High Yield Single-Walled Carbon Nanotube Synthesis Through Multilayer Porous Mesh Substrates*

Naoyuki Matsumoto, Sachiko Ishizawa, Kenji Hata, and Don N. Futaba
National Institute of Advanced Industrial Science and Technology (AIST),
CNT-Application Research Center, Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

(Received 9 January 2018; Accepted 5 May 2018; Published 16 June 2018)

We demonstrate the high yield synthesis of single-walled carbon nanotubes (SWCNTs) using a multi-layer, three-dimensional (3-D) metal mesh porous substrate consisting of eight parallel and evenly spaced mesh substrates. SWCNT yield in this synthesis improved 78-times compared to that of a single flat nonporous substrate. In addition, the total SWCNT yield was greater than eight-fold (mesh layered number). This yield improvement was caused from the two reasons. First, mesh substrate could play a role as higher surface substrates than that of a flat nonporous substrate. Second, it also could achieve gas heating elements to allow the uniform delivery of heated gas source sources. In addition, CNTs grown were sustained the single-walled structure from the first layer to the final (8th) layer. This architecture leads to achieve the total carbon conversion efficiency of above 80% with single-walled structure (average: 1.2 number of walls). We can demonstrate this process as an interesting alternative approach for the efficient synthesis of high yield SWCNT synthesis for mass production through simply a change to the layered porous substrates (metal meshes). [DOI: 10.1380/ejssnt.2018.279]

Keywords: Carbon nanotubes; Chemical vapor deposition; Growth; Mesh structure; Growth enhancer

I. INTRODUCTION

The development of single-walled carbon nanotube (SWCNT)-based applications has shown great advances as represented by composite materials, strain sensors, and fibers have taken great strides [1–3]. Vital to this progress is the ability to synthesize long (100s of micrometers) carbon nanotubes in large quantities, because the high production cost is now the limiting factor for these applications to reach commercialization. Therefore, the improvement of growth efficiency and large throughput of SWCNT synthesis, which result in mass production, is important for practical use of SWCNT applications.

We have reported a water-assisted chemical vapor deposition with highly efficient growth of high purity and millimeter-tall CNT forests [4]. This synthesis method achieves the improvement of growth rates and long catalyst lifetime [5]. However, an inverse relationship between the CNT forest growth rate and the catalyst lifetime has been reported, which can limit the ultimate CNT forest height [6].

As previous reported, high volumetric synthesis efficiency is important for the development of mass production technology, which is the quotient of the mass of grown carbon nanotubes (CNTs) and the reactor volume. Therefore, the natural solution to this issue is to design a three-dimensional (3-D) substrate to grow to CNTs. In contrast to the high efficient (water-assisted) synthesis on substrates, which can grow SWCNT forests in millimeter scale from the flat substrates, the ideal condition would be to expand this concept three-dimensionally. The fluidized bed approach has demonstrated this concept to have beads coated with catalyst nanoparticles and grow CNTs [7–10]. This process has demonstrated high volume and low cost synthesis of CNTs. However, in this process, the control of SWCNT structure and to synthesize long CNTs in the 100s of micrometers is difficult. The fluidized bed approach overcomes the difficulty to deliver gas uniformly to all surfaces of a three-dimensional substrate to enable uniform SWCNT growth. However, because high gas velocities are required to fulfill particle fluidization requirements, reactive gas heating is limited which then reduces the necessary heating of the gases for efficient CNT synthesis. This aspect has been previously reported to be critically important [6, 11].

Another approach to increase the overall yield of SWCNTs is to use high area substrates, such as metal meshes. It has been previously shown that by using metal mesh substrates, uniform gas delivery could be achieved resulting in the exceptionally high speed synthesis as high as 1 mm/min of SWCNTs and the catalyst-substrate system could be grown for arbitrarily long periods, independent of a fluidization requirement [12]. While this report did demonstrate that a mesh substrate could increase SWCNT yield by ∼8-fold, a single layer would be insufficient for mass production purposes. The question remains how this system would scale if expanded into a multilayer, 3-D system and if the SWCNT quality could be maintained and if the yield would increase proportionally with the layer number.

Here, we report the high yield synthesis of long (millimeter-order) SWCNTs through the design of a 3-D substrate composed of a multiple, stacked porous metal mesh substrates. Each substrate allows for the uniform gas delivery across its surface as well as an increase in total available catalyst surface area. Importantly, the yield of SWCNTs could be improved 78-times when compared to that of flat nonporous substrate. Furthermore, we observed little to no structural variance from the first to last layer as they were all ∼2.9 nm-diameter SWCNTs. Interestingly, the yield for each layer progressively increased which led to a total yield greater than eight mesh layers. Examination into the origins of this increase found that the porous metal substrates overcame the two critical obstacles for high yield synthesis, uniform
FIG. 1. 3D-synthetic processes of SWCNT. (a) Setting 8-layered mesh substrate with 1 cm spacing. (b) Photograph of 8-layered mesh substrate after synthesis. (c), (d) SEM images of 1st- and 8th-layered mesh substrate from top and cross-section after SWCNT growth, respectively.

Synthesis of SWCNTs was performed by the water-assisted CVD method using sequentially sputtered alumina (40 nm) and Fe (1.8 nm) as the catalyst support and catalyst, respectively [4]. In place of silicon substrates, stainless steel (SUS) mesh substrates with aperture size (0.35 mm), wire diameter (0.21 mm) and open porosity of 29.9% and sputtered on both sides were used. This variety was chosen as it was found to be the optimum structure for achieving high efficiency SWCNT growth [12]. It should be noted that the catalyst thickness was chosen because it is well-known to grow SWCNT forests in high efficiency from silicon substrates. The growth process was performed in a 1” synthetic reactor with the substrates perpendicular to flow the source gases with a spacing of ~1 cm. [Fig. 1(a)] In this arrangement, the separation between consecutive layers was 1 cm as the yield was found to increase monotonically with separation until this value. Through our empirical data, we found that this separation is related to the relative gas conductivity of each layer (i.e., mesh porosity) and the conductivity of the remaining gap between the edge of the mesh and inner surface of the quartz tube. The growth conditions were fixed at optimum conditions: a total flow of 1000 scm, an acetylene (C$_2$H$_2$) carbon feedstock at 0.75% concentration, H$_2$O at ~1000 ppm in a helium (He) carrier gas at 750°C in 10 min growth time at atmospheric pressure.

Following the synthesis, the SWCNT forest growth efficiency and uniformity were characterized by the SWCNT yield (CNT mass/substrate area), and forest height which measured by scanning electron microscopy (SEM; Keyence, VE-9800). In addition, we evaluated the G-band/D-band (G/D) ratio in Raman spectra as the grown CNT quality, and the average wall number of the CNTs by using a transmission electron microscopy (TEM, TOP-COM EM-002B).

III. RESULTS AND DISCUSSION

To begin, we determined the growth conditions for a single layer mesh substrates capable of growing long
FIG. 2. SWCNT yield, quality change, gas dwell time as each mesh layered position. (a) CNT yield, (b) Raman spectra of the grown CNTs at 1st, 4th, and 8th layers, (c) Raman G-band/D-band ratio and average wall number of CNTs, and (d) gas dwell time and CNT yield at each mesh position.

SWCNTs. For this we placed a single layer upright in the reactor as shown in Fig. 1. The growth of CNTs was achieved from both sides of the mesh surface in a 10-min growth time. Quantitatively, the yield was determined to be 10.5 g/cm², which is 10-times that of a flat substrate. TEM examination showed that this was 95.5% SWCNTs with an average diameter of ~3.0 nm.

Using these growth conditions and mesh position as reference, we centered an eight layer 3-D substrate at that position and tested the synthesis of CNTs using the same growth conditions. As seen in Fig. 1 growth of CNTs was achieved on surfaces of every layer of the 3-D substrate. Examination of the yield showed that the total yield increased by 11-times compared to the single layer. The CNT yield was examined for each layer by change in the mass and plotted in Fig. 2(a). As the mesh position increased (toward downstream), the SWCNT yield increased from 10.5 mg/cm² for the first layer to 117 mg/cm² on the final eighth layer: the yield did not increase linearly.

Importantly, the grown CNTs were found to be SWCNTs for all layers and similar in quality as demonstrated by TEM and Raman spectroscopy analysis [Fig. 2(b, c)]. To demonstrate the uniform quality of SWCNT at each layer, the G/D ratio and wall number of the grown CNT were investigated by Raman measurement and TEM observations [Fig. 2(c)]. As shown in Fig. 2(c), almost no change in both the G/D ratio and the wall number of CNT at each layer (fixed position of the mesh) was observed showing that homogeneous SWCNT could be grown throughout the 3D substrate. This is significant because typically the homogenous growth of CNTs synthesized by CVD using a multilayer fixed bed substrates, such as zeolites, is difficult due to uniform gas diffusion throughout the substrate. In our case of using the 3D-mesh substrate, essentially allows for the adjustment of layer-to-layer pore size and thus allow uniform gas diffusion. If the mesh separation were zero, then we would expect that our substrate would approach the conditions for a fixed bed of powder particles. This aspect allows for the homogeneous growth of SWCNTs across all surfaces. Further, these results indicate that the SWCNT growth using the layered mesh substrate is a productive method for high efficiency of homogeneous SWCNT growth.

To examine the origin of this increase, we focused on two aspects: carbon conversion efficiency and gas heating. We first calculated the carbon conversion efficiency. Carbon conversion efficiency was defined as the percentage of the input carbon feedstock that is converted to CNTs: the estimated carbon conversion efficiency for a single nonporous substrate with a yield of ~1.4 g/cm² can be simply estimated by the quotient of the carbon nanotube mass and the input carbon mass. In this case, the carbon conversion efficiency was estimated to be ~1.6% for a silicon substrate, and for a porous metal mesh substrate, about 30%. This means that much of the carbon feedstock is left unused (above 70%) due to both lack of appropriate heating and lack of contact to the catalytic surface, i.e., the low carbon values indicate that much of the gas can still be used.

The second aspect is gas heating. We clarified this factor that increased CNT growth efficiency in each layer from the viewpoint of dwell time. By employing the previously reported calculation methodology [6], the dwell
time \( (t) \) was calculated as described below:
\[
t = 273 (Ad / FT_{GT})
\]
where \( A \) is the cross sectional area of the furnace tubes (one inch), \( d \) is the length of the gas heating zone, \( F \) is the total inlet gas flow (1000 sccm), and \( T_{GT} \) is the furnace temperature (1023 K), respectively. The gas heating zone is the distance from the furnace edge in the horizontal synthesis furnace in this study, and the center of the mesh holder is 25 cm from the furnace edge.

Fig. 2(d) shows the CNT yield and the calculated dwell time at each mesh position. In Fig. 2(d), the dwell time is expected to increase linearly with each mesh position, and, in fact, the CNT yield also increased with increase accordingly. It has been previously reported that gas heating, which is dependent on heating time, heating surface area etc., is one critical aspect in improving carbon nanotube growth efficiency \([6, 11]\); CNT yield increase with increasing dwell time if dwell time is small (less than 8 s) as in this study \([6]\).

When considering the mechanisms for heat transfer from the reactor to the gases, the heating surface area from the metal meshes more than doubles. It is reasonable that each mesh layer acts as both a growth substrate and as a gas heating element for the downstream substrates. Therefore, gas heating uniformity is increased greatly, which mimics one of the strengths of the fluidized bed process. To quantitatively examine the difference, we estimated the heating area.

The surface area of each mesh was estimated as a sum of two individual arrays of aligned wires scaled by the pitch. The increase in surface area increased linearly, but more significantly, the amount of heating surface area doubles by the 8th (final) mesh substrate layer. This architecture leads to a nearly step-wise progression in heating efficiency and carbon consumption, which is supported by the total carbon conversion efficiency of above 80% with single-walled structure (less than 1.2 of CNT wall number).

IV. CONCLUSION

We demonstrated the high yield synthesis of SWCNTs in the process of a multi-layer, 3-D metal mesh porous substrate: the equivalent of eight parallel and evenly spaced mesh substrates. In this synthesis, the SWCNT yield could be improved 15-times when compared to that of flat nonporous substrate. The SWCNT yield increased with increase in each layer, which led to a total yield greater than eight-fold. This yield improvement was attributed to the two critical reasons. One, they acted as high surface growth substrates. Two, due to the porosity, they acted gas heating elements to allow the uniform delivery of heated gas to subsequent substrates. As a result, the carbon conversion efficiency was found to be about 78% (49-hold as nonporous substrate, and 2-hold as one mesh substrate). In addition, CNTs grown on all layers were single-walled structure. We do believe that the yield can be further increased through the further balance of the mesh porosity, mesh pitch, growth conditions, and gas flow simulations. Therefore, we believe that these results represent an interesting seed in developing synthesis processes combining the strengths of substrate supported and fluidized bed growth of SWCNTs. Finally, in principle, we trust that this methodology can be applied to other aspects of CNT synthesis, such as structural control (i.e., CNT wall number control and metal-semiconductor selective synthesis \([13, 14]\)).

ACKNOWLEDGMENTS

This work was supported by JSPS Grant-in-Aid for Young Scientists (B) Number JP 17K14091.

[1] G. Mittal, V. Dhand, K. Y. Rhee, S. J. Park, and W. R. Lee, J. Ind. Eng. Chem. 21, 11 (2015).
[2] T. Yamada, Y. Hayamizu, Y. Yamamoto, Y. Yomogida, A. Izadi-Najafabadi, D. N. Futaba, and K. Hata, Nat. Nanotechnol. 6, 296 (2011).
[3] T. W. Chou, L. M. Gao, E. T. Thostenson, Z. G. Zhang, and J. H. Byun, Compo. Sci. Technol. 70, 1 (2010).
[4] K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, and S. Iijima, Science, 306, 1362 (2004).
[5] T. Yamada, A. Maigne, M. Yudasaka, K. Mizuno, D. N. Futaba, M. Yumura, S. Iijima, and K. Hata, Nano Lett. 8, 4288 (2008).
[6] S. Yasuda, D. N. Futaba, T. Yamada, M. Yumura, and K. Hata, Nano Lett. 11, 3617 (2011).
[7] Q. Zhang, J. Huang, M. Zhao, W. Qian, and P. Wei, ChemSusChem 4, 864 (2011).
[8] D. Y. Kim, H. Sugime, K. Hasegawa, T. Osawa, and S. Noda, Carbon 50, 1538 (2012).
[9] Z. Chena, D. Y. Kim, K. Hasegawa, T. Osawa, and S. Noda, Carbon 80, 339 (2014).
[10] C. H. See and A. T. Harris, Chem. Eng. J. 171, 841 (2011).
[11] S. Yasuda, D. N. Futaba, T. Yamada, J. Satou, A. Shibuuya, H. Takai, K. Arakawa, M. Yumura, and K. Hata, ACN Nano 3, 4164 (2009).
[12] N. Matsumoto, A. Oshima, S. Ishizawa, G. Chen, K. Hata, and D. N. Futaba, RSC Adv. 8, 7810 (2018).
[13] T. Yamada, T. Namai, K. Hata, D. N. Futaba, K. Mizuno, J. Fan, M. Yudasaka, M. Yumura, and S. Iijima, Nat. Nanotechnol. 1, 131 (2006).
[14] S. Sakurai, M. Yamada, H. Sakurai, A. Sekiguchi, D. N. Futaba, and K. Hata, Nanoscale 8, 1015 (2016).