Reduction of carbon byproducts for high-purity carbon nanocoil growth by suppressing catalyst collision

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Carbon nanocoils (CNC) are promising nanocarbon materials for application as functional composites such as electromagnetic wave absorbers. However, the suppression of carbon byproducts during CNC growth is necessary to obtain high purity CNCs with high yield. Here, we demonstrate a simple but efficient method for the reduction of carbon byproducts using a patterned thin film catalyst. Results show that the collision of tip catalysts of growing CNCs to the substrate or other CNCs inhibits the smooth growth of CNCs because of the deactivation of the catalyst. The collision also stimulates the formation of a carbon byproduct layer underneath the CNC layer. The well-controlled thin film catalyst with checkerboard pattern brings us four-times-higher efficiency of the catalyst and suppresses the carbon byproduct layer to $\sim 1/3$.

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1. Introduction

Because of their helical structure, carbon nanocoils (CNCs) [1, 2] are promising as functional nanocarbons for applications such as nano-mechanical components [3, 4], field emission sources [5-8], and electromagnetic wave absorbers [9-12]. For these and similar applications, mass-production synthesis is indispensable. Many attempts have been made to improve the synthetic yield of CNCs. Thermal chemical vapor deposition (CVD) is commonly used to synthesize CNCs in which catalyst metals play an important role. Therefore, many studies related to catalyst for growth of CNCs have been conducted to develop highly efficient catalysts for CNC growth based on transition-metal based catalysts, including the use of Co, Fe, and Ni [1, 2], and multicomponent-catalysts such as Fe/Sn, Fe/In/Sn alloys [8, 13-16], and K/Ag [17]. Aside from these efforts for the development of catalysts, the interaction between the substrate and catalyst reportedly affects CNC growth [18-20]. The additional Sn buffer layer strongly supports the formation of highly efficient catalytic particles at the very early stage of CNC growth, which results in the high yield synthesis of CNCs. Consequently, the catalyst formation at an early stage is a key parameter to realize the mass synthesis of CNCs.

In addition to the catalyst formation at an early stage, the positioning of the catalyst including the density of catalyst on the substrate must be important. In the case of thin film type catalyst, however, little attention has been devoted to this issue, where the whole substrate was covered with the catalyst layer. The lifetime of the catalyst particle is also important for high yield synthesis. Recently, we investigated the growth of individual CNCs using in-situ optical microscopy to reveal the growth mechanism of CNCs [21]. Results showed that the smooth growth of some CNCs was inhibited by the collision of catalyst particles at the tips of the CNCs. Furthermore, we observed very long CNCs longer than 100 μm at the substrate edge, whereas the average length of CNCs was approximately 10 μm ,

which implies that a lower collision rate at the edge is preferred for CNC growth in comparison to the central part of the substrate, where the density of grown CNCs is higher than that at the substrate edge. Consequently, the position or arrangement of the catalyst is an important parameter to realize an efficient catalyst with a long lifetime.

This study investigated the effects of collision on CNC growth by changing the distance between the catalysts to control the collision probability. We also demonstrated a simple but efficient method for the reduction of the carbon byproduct by controlling the arrangement of catalyst pattern.

2. Experiments

Fig. 1 presents a schematic of the catalyst arrangement on a substrate for investigation of collision effects on CNC growth. In this arrangement, we expect that the collision probability of CNC tips between the catalyst stripes can be varied by changing the gap of the catalyst stripe. A narrower gap is expected to be attributable to the higher collision rate because of the presence of the CNC grown from the counter stripe in addition to the collision to surrounding CNCs on the same stripe. The growth of CNCs on top of the catalyst is also affected by the collision of surrounding CNCs. These effects will be discussed.

Figure 1(a) Schematic illustration of the arrangement of thin film catalyst to investigate the collision of the growing CNCs, where a tri-layer catalyst was deposited on the SiO₂/Si substrate. (b) Schematic illustration of cross-sectional view for grown CNCs around the catalyst.

In this experiment, thin film catalysts were used because they can form a stripe pattern using photolithography, and vary its composition ratio merely by changing each thickness. The multilayered thin film catalysts of Fe, SnO₂ (~15 nm), and In₂O₃ (~ 20 nm) were prepared by sputtering deposition on a 10 × 10 mm SiO₂ substrate. The Fe–Sn–In catalyst was reported as a high-yield catalyst for CNC growth [13], where the Fe:Sn=5:1 catalyst provides the best results for stable growth of CNCs with small distribution of coil diameters, about 0.5–1 μm (see "supporting information" for optimization of growth condition). After the deposition, the catalyst on the substrate was oxidized at 600 °C in ambient conditions for 10 min.

The CNCs were grown using atmospheric CVD, using C₂H₂ as a carbon feedstock with a flow rate of 5 standard cubic centimeters per minute (sccm), mixed with 50 sccm Ar. CNCs

were synthesized at different temperatures of 800 °C. To perform in-situ observation of CNC growth, we use a small reactor (cross-sectional area: 5×20 mm) and a furnace with an optical microscope, as described in an earlier report of the literature [21].

3. Results and discussion

3.1 *Effect of collision of catalyst particle on CNC tip*

Fig.2(a) presents the gap-distance dependence of the CNC layer thickness between two adjacent stripes measured from the cross-sectional SEM images for each gap, where the reaction time was also varied: 5, 10, 20, and 30 min. The CNC layer thickness between the adjacent stripes increases concomitantly with the increase of the gap. A straight line in Fig.2(a) shows the half length of the gaps. It is readily apparent that the CNC layer thickness between the adjacent stripes for all deposition times is thinner than the half length of the gap, even after the growth of 30 min. **It should be noted that the impurity layer at the root of CNCs is still grown owing to the excess supply of carbon source to the remaining catalyst on the substrate. As a result of the growth of amorphous carbon layer, the roots of CNCs are covered with the amorphous carbon layer. Thus, the total CNC length at 30 min is shorter than that at 20 min as observed in Fig.2(a).** The CNC layer thickness on top of the catalyst layer, which corresponds to the free from the collision from the adjacent stripe, shows no clear gap dependence. It saturates to approx. 55 μm after the growth of 30 min, even for the gap of 20 μm , as portrayed in Fig.2(b). **In the case of no collision of CNCs in the gap, the grown CNC length in between portrayed in Fig.2(a) is almost identical to the thickness corresponding to the CNC length on top of the catalyst layer.** Fig.2(c) presents a series of the temporal variation of in-situ optical microscopy images of CNC growth on the stripe patterned catalyst. The entangled fibrous carbon layer as presented in Fig. 1 gradually occupies the gap separating the adjacent stripes with the growth and results in no space for CNC growth at the gap in the case

Figure 2 Effect of gap distance dependence on CNC growth: (a) Gap distance dependence of CNC length grown between adjacent strips with several growth time. A straight line represents half of the gap distance. (b) Gap distance dependence of CNC length on top of the catalyst center with several growth time. (c) Temporal variation of the in-situ optical microscope image of growing CNCs around the different stripe gaps with 20 μm and 40 μm .

of gap less than 20 μm and the reaction time longer than 5 min as portrayed in Fig.2(c). These results strongly support the model by which the collision of the catalyst particle on the tip of CNCs inhibits the CNC growth.

Fig.3(a) presents a cross-sectional SEM image of the grown CNCs using stripe catalyst with a growth time of 20 min. A tri-layered structure, shown schematically in Fig. 1, is readily apparent: outermost, middle, and innermost layers are composed respectively by CNCs,

shortened and dense fibrous carbon layer (Fig.3(b)), and dense carbon layer (Fig.3(c)). Based on the model that the collision of each CNC inhibits the growth of CNC, the middle carbon layer depicted in Fig.2(b) was formed by the collision of CNCs. Only the survived CNCs form the outermost CNC layers. Results show that the cross section of the shortened and dense fibrous carbon layer is a hog-back shape, i.e., the middle carbon layer around the center is thicker than that edge region, which suggests that the collision probability of CNCs around the center is greater than that around the edge region. As shown in Fig. 3(d), the ratio of CNC layer area in the cross sectional SEM image increases with increasing the gap length to 60% and saturates around 74%. This result suggests that the elimination of collision of the catalyst particle on the tip of CNCs is efficient to improve the purity of CNC.

Figure 3 Cross-sectional SEM image of stripe catalyst: (a) SEM image of the cross section around the stripe catalyst (scale bar is 50 μm). (b) Expanded view at the carbon byproduct layer consisting from dense and shortened CNCs (scale bar is 2 μm). (c) Expanded view of the carbon byproduct layer consisting of dense amorphous carbon. (d) Gap length dependence of the ratio of areas between CNC and byproduct measured from the cross sectional SEM image.

3.2 Growth model based on catalyst collision

Based on the collision model, because the entangled fibrous carbon layer is formed mainly by the collision of the growing CNCs or carbon fibers as described previously, the analysis of

the formation mechanism of the entangled fibrous layer is important to realize the high-yield synthesis of CNCs. Fig.4 presents the growth model of CNCs. We have reported that the catalyst color was changed suddenly from a metallic color to black with volume expansion when C_2H_2 gas had reached the catalysts from the in-situ observation using optical microscopy [21] as presented schematically in Fig.4(a). At this time, C_2H_2 , the source gas, was decomposed thermally when it reached the reaction area and the dehydrogenation reaction was happened on the catalyst surface. Then the carbon atoms were diffused into catalyst metals, forming the bottom a-C layer presented in Fig.4(b). As presented in Fig.4(b) (see also Fig.3(c)), the bottom a-C layer is a rectangular cross section and much thicker than the initial catalyst thin film. Then, the catalyst particles of Fe_3SnC or Fe_3C for growth of CNCs or carbon nanofibers (CNFs) were formed on the surface of the bottom a-C layer. The catalyst particle density on the bottom a-C layer is expected to be high. Although the growth of CNC is initiated at the catalyst particles as presented in Fig.4(c), the continuous growth of the most of CNCs is stagnated by collisions because of excess density of the catalyst particle. Stagnated CNCs were piled up, forming a shortened and dense fibrous carbon layer on the bottom a-C layer, as depicted in Fig.4(d) (see also Fig.3(b)). This collision process is repeated. The shortened and dense fibrous carbon layer continues to expand as described in Fig.2(c).

Figure 4 Growth model of CNCs: (a) immediately after the introduction of source gas, (b) nanoparticles and a-C layer formation after 10 s, (c) very early stage of CNC formation on the catalyst surface, (d) beginning of collision of adjacent CNCs, (e) beginning of formation of shortened and dense fibrous C layer and of collision of CNCs at the gap, and (f) the gap is occupied by collided CNCs.

The survived CNCs in the collisions continue to grow as presented in Fig.4(e). In this case, the collision probability is much lower than that for the initial growth stage because of the expansion of distance between the growth sites. These CNCs can be observed as filament-like structures grown from the edge of expanded stripe pattern as observed by the in-situ optical microscopy portrayed in Fig.2(c). Long CNCs (longer than 2-3 μm) begin to vibrate because of increased flexibility, heat, and turbulence of source gases. This vibration causes an increase of the collision probability to the surrounding CNCs. It inhibits the growth of long CNCs, as presented in Fig.2(c). This situation closely resembles the case in which the gap separating the adjacent stripes as discussed in Fig.2. Finally, very few CNCs without collisions are able to grow until the catalyst life time. In this way, the CNC growth is affected strongly by the collision of others including the substrate at each growth stage.

3.3 Suppression of collision of tip catalyst toward mass synthesis

Figs. 5(a)–5(c) show cross-sectional SEM images for catalyst pattern dependence of grown CNCs, where catalyst patterns are depicted schematically in the insets, (a) fully covered with the catalyst layer, (b) stripe pattern with the width of 20 μm , and (c) checkerboard pattern with 2 μm square with a 2 μm gap. The dense carbon layer with 15 μm is observed clearly in Figs. 5(a) and 5(b). The thicknesses of "the shortened and dense fibrous carbon layer" are also similar for both cases. At the gap region for adjacent catalysts, the grown CNCs from the edge region are visible. In both cases, the growth directions of CNCs to the substrate are distributed randomly and the grown CNCs are entangled. These characteristics imply that the collision between growing CNCs prevent the smooth growth of CNCs. Consequently, the central region of the 20- μm -width stripe catalyst is insufficient for suppression of the tip catalyst collisions.

Figure 5 Suppression of dense a-C and shortened and dense fibrous layer: cross-sectional and top view SEM images of CNCs grown from (a) and (d) a substrate fully covered with catalyst layer, (b) and (e) stripe catalyst with a width of 20 μm and (c) and (f) checkerboard pattern with 2 μm square. Yellow parts are insets of (a)–(c), showing the catalyst pattern on the substrate. All scale bars are 100 μm .

In the case of Fig.5(c), the ratio of the circumference length of the square catalyst to the surface area of the square catalyst is much higher than that both for the fully covered and stripe catalyst. This height induces the reduction of the tip catalyst collision at the early growth stage around the edge of the catalyst, which results in the suppression not only of the "shortened and dense fibrous carbon layer" but also of the "dense carbon layer" less than 5 μm . Additionally, it is difficult to find a clear boundary separating "the shortened and dense fibrous carbon layer" to the CNC layer. The growth of the CNCs to the substrate is perpendicular to the substrate in comparison with the former cases and the grown CNCs are less entangled and less wavy shape. Furthermore, although the coverage ratio of the catalyst layer to the substrate is only 25% for the checkerboard pattern, the total thickness of the CNC layer is almost equal to that of the fully covered with catalyst layer depicted in Fig.5(a), which indicates that the catalyst efficiency of the checkerboard pattern for growth of CNCs is four times higher than that for conventional (fully covered with catalyst layer) thin film catalyst. Figs. 5(d)–5(f) respectively present SEM images of top views of Figs. 5(a)–5(c). The CNCs observed in Fig.5(d) shows a wavy shape. In contrast, many CNCs depicted in Fig.5(e) and 5(f) corresponding to the smaller collision probability are observed as straight rods.

We have performed additional experiments to investigate the effect of the gap length for checkerboard pattern. In the case of the wide gap of 24 μm , the thickness of byproduct layer could be greatly reduced as shown in Fig. 6 and the purity defined by the ratio of areas between the CNC and byproduct reaches to 88.7%. In this case, however, the wider gap must result in the reduction of CNCs layer thickness as shown in Fig. 6 because of the reduction of the total catalyst area on the substrate, even though the larger gap is effective to reduce the byproduct. For instance, in the case of 3 μm square with 24 μm gap shown in Fig. 6(c), the catalyst area on the substrate is only 1.2%. Surprisingly, the whole of substrate was covered with ~ 50 μm -thick CNC layer even under the condition that the catalyst covers only 1.2% as

shown in Fig. 7. The catalyst efficiency for this case is ~50 times higher than that for fully covered catalyst estimated from the CNC layer thickness and coverage of catalyst on the substrate.

Figure 6 SEM images of grown CNCs with different gaps with (a) 2 μm , (b) 6 μm , and (c) 24 μm for checker board pattern catalyst. Arrows of bottom images indicate the substrate edges.

Figure 7 (a) Catalyst pattern on the substrate with a gap of 24 μm for checker board pattern catalyst. (b)-(d) SEM images with different magnification of grown CNCs.

The optimization of the ratio of the gap and catalyst size is important to realize the high yield syntheses of CNCs. In our experiments, the optimum condition for the yield of CNCs is 2 μm square with a gap of 2 μm without significant reduction of CNC layer thickness. Note that we have intended to investigate the effect of the collision of catalyst, so that the optimization for high yield synthesis is the subject for further study. Consequently, suppression of the collision of growing CNCs at the early growth stage is extremely efficient for the smooth growth of CNCs. The highest purity (the ratio of cross sectional areas of CNC and carbon byproducts) of 88.7% is achieved with nearly isolated island pattern as shown in Figs. 6 and 7. We believe that this simple strategy to suppress the collision of the tip catalyst at CNC presents opportunities for the mass synthesis of CNCs.

4. Conclusions

We investigated the effects of the collisions of the catalyst on the growing CNC tip on CNC growth using a thin film catalyst with a stripe pattern. The grown length at the gap separating the adjacent catalyst stripes along the substrate depends strongly on the gap distance, whereas the growth length on top is independent of the gap length, which indicates that the collision of each CNC inhibits the smooth growth of CNCs and forms the dense entangled and shortened CNC layer under the CNC grown layer because of the deactivation of the catalyst at the growing CNC tip. Results show that the well-controlled thin film catalyst with a checkerboard pattern (2 μm square) brings four-times-higher efficiency of catalyst **without significant degradation of CNC yield** and the suppression of carbon byproduct layer to $\sim 1/3$. We believe that this simple strategy to suppress the collision of the tip catalyst at growing CNCs might facilitate the mass production of CNCs.

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Figure captions

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