Over 99.6 wt%-pure, sub-millimeter-long carbon nanotubes realized by fluidized-bed with careful control of the catalyst and carbon feeds

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Abstract

To establish a method for sub-second conversion of acetylene to sub-millimeter-long carbon nanotubes (CNTs), we have proposed and developed an internal heat-exchange reactor for fluidized-bed chemical vapor deposition (FBCVD). This reactor enabled sufficient heating of the reaction gas and uniform heating of the bed of alumina beads at a space velocity as high as 3600 h^{-1} . The direct feeding of the catalyst vapors (aluminum isopropoxide for the alumina support layer and ferrocene for the iron particles) to the bed separately from the other gases, which were fed through the heat-exchange and preheating zone and the distributor, enabled the careful control of the catalyst particles deposited on the beads. By decreasing the

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acetylene feed concentration and preventing the deactivation of small Fe particles, we realized semi-continuous production of 99.6–99.8 wt%-pure, sub-millimeter-long, few-wall CNTs with an average diameter of 6.5 nm at a carbon yield of 42%. The FBCVD reactor with an internal heat-exchanger can be scaled-up for practical mass production with uniform and energy-saving heating.

1. Introduction

Carbon nanotubes (CNTs) have attracted a lot of attention owing to their unique one-dimensional nanostructure and extraordinary electrical, thermal, mechanical, and optical properties. Their ability to form self-organized conductive networks as well as their large specific surface area, high chemical/mechanical stability, and light weight make them an attractive candidate for electrodes of batteries, capacitors, and solar cell devices [1–6]. The low-cost production of carbon nanotubes (CNTs) will open many opportunities for their practical application. Different methods have been used to produce high-quality CNTs, including electric arc discharge [7,8], laser vaporization [9], chemical vapor deposition (CVD) [10–12], and plasma-enhanced CVD [13]. Among these methods, CVD is one of the most commonly used techniques for laboratory- and commercial-scale controllable growth of CNTs [14,15]. Fluidized-bed CVD (FBCVD) is one of the most popular ways for the mass production of CNTs because of advantages in terms of providing sufficient surface area for supporting catalysts and growing CNTs, excellent mass and heat transfer, easy scale-up, and continuous operation [14–20]. Single-wall CNTs (SWCNTs) to multi-wall CNTs (MWCNTs) have been mass produced by FBCVD. However, CNTs tend to entangle with catalysts and supports and thus need post treatment, which creates additional costs and damages the CNTs.

Since the report in 1996 [21], vertically aligned (VA) CNT arrays have been a focus in CNT production because of the uniform tube length, uniform orientation, and extra high purity. Impurity-free, millimeter-long, SWCNTs have been produced by the water-assisted CVD method [22], and such synthesis is now possible using several CVD recipes on catalyst-supported flat substrates [23–26]. However, the limited surface area of the two-dimensional (2D) growth substrate is a major obstacle for the mass-production of such CNTs. To improve the productivity of CNT arrays, some researchers have chosen

three-dimensional (3D) support materials to extend the reaction surface. Wei and coworkers used spherical ceramic beads in a thin fixed-bed and synthesized MWCNT arrays [27–29]. They also used vermiculite as a catalyst carrier and grew micrometer-tall MWCNT arrays among the layers of vermiculite via FBCVD, and realized the mass production of CNTs at 3.0 kg h^{-1} using a pilot plant reactor with an inner diameter of 0.5 m [18,30].

We previously developed an original FBCVD method and realized semi-continuous production of sub-millimeter-long few-wall CNTs (FWCNTs) from acetylene (C_2H_2) at a high carbon yield $\geq 70\%$ and short gas residence time of $\sim 0.3 \text{ s}$ [19]. The high gas feed enabled the rapid conversion of C_2H_2 to CNTs but caused insufficient heating of the bead bed when scaled up. In situ catalyst deposition on spherical alumina (Al_2O_3) beads by the FBCVD enabled the semi-continuous operation of catalyst deposition, CNT growth, and CNT separation/collection. However, the catalyst vapor fed through the distributor caused stacking after ~ 20 cycles and resulted in an interrupted semicontinuous operation. In this study, we designed and developed a new FBCVD reactor with an internal heat-exchange and preheating zone, and investigated its performance in producing sub-millimeter-long CNTs.

2. Experimental

All processes for catalyst (re)deposition, catalyst reduction, CNT growth, CNT separation, and removal of residual carbon were performed in a single FBCVD reactor (Fig. 1), similar to our previous work [19] but using a new reactor tube with an internal heat-exchange and preheating zone. Commercially available Al_2O_3 beads (purity $> 99.95 \text{ wt.}\%$, 0.5 mm average diameter, and 3.89 g cm^{-3} density, Taimei Chemicals, Japan) were loaded in the reactor with a static bed height of 30 mm. All of the gases except for the catalyst vapor were fed into the outer tube (inner and outer diameters of 50 and 55 mm, respectively).

The gas flowed down and was preheated by the furnace and the hot effluent gas in the inner tube, and then flowed into the inner tube (inner and outer diameters of 40 and 44 mm, respectively) through the distributor at the bottom of the reactor tube. Catalyst vapors of aluminum-isopropoxide and ferrocene were fed directly into the bed through the catalyst line penetrating the distributor from the bottom, minimizing their decomposition in the catalyst line while promoting their decomposition on the “hot beads” (Fig. 1a) (see also the detailed structure in Supplementary data, Fig. S1). An AlO_x support layer was formed on the beads in 2 min by supplying aluminum isopropoxide vapor, which was sublimated in an evaporator at 130 °C and carried in 450 standard cm^3 Ar gas [225 standard cubic centimeter (sccm), 3 atm for 2 min]. AlO_x support layer of a few tens of nanometers in thickness is very important to activate the Fe particles, not only for the growth on flat substrates [23,25] but also for the FBCVD growth on Al_2O_3 beads with sputtered catalyst [20]. We have carefully adjusted the Ar carrier gas volume to make Fe particles active and fixed it at 450 standard cm^3 . Then, Fe particles were formed on the AlO_x layer in 2 min by supplying ferrocene vapor, which was sublimated at 120 °C and carried in 50–250 standard cm^3 Ar gas (25–125 sccm, 2.2–2.5 atm for 2 min) to adjust the amount of Fe. Deposition of both AlO_x and Fe was performed with 4 vol% O_2/Ar to completely decompose the vapor, and at 20 slm to fluidize the bed well and uniformly deposit the catalyst on the beads. After reducing the deposited Fe by flowing 26 vol% $\text{H}_2/0.06$ vol% $\text{H}_2\text{O}/\text{Ar}$ at 9.48 slm for 10 min, CVD was performed by flowing 0.37–1.1 vol% $\text{C}_2\text{H}_2/26$ vol% $\text{H}_2/0.06$ vol% $\text{H}_2\text{O}/\text{Ar}$ at 9.48 slm for 10–20 min (Fig. 1b). Note that, the time for catalyst deposition was separated from that for CNT growth to obtain better control of the catalyst diameter (and thus the CNTs) and to ensure the continuous growth of CNTs from the catalysts on the bead’s surface [19]. The CNTs were then separated from the beads by vigorously fluidizing the bed with Ar gas at 20 slm for 10 min (Fig. 1c). The residual carbon on the beads was removed by oxidizing with 20 vol% O_2/Ar at 5 slm for 5 min. The

cycle was then moved to the redeposition process. Note that the AlO_x support layer was deposited every cycle to cover the coarsened Fe particles and have fresh Fe particles to maintain the small diameter of the catalyst particles and CNTs for further cycles [19]. These processes were repeated at a constant bed temperature of 745 °C by changing the gas flow to minimize the time and energy consumed for cooling/heating the bed [19]. Al_2O_3 beads with a relatively large diameter of 0.5 mm were used to keep the beads in the reactor tube under a high gas flow for growth and separation of CNTs. For such big beads, the minimal fluidization velocity is about 0.1 m s^{-1} [19]. We kept the flow rates and thus the gas velocities high enough for all steps of catalyst deposition (20 slm total flow rate and 1.0 m s^{-1} gas velocity), catalyst reduction (9.48 slm and 0.47 m s^{-1}), CNT growth (9.48 slm and 0.47 m s^{-1}), CNT separation (20 slm and 1.0 m s^{-1}), and oxidation of the residual carbon (5 slm and 0.25 m s^{-1}), resulting in a slugging fluidized bed (ambient pressure for all steps).

Fig. 1 – Schematics of the semi-continuous fluidized-bed process: (a) deposition of AlO_x support layer from aluminum-isopropoxide followed by deposition of Fe catalyst particles from ferrocene; (b) reduction of Fe catalyst by introducing H_2 followed by CNT growth by feeding C_2H_2 ; and (c) separation of CNTs from beads by increasing Ar gas flow. After removing the residual carbon on the beads by introducing O_2 , the next cycle is carried out starting at step (a). The whole process can be repeated by just changing the gas flow while keeping the bed heated at a fixed temperature for tens of cycles without changing the beads.

The synthesized CNT samples were characterized by field emission scanning electron microscopy (SEM; Hitachi S-4800, Tokyo, Japan). Some VA-CNTs were transferred from the beads to copper microgrids using tweezers and observed via transmission electron microscopy (TEM; JEOL 2000EX, Akishima, Japan). The CNT powders after separation were characterized by thermogravimetric–differential thermal analysis with a ramp rate of $5\text{ }^{\circ}\text{C min}^{-1}$ in air (TG-DTA; Rigaku TG8120, Akishima, Japan). The Brunauer–Emmett–Teller (BET) surface areas of the CNT samples were determined by N_2 (77 K) volumetric adsorption (Quantachrome Instruments Autosorb 1C, Boynton Beach, FL, USA) after pre-evacuation at

423 K and 10^{-4} Pa for 2 h. The CNT paper made by dispersion in ethanol and vacuum filtration was analyzed by X-ray fluorescence spectroscopy (XRF; Rigaku ZSX Primus 2, Akishima, Japan) to determine its elemental composition. The nominal thickness of the deposited Fe on the beads and the composition of the ash of the CNTs after the TG-DTA measurement were analyzed using an energy dispersive X-ray spectrometer (EDS; AMETEK EDAX Genesis, Berwyn, PA, USA) coupled with SEM. The catalysts deposited on the bead surface was analyzed by atomic force microscopy (AFM; SPM 9600; Shimadzu, Kyoto, Japan). The composition of the effluent gas from the FBCVD reactor was measured using a gas chromatograph (GC; Shimadzu GC-2014, Kyoto, Japan) equipped with a flame ionization detector.

3. Results and discussion

3.1 Heating state of the bed in the reactor with an internal heat-exchange and preheating zone

We first investigated and compared the heating states of the bead bed (30 mm static height) using the old single tube (22 mm in inner diameter, Fig. 2a) and the new coaxial double tube (40 mm in inner diameter for the bed, Fig. 2b) using the same furnace (300 mm in length, the distributor set at 32 mm from the furnace bottom, and the thermocouple for furnace control set outside of the reactor tube at 150 mm from the furnace bottom) with the same set temperature of 820 °C and various Ar flow rates. As with the old reactor tube (Fig. 2a), the top region of the bed was heated well to 830 °C at 140 mm from the distributor, but the bottom of the bed was insufficiently heated (690 °C) for an Ar flow rate of 3.16 slm. The temperature of the distributor of the reactor tube decreased to 630 °C with an Ar flow rate of 10 slm. Although fluidized beds are known to effectively enhance mass and heat transport,

rapid gas feed with a residence time ≤ 0.3 s causes insufficient heating. Such insufficient heating becomes more serious for larger reactor tubes. In contrast, for the new reactor tube with two feed lines (Fig. 2b), one line from the bottom directly to the bed for catalyst vapors and the other line for the other gases from the top through the heat-exchange and preheating zone and the distributor at the bottom, the temperature was more uniform. For the low total gas feed rate of 5 slm, the temperature at the distributor of the reactor tube was 750 °C because 1 slm Ar gas was directly fed into the bed from the catalyst line without preheating. With the increase in the total gas feed, the effect of the cold Ar gas decreased, the temperature became more uniform, and the temperature at the bottom of the reactor tube increased, reaching 780 °C at a high Ar gas feed rate of 30 slm (corresponding to a space velocity as high as 3600 h⁻¹). It should be noted that this more uniform heating was achieved for a reactor tube with a larger diameter (40 mm) than the old reactor tube (22 mm). The uniform heating even with the cold catalyst line gas will realize the efficient control of CNT growth by FBCVD with minimal catalyst stuck in the feed line. In addition, improved heating for the increased gas feed rate suggests good compatibility with scale-up. Furthermore, the heat-exchange zone will enable the reduction of the heating power consumption by heating the cold inlet gas with the hot effluent gas.

Fig. 2 – Schematics of (a) the old single tube and (b) the new coaxial double tube with temperature distributions for various Ar gas feeds. In (a), Ar gas was fed at 3.16–10 slm to the bed through the distributor at the bottom. In (b), Ar gas was fed through two inlets: constantly from the catalyst line at the bottom at 1 slm and from the top through the heat-exchange and preheating zone and the distributor at the bottom at 4–29 slm. The inner tube diameter for the bed was 22 mm for (a) and 40 mm for (b), and the set temperature was 820 °C for both (a) and (b).

3.2 Semi-continuous production of CNTs and resulting CNT structure

Photos of the fluidized-bed reactor were taken without gas flow at each step by interrupting the semi-continuous operation (Fig. 3). 82 g of pristine Al_2O_3 beads initially had a bed height of 3 cm (Fig. 3a). After depositing the Fe/AlO_x catalyst on the beads and reducing them with H_2 , CVD was carried out for 20 min. The bead bed remarkably increased in height (by more than four times) from 3 to 13 cm owing to the sub-millimeter-long CNT arrays grown on the bead surfaces (Fig. 3b). These CNT arrays were easily separated from the beads by vigorously fluidizing the beads with an increased Ar carrier gas flow and 0.82 g of CNTs,

which corresponds to a carbon yield of 37% (note that 2.23 g carbon was fed as 1.1 vol% C_2H_2 in 20 min), were collected in a 0.5 L bottle (Fig. 3d). The bead bed height decreased from 13 to around 3 cm (Fig. 3c), indicating rather efficient separation of CNTs from the beads. Then, the residual carbon on the beads was removed by oxidation with O_2/Ar for 5 min.

Fig. 3 – Photos of the fluidized-bed reactor taken by stopping the gas flow and interrupting the cycle at each step of the semi-continuous operation: (a) the bed with pristine beads before CVD; (b) the bead bed after CVD; (c) the bead bed after CNT separation; and (d) CNTs collected in a 0.5 L container in one cycle. All steps were performed by gas flow modulation at a fixed set temperature of 745 °C in a single fluidized-bed reactor.

Fig. 4a,b shows the SEM images of the CNT arrays collected in the container (Fig. 3d). The CNTs were 0.3–0.4 mm long and appeared well-aligned (Fig. 4a). Note that CVD was carried out with a lower gas flow rate of 9.48 slm than for CNT separation (~20 slm) so that CNTs could continuously grow without separation during CVD. However, in the enlarged image in Fig. 4b, the CNT array had rather poor alignment, which is sometimes observed for

VA-CNT arrays. Fig. 4d–f shows the TEM images of the CNTs taken near the top (Fig. 4d), middle (Fig. 4e), and bottom (Fig. 4f) of a single piece of the CNTs taken out of the array. The inset histograms of the CNT diameter distributions show that the diameter increased with increasing depth. Fig. 4c shows the average diameter of the CNTs at different depths from the top of the VA-CNTs. The diameter increased from 9.9 to 12.5 nm with an average diameter of 11 nm. Because CNTs grow in root growth mode, this result indicates that the diameter of the CNTs increases with time because of gradual coarsening of the catalyst particles during CVD, which is in good agreement with the diameter increase in growing SWCNTs during rapid growth on flat substrates by CVD [25,26,31–33]. We have achieved the semi-continuous production of sub-millimeter-long CNTs using the new reactor tube with a larger cross-section than our previous method. However, the resulting CNTs had a rather disordered structure with a large diameter. Next, we carried out the experiment with careful control of the catalyst and CVD conditions.

Fig. 4 – (a, b) SEM images of the CNTs separated from the beads by the gas flow and collected in the container bottle. (c) The change in the average diameter of the CNTs plotted against the depth from the top of the CNT arrays. The error bars show the standard deviation. (d–f) TEM images and diameter distributions of CNTs at the top, middle, and bottom of a single piece of the CNTs taken out from the array, respectively.

3.3 Controlling the amount and size of Fe particles and resulting CNTs

Control of the catalyst particle size is crucially important to control the diameter of CNTs. Because the catalyst particle size can be largely controlled by the nominal thickness of the catalyst layer [24,34], we changed the Ar carrier gas volume for ferrocene and examined the structure of the resulting Fe particles by AFM.

Fig. 5a shows the nominal thickness of Fe deposited on the AlO_x layer on the Al_2O_3 beads measured by SEM-EDS. To determine the average value for different beads, three different points were measured for each bead and five beads were measured for each condition. The nominal Fe thickness was 1.77 nm with 250 standard cm^3 Ar gas used to carry ferrocene, and it linearly decreased with Ar carrier gas volume to 0.28 nm with 50 standard cm^3 Ar gas. Fig. 5b–d shows AFM images of the Al_2O_3 bead surface with AlO_x support layer (Fig. 5b) and Fe catalyst particles on the AlO_x support layer (Fig. 5c and d). The AlO_x support layer had a roughness with in-plane size of several tens of nanometers (Fig. 5b). Ferrocene carried by 250 standard cm^3 Ar gas formed Fe particles with around 20–40 nm diameter (Fig. 5c), while ferrocene carried by 50 standard cm^3 Ar gas formed smaller Fe particles with around 10–20 nm diameter (Fig. 5d). The nominal Fe thickness was in a similar range to the sputtered catalyst used to produce millimeter-tall SWCNTs on flat substrates (typically 0.5–1.0 nm) [23,25,26]. However, the number density of Fe particles was about one order of magnitude smaller ($10^{10-11} \text{ cm}^{-2}$) than the sputtered catalyst (typically $\sim 1 \times 10^{12} \text{ cm}^{-2}$ [26]). The difference possibly arises from the different reactivity of the depositing Fe species: sputtered Fe atoms attach to both the AlO_x support layer and the nucleated Fe particles whereas ferrocene preferentially reacts with the nucleated Fe particles, resulting in larger Fe particles with smaller number density.

Fig. 5 – (a) Relationship between the nominal Fe thickness and the Ar carrier gas volume for ferrocene. AFM images of the alumina bead surface with different catalyst layers: (b) AlO_x, (c) 1.77 nm Fe on AlO_x, and (d) 0.28 nm Fe in AlO_x. The AlO_x layer was deposited by carrying aluminum isopropoxide using 450 standard cm³ Ar gas in all cases. The Fe catalyst was deposited on the AlO_x layer by carrying ferrocene using (c) 250 and (d) 50 standard cm³ Ar gas and reduced with 26 vol% H₂/0.06 vol% H₂O/Ar at 9.48 slm for 10 min.

Using these catalysts, we next synthesized CNTs by FBCVD under the same conditions as for Figs. 3 and 4 (i.e., 1.1 vol% C₂H₂/26 vol% H₂/0.06 vol% H₂O/Ar at 9.48 slm and 745 °C). Fig. 6 shows the SEM images, array lengths, and weight of the CNT arrays collected in the container bottle. From the SEM images, all of the CNTs are aligned and sub-millimeter long, even after separation by vigorous fluidization. The array lengths were longer for larger Ar carrier gas volume of ferrocene (i.e., larger Fe particles with larger nominal Fe thickness,

Fig. 5) and for longer CVD time of 20 min (Fig. 6k). For 10 min CVD, the weight of CNTs collected in the container bottle was 0.4–0.5 g per cycle, and similar for different Fe feeds. For 20 min CVD, the weight of CNTs increased from 0.45 to 0.82 g per cycle with increasing Fe catalyst feed from 50 to 250 cm³. The large Fe catalyst particles formed with 250 standard cm³ Ar carrier gas for ferrocene (Fig. 5c) gave a larger amount of CNTs after 20 min (0.82 g) than after 10 min (0.52 g), meaning that the catalyst remained active for 20 min. In contrast, the small Fe catalyst particles formed with 50 standard cm³ Ar carrier gas for ferrocene (Fig. 5d) gave a similar amount of CNTs after 10 (0.40 g) and 20 min (0.45 g), meaning that this catalyst was mostly deactivated in 10 min. To produce CNTs with small diameter at a high yield, it is essential to find the conditions that keep small Fe particles active for long CVD time.

Fig. 6 – (a–j) SEM images, (k) array lengths, and (l) weight of CNT arrays collected in the container bottle. The Ar carrier gas for ferrocene was varied between 50 and 250 standard cm^3 , and CVD was carried out under the same conditions as Figs. 3 and 4, using 1.1 vol% C_2H_2 for either 10 or 20 min. The array lengths were measured for 10 arrays of each sample and the average value is plotted in (k) with the maximum and minimum values as error bars. The weight of CNTs collected in one cycle of ~1 h is shown in (l).

3.4 Maintaining the activity of small catalyst particles by moderating C₂H₂ feed to produce sub-millimeter-long FWCNTs with reduced diameter and improved purity

Because small catalyst particles are more easily deactivated by C₂H₂ with high concentration [25,32], we reduced the C₂H₂ feeds to maintain the activity of the small Fe particles. Fig. 7a–h shows the SEM images of CNT forests collected in the container bottle. The CNTs were sub-millimeter-long and well-aligned for all the conditions considered: large and small Fe catalyst particles (250 and 50 cm³ Ar carrier gas for ferrocene, respectively), 0.73 and 0.37 vol% C₂H₂, and 10 and 20 min CVD. The amounts of CNTs are shown in the histograms for different C₂H₂ concentrations in Fig. 7i–k. With a high C₂H₂ concentration of 1.1 vol% (Fig. 7i), increasing the CVD time from 10 to 20 min only increased the amount of CNTs for large Fe particles, meaning that the small catalyst particles were rapidly deactivated within about 10 min. With a low C₂H₂ concentration of 0.37 vol% (Fig. 7k), increasing the CVD time from 10 to 20 min resulted in an increased amount of CNTs for both large and small Fe particles, because of the increased lifetime of the small Fe particles. However, the significant decrease in the C₂H₂ concentration from 1.1 to 0.37 vol% resulted in a significant decrease in the amount of CNTs collected, because of not only the decreased amount of synthesized CNTs but also the decreased separation efficiency of the short CNT arrays from the beads. The moderate C₂H₂ concentration of 0.73 vol% (Fig. 7j) resulted in an increased CNT amount with increasing CVD time from 10 to 20 min for both large and small Fe particles. In addition, the CNT arrays were sufficiently long to be well-separated after 20 min CVD for both the catalysts, resulting in more than twice the amount of CNTs collected than for 10 min CVD. The moderate C₂H₂ feed of 0.73 vol% had the best balance between CNT growth rate and catalyst lifetime, and gave more CNTs (0.62 g, corresponding to a carbon yield of 42%) after 20 min with small Fe particles (50 cm³ Ar gas for ferrocene) than the high C₂H₂ feed of 1.1 vol% (0.45 g, corresponding to a carbon yield of 20%).

Fig. 7 – (a–h) SEM images and (i–k) weights of CNT arrays collected in the container bottle. The large and small Fe catalyst particles were prepared with (a–d) 250 and (e–h) 50 standard cm³ Ar carrier gas for ferrocene, respectively. The CNTs were synthesized by 10 min CVD for (a, c, e, g), and 20 min CVD for (b, d, f, h). The C₂H₂ concentrations were 0.73 vol% for (a, b, e, f), and 0.37 vol% for (c, d, g, h). The weights of CNTs obtained with C₂H₂ concentrations of (i) 1.1 (the same data as in Fig. 6), (j) 0.73, and (k) 0.37 vol%.

We then examined the diameter of the CNTs synthesized with the moderate C₂H₂ concentration of 0.73 vol% by TEM (Fig. 8). The CNTs produced using small Fe particles (50 standard cm³ Ar gas for ferrocene) with 0.73 vol% C₂H₂ (Fig. 8d–f) had smaller diameters, thinner walls, and cleaner surfaces than those produced using the large Fe particles (250 standard cm³ Ar gas for ferrocene) with both 1.1 (Fig. 4d–f) and 0.73 vol% (Fig. 8a–c) C₂H₂. The inset histograms of the CNT diameter distributions as well as the graph of the average diameter versus the depth from the top of the array (Fig. 8g) show that there was a gradual

increase in diameter from the top to the bottom in both cases. The average diameter increased from 8.7 to 11.6 nm using the large Fe particles with an average diameter of 10.1 nm, while it increased from 5.6 to 7.3 nm using the small Fe particles with an average diameter of 6.5 nm. Because CNTs grow via the root growth mode, the diameter of CNTs increased with time during CVD. Although the CNTs increased in diameter regardless of the Ar carrier gas volume for ferrocene, and thus the Fe particle size, CNTs with smaller diameters nucleated and grew from the smaller catalyst particles, and retained their smaller diameters when CVD was performed at a moderate carbon feed of 0.73 vol% C₂H₂. The N₂ adsorption measurement (Figs. S2, S3) at 77 K showed that the CNTs had a BET specific surface area of 440 m² g⁻¹ for the CNTs synthesized with the small Fe particles and moderate C₂H₂ feed of 0.73 vol% (Fig. S3), while it was 367 m² g⁻¹ for the large Fe particles and high C₂H₂ feed of 1.1 vol% (Fig. S2). The value of 440 m² g⁻¹ is about one-sixth of the theoretical value for monolayer graphene (2730 m² g⁻¹), and thus about one-third of that of SWCNTs with closed ends [35,36]. This result indicates that the average number of walls of the synthesized CNTs was three for the small Fe particles (50 cm³ Ar gas for ferrocene) with the moderate carbon feed (0.73 vol% C₂H₂).

Fig. 8 – TEM images and diameter distributions of CNTs synthesized with 0.73 vol% C_2H_2 for large and small Fe catalyst particles prepared with (a–c) 250 and (d–f) 50 standard cm^3 Ar carrier gas for ferrocene, respectively: (a, d) top, (b, e) middle, and (c, f) bottom of a single piece of CNTs taken out of the array. In (g), the changes in the average diameter of the CNTs with 250 cm^3 and 50 cm^3 Ar carrier gas for ferrocene are plotted against the depth from the top of the CNT arrays. The error bars show the standard deviation.

We analyzed the purity of CNTs synthesized with small Fe particles (50 cm^3 Ar gas for

ferrocene) and moderate carbon feed (0.73 vol% C₂H₂) by XRF and TG-DTA. We prepared two CNT papers for analysis by XRF. One paper is prepared by dispersing CNT powders (3 mg) in ethanol (30 mL) by ultrasonication (3 min) and filtrating all of the dispersion. The other is prepared by dispersing CNT powders (4 mg) with sodium dodecylbenzenesulfonate surfactant (SDBS, 50 mg) in water (40 mL) by ultrasonication (3 min), centrifuging the dispersion mildly (3000 rpm, 10 min), and then filtrating the supernatant. Note that no other purification, such as acid treatment, was applied in making these papers. Table 1 shows the elemental composition of these papers. The paper prepared by filtrating all dispersion without centrifugation (and thus without any purification) had a high carbon purity of 99.8 wt%. Such high purity is sometimes reported for SWCNT arrays synthesized on flat substrates [22] but not for FBCVD. The other paper prepared by filtrating the supernatant after a mild centrifugation showed even smaller contaminations of Al and Fe (1/6–1/7 of the paper without centrifugation). These Fe and Al contaminations should be contained mainly as powders just mixing with CNTs, which are easily separated from the CNT dispersion by settling during centrifugation. Note that if these catalyst impurities are encapsulated by CNTs, they cannot be removed just by dispersion and centrifugation. The TG-DTA result shows that the as-synthesized CNT powder had a carbon purity of 99.6 wt% with amorphous carbon of ~2 wt% and a high oxidation stability of ~650 °C (Fig. 9a). We analyzed the compositions of the ash after TG-DTA by EDX (Fig. 9b). The ash contained Fe and Al, which are attributed mainly to the Fe catalyst and AlO_x support layer being scraped off during the vigorous fluidization for CNT separation. The small Si content can be attributed to the reactor tube made of quartz glass being slightly scraped off. The weight of the ash was 0.05 mg, which is in good agreement with the 0.4 wt% impurity in the 10.2 mg CNTs used for the TG-DTA measurement when we take into account the weight increase from 0.019 mg Fe in the CNT powder to 0.027 mg Fe₂O₃ in the ash. There was a slight deviation in the carbon purity and

Fe/Al ratio between the two measurements (XRF in Table 1 and TG-DTA with SEM-EDS in Fig. 9). However, it is clear that the CNTs synthesized by our FBCVD method with careful control of the catalyst and carbon feeds gave 99.6–99.8 wt%-pure sub-millimeter-long CNT arrays, and that the small catalyst contamination can be reduced further easily by dispersion and centrifugation. Such pure and long CNTs are attractive especially for use as electrodes and 3D current collectors in secondary batteries [37] and electrochemical capacitors [38].

Table 1 – Elemental composition of the CNT papers* by XRF

Element	C	O	Al	Si	Fe
without centrifugation	99.81	0.10	0.06	0.01	0.02
with centrifugation**	99.84	0.14	0.01	0.01	0.003

*No chemical purification was applied in making the CNT papers.

**S is also contained at 0.61 wt% due to SDBS used in dispersion.

Fig. 9 – (a) TG-DTA curves of the CNTs synthesized using small Fe particles (50 cm³ Ar carrier gas for ferrocene) with 0.73 vol% C₂H₂. The sample was the same as that in Fig. 8d–f. (b) Elemental composition of the ash after the TG-DTA measurement.

We analyzed the composition of the carbon-containing species in the effluent gas from the FBCVD reactor by GC-FID at 2 min intervals for 20 min CVD (Fig. 10). We first supplied the CVD gas to the tube filled with pristine beads at room temperature (r. t.) to eliminate the influence of the catalytic reaction, and used this data as the reference. For the effluent gas during CVD, CH₄, C₂H₂, CO₂ and C₂H₄ were the main carbon-containing species. Small peaks for C₂H₆ and CO were also detected. The concentrations of CO₂ and CO were around 0.1 and 0.03 vol%, respectively, which are somewhat higher than the expected values from the 0.06 vol% H₂O feed, presumably because of some species desorbing from the beads, gas-lines, and/or the reactor walls. There were two stages of CNT growth: an early stage from 0 to 10 min, where the conversion of C₂H₂ to undetectable carbon (mostly CNTs) was as high as 70–80%; and a later stage from 10 to 20 min, where the catalyst gradually deactivated and the conversion decreased to 40–70%. The total conversion was around 60%. There was a deviation in the conversion of C₂H₂ to undetectable carbon (~60% by GC) and the carbon yield of CNTs (42% from the weight of collected CNTs). To clarify the reason, we analyzed the CNT arrays on beads without separating them by the gas flow (Fig. S4). Both the pristine beads and the beads with CNTs had certain distributions in radius. The CNT arrays on beads also had a certain distribution in height and were shorter on the beads (Fig. S4d) than in the container bottle (Fig. 6k). The catalyst line directly feeding the catalyst vapors to the center of the bed (Fig. S1) prevented the stacking of the distributor while caused some distribution in the catalyst thickness among different beads, resulting in the distribution in the CNT array height. It is probable that long CNT arrays were separated from the beads while the short CNT arrays remained on the beads, resulting in the smaller CNT yield than the C₂H₂ conversion. Development of a more efficient separation method is currently underway.

Fig. 10 – Composition of the effluent gas from the FBCVD reactor for different CVD times analyzed by gas chromatography. CVD was carried out with the moderate carbon feed of 0.73 vol% C₂H₂ and the small Fe particles with 50 cm³ Ar carrier gas for ferrocene.

4. Conclusions

In this study, we proposed and developed a new FBCVD reactor with internal heat-exchanger and preheater with the aim of efficiently synthesizing CNTs with controlled structure. The new heater realized uniform heating of the bed even for a space velocity as high as 3600 h⁻¹ (corresponding to a gas residence time <0.3 s at 745 °C) and direct feeding of cold catalyst vapor source into the bed. Using this new reactor, sub-millimeter-long CNTs were semi-continuously produced from C₂H₂ using a Fe/AlO_x catalyst at 745 °C with careful control of the structures of the catalyst and CNTs. The nominal thickness and size of the catalyst Fe particles could be easily controlled by the amount of ferrocene feed, whereas it was difficult to control the number density of the Fe particles, which remained at around 10¹⁰–10¹¹ cm⁻² (one order of magnitude smaller than those prepared on flat substrates by sputtering). With a high C₂H₂ feed (1.1 vol% C₂H₂), the weight of produced CNTs remained almost constant for different Fe catalysts for a short reaction time (10 min), whereas the small

Fe particles were easily deactivated within 10 min. A moderate C_2H_2 feed (0.73 vol%) increased the catalyst lifetime to ~20 min and realized the efficient production (carbon yield >40 at%) of small diameter FWCNTs (6.5 nm on average) at a purity of 99.6–99.8 wt%. This semi-continuous FBCVD process with careful control of the CNT structure can be used to produce CNTs for various practical applications, including electrodes for electric storage devices.

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Captions

Table 1 – Elemental composition of the CNT papers* by XRF

Fig. 1 – Schematics of the semi-continuous fluidized-bed process: (a) deposition of AlO_x support layer from aluminum-isopropoxide followed by deposition of Fe catalyst particles from ferrocene; (b) reduction of Fe catalyst by introducing H_2 followed by CNT growth by feeding C_2H_2 ; and (c) separation of CNTs from beads by increasing Ar gas flow. After removing the residual carbon on the beads by introducing O_2 , the next cycle is carried out starting at step (a). The whole process can be repeated by just changing the gas flow while keeping the bed heated at a fixed temperature for tens of cycles without changing the beads.

Fig. 2 – Schematics of (a) the old single tube and (b) the new coaxial double tube with temperature distributions for various Ar gas feeds. In (a), Ar gas was fed at 3.16–10 slm to the bed through the distributor at the bottom. In (b), Ar gas was fed through two inlets: constantly from the catalyst line at the bottom at 1 slm and from the top through the heat-exchange and preheating zone and the distributor at the bottom at 4–29 slm. The inner tube diameter for the bed was 22 mm for (a) and 40 mm for (b), and the set temperature was 820 °C for both (a) and (b).

Fig. 3 – Photos of the fluidized-bed reactor taken by stopping the gas flow and interrupting the cycle at each step of the semi-continuous operation: (a) the bed with pristine beads before CVD; (b) the bead bed after CVD; (c) the bead bed after CNT separation; and (d) CNTs collected in a 0.5 L container in one cycle. All steps were performed by gas flow modulation at a fixed set temperature of 745 °C in a single fluidized-bed reactor.

Fig. 4 – (a, b) SEM images of the CNTs separated from the beads by the gas flow and collected in the container bottle. (c) The change in the average diameter of the CNTs plotted against the depth from the top of the CNT arrays. The error bars show the standard deviation. (d–f) TEM images and diameter distributions of CNTs at the top, middle, and bottom of a single piece of the CNTs taken out from the array, respectively.

Fig. 5 – (a) Relationship between the nominal Fe thickness and the Ar carrier gas volume for ferrocene. AFM images of the alumina bead surface with different catalyst layers: (b) AlO_x , (c) 1.77 nm Fe on AlO_x , and (d) 0.28 nm Fe in AlO_x . The AlO_x layer was deposited by carrying aluminum isopropoxide using 450 standard cm^3 Ar gas in all cases. The Fe catalyst was deposited on the AlO_x layer by carrying ferrocene using (c) 250 and (d) 50 standard cm^3 Ar gas and reduced with 26 vol% H_2 /0.06 vol% H_2O /Ar at 9.48 slm for 10 min.

Fig. 6 – (a–j) SEM images, (k) array lengths, and (l) weight of CNT arrays collected in the container bottle. The Ar carrier gas for ferrocene was varied between 50 and 250 standard cm^3 , and CVD was carried out under the same conditions as Figs. 3 and 4, using 1.1 vol% C_2H_2 for either 10 or 20 min. The array lengths were measured for 10 arrays of each sample and the average value is plotted in (k) with the maximum and minimum values as error bars. The weight of CNTs collected in one cycle of ~1 h is shown in (l).

Fig. 7 – (a–h) SEM images and (i–k) weights of CNT arrays collected in the container bottle. The large and small Fe catalyst particles were prepared with (a–d) 250 and (e–h) 50 standard cm^3 Ar carrier gas for ferrocene, respectively. The CNTs were synthesized by 10 min CVD for (a, c, e, g), and 20 min CVD for (b, d, f, h). The C_2H_2 concentrations were 0.73 vol% for (a, b,

e, f), and 0.37 vol% for (c, d, g, h). The weights of CNTs obtained with C_2H_2 concentrations of (i) 1.1 (the same data as in Fig. 6), (j) 0.73, and (k) 0.37 vol%.

Fig. 8 – TEM images and diameter distributions of CNTs synthesized with 0.73 vol% C_2H_2 for large and small Fe catalyst particles prepared with (a–c) 250 and (d–f) 50 standard cm^3 Ar carrier gas for ferrocene, respectively: (a, d) top, (b, e) middle, and (c, f) bottom of a single piece of CNTs taken out of the array. In (g), the changes in the average diameter of the CNTs with 250 cm^3 and 50 cm^3 Ar carrier gas for ferrocene are plotted against the depth from the top of the CNT arrays. The error bars show the standard deviation.

Fig. 9 – (a) TG-DTA curves of the CNTs synthesized using small Fe particles (50 cm^3 Ar carrier gas for ferrocene) with 0.73 vol% C_2H_2 . The sample was the same as that in Fig. 8d–f. (b) Elemental composition of the ash after the TG-DTA measurement.

Fig. 10 – Composition of the effluent gas from the FBCVD reactor for different CVD times analyzed by gas chromatography. CVD was carried out with the moderate carbon feed of 0.73 vol% C_2H_2 and the small Fe particles with 50 cm^3 Ar carrier gas for ferrocene.