmed by TEM. Similar result was obtained when we only increased the feeding rate of catalyst while kept the carbon source the same by using a higher concentration ferrocene in cyclohexane. Apparently, this deterioration of the product is due to the higher concentration of catalyst precursor in the CVD atmosphere. When the concentration of catalyst precursor was the same while carbon source was lowered, the growth rate decreased significantly and the

efficiency is usually not higher than 10% (not shown). It is also not a preferable way.

When we examined the remaining product carried out by Ar/H_2 with a gas chromatography (GC), the exhaust was found as a mixture of different hydrocarbons, which contained both gases (C_1–C_4) like methane, ethane, ethylene, etc., liquid (C_5, C_6) and even some naphthalene (C_{10}, solid at room temperature). Interestingly, most of these hydrocarbons have been used as carbon source for CNT production previously. Therefore, for another simple consideration, we may introduce this mixture into some other processes to use it while keeping the growth of aligned CNT arrays untouched. One promising approach is shown in experiment 9 and 10. We combined this ferrocene CVD with our existing CVD process by placing some Fe/Mo/Al_2O_3 catalyst at the downstream of the reactor. As expected, aggregated multi-walled CNT network was obtained at downstream using exhaust of ferrocene CVD as the carbon source. Meanwhile, aligned CNT arrays grew without any influences. Owing to the further reaction on downstream catalyst, the overall carbon efficiency was improved to 35% (No.9) or even above 50% (No.10 at lower space velocity). GC analysis revealed that the heavy hydrocarbons were significantly suppressed (converted into lighter molecules and CNTs). This can also be easily noticed at the outlet of the reactor (inset in Fig. 2a.). The optical, SEM, TEM images of the product are presented in Fig. 2a, b and c. HRTEM and Raman spectroscopy confirmed the product as well-graphitized MWNTs.

After this ferrocene CVD process optimized and product cost also considerably decreased, better control on the CNT product, especially, several key structure parameters of a CNT became our next target.

The length of a CNT array can be easily tailored by simply changing the growth time. We have confirmed both theoretically [22] and experimentally [23] that this process is not limited by carbon source diffusion. The MWNT film will not meet high diffusion resistance until it approaches 1 m thick. Now we are able to produce several mm on our 1-mm-diameter spheres and up to 15 mm on quartz substrates.

Diameter of the produced MWNTs can also be adjusted. Fig. 3a and b show two typical aligned CNT samples from CVD with different
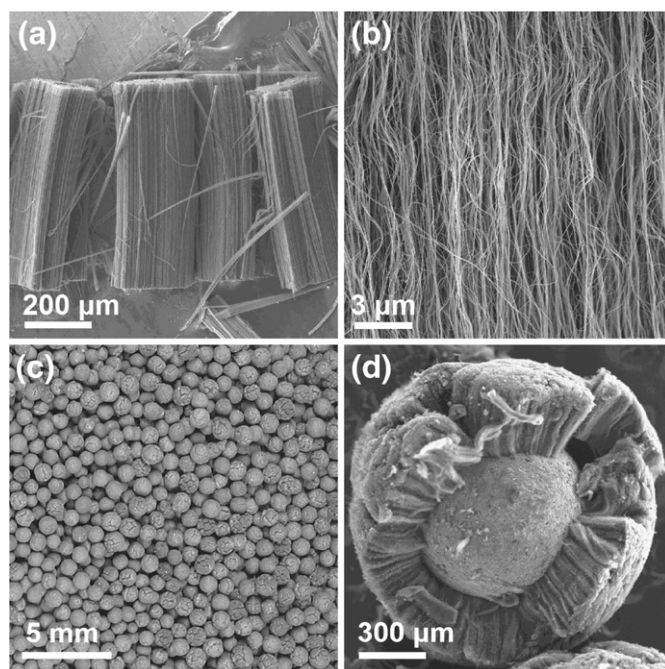
Fig. 1. Morphologies of aligned CNT arrays: (a) SEM micrograph of CNT arrays grown on flat quartz wafer, (b) enlarged SEM micrograph showing the CNT alignment, (c) optical image of CNT arrays grown on large amounts of spheres, (d) SEM micrograph of single sphere-CNT structure.
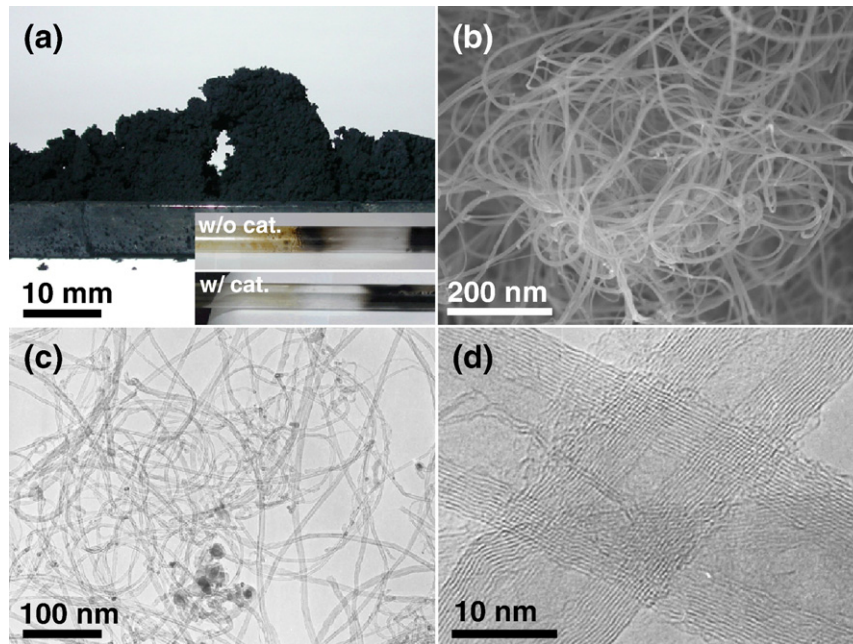
Fig. 2. Morphologies of aggregated CNTs at the downstream of reactor: (a) optical image of the powder-like product, inset shows the difference in the reactor outlet with and without downstream catalyst, (b) SEM micrograph of the random oriented CNT aggregates, (c) TEM micrograph of the product, (d) HRTEM micrograph of the product.
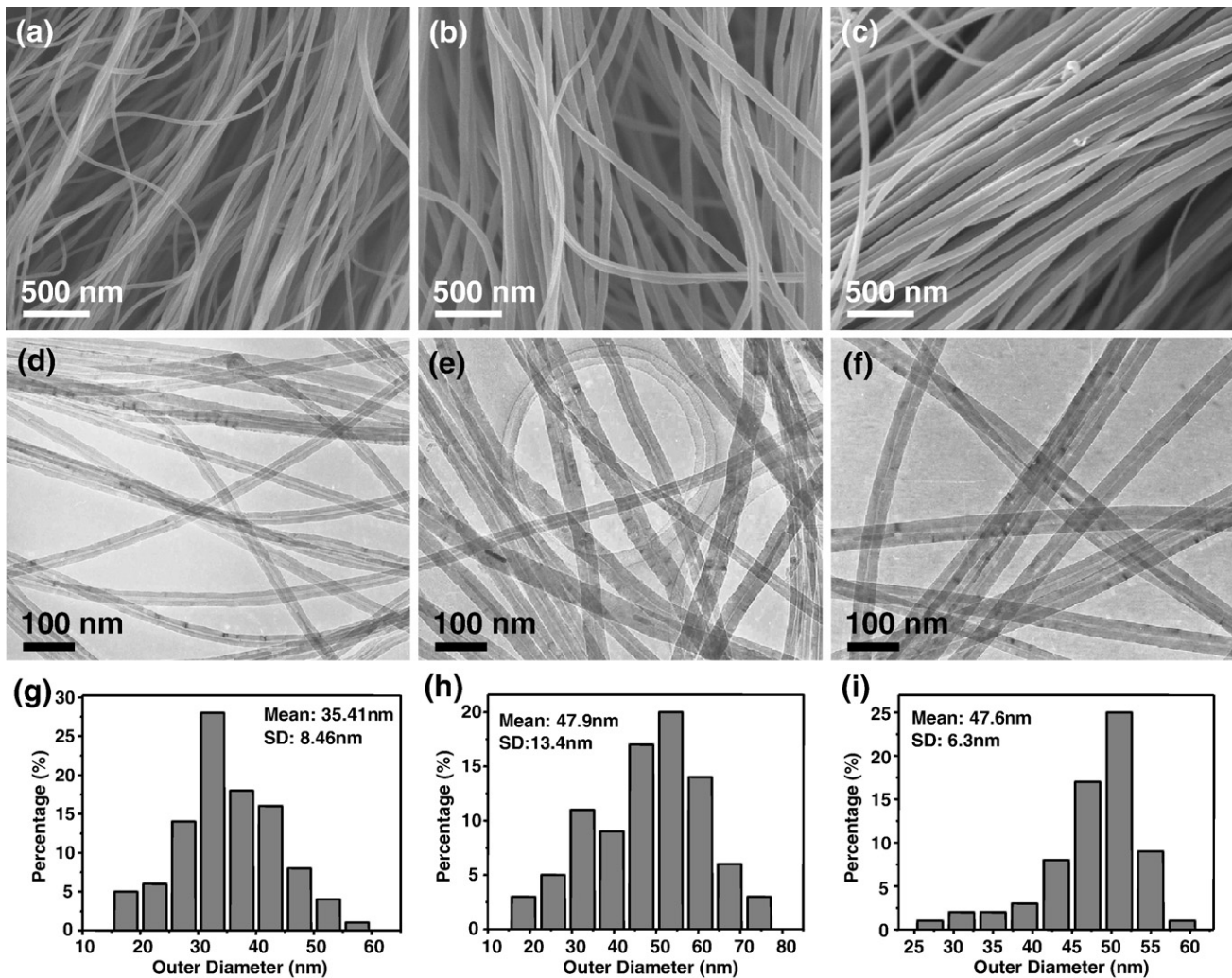
Fig. 3. SEM, TEM micrographs and diameter histograms of aligned CNT arrays produced at different conditions, showing that both the average value and distribution of outer diameter can be adjusted: (a)(d)(g) ferrocene/cyclohexane, feeding rate 7.2 ml/h (b)(e)(h) ferrocene/cyclohexane, feeding rate 9.6 ml/h (c)(f)(i) nickelocene/cyclohexane, feeding rate 7.2 ml/h.

feeding rates of the precursor solution (importantly, catalyst concentration inside of reactor). For the outer diameter, the histograms (Fig. 3g and h) obtained from TEM (Fig. 3d and e) clearly show that the average value can be easily controlled by this single parameter. It can be adjusted from 25 nm to 100 nm continuously. In addition, if other catalyst precursors are used, the diameter distribution can also be controlled to some extent. Fig. 3c is an aligned CNT sample obtained from nickelonece/cyclohexane solution. Although the average diameter is slightly larger than products from ferrocene at similar condition (Fig. 3a), the distribution is much narrower, as shown in Fig. 3f, than the CNTs with similar average diameter produced from ferrocene-base catalyst (Fig. 3b). As to the inner diameter, however, there was no significant change for different catalyst concentrations. The inner diameter is from 5 to 15 nm with the mean value of about 10 nm in all three samples, the reason of which needs further investigation. Nevertheless, we can tailor the number of walls of a MWNT by using different carbon source, which means the size of the inner channel can also be adjusted. [24] More precise control over this process and the product can be achieved by now.

In summary, firstly, we studied the operation parameters on the yield of the aligned CNT arrays in this ferrocene-based CVD for the mass production of long MWNT arrays. After we optimized several key parameters and proposed a promising coupling strategy, the overall carbon efficiency was improved from around 1% to over 50%. It also allowed us to produce high quality aligned and aggregated CNT at the same time. Furthermore, the length, average diameter and also diameter distribution of mass produced MWNT arrays become adjustable over a wide range. It is reasonable to believe this large scale, low cost and controllable growth will facilitate the research on the applications of these fascinating long CNTs.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.matlet.2008.09.015.

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