



Growth of high-density horizontal SWNT arrays using multi-cycle in-situ loading catalysts



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ABSTRACT

Density of horizontal single-walled carbon nanotube (SWNT) array is considered as one of most important index in SWNT-based integrated circuits. However, it is still a challenge to directly obtain horizontal SWNT arrays with ultra-high density on quartz. Herein, we developed multi-cycle in-situ loading catalysts method to directly grow horizontal SWNT arrays with high density on quartz substrate. In this method, Cu catalysts showed much higher efficiency to grow SWNT, which were in-situ loaded through depositing Cu vapor produced by hot copper mesh. Density and size of catalysts could be directly controlled by depositing temperature and time. Moreover, the high efficiency of in-situ loaded Cu catalysts can be maintained after multi-cycle loading, which leads to the linear increase of SWNTs density with loading times. Finally, further optimizing depositing temperature and time, horizontal SWNT arrays with the average density higher than 60 SWNTs/ μm and area larger than $8 \times 12 \text{ mm}$ on quartz have been obtained. This method opens up an opportunity for obtaining SWNT arrays with any density, which shows great potential in the nanoelectronics application in the future.

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1. Introductions

In 2013, the scientists in IBM pointed out that the density of SWNT arrays should be more than 125 SWNTs/ μm to realize SWNT-based integrated circuits with high performance [1]. Generally, there are two methods to get high-density SWNT arrays. One is the post-treatment approaches, such as multiple-cycle transfer [2,3] and solution-based SWNT assembly methods [4–8]. Although high density of up to 500 SWNTs/ μm can be obtained through these methods [4], the alignment and purity of the arrays are usually poor, which significantly decrease the device performance. The other is directly growth by chemical vapor deposition (CVD) method [9–11]. Compared with post-treatment methods, SWNT arrays directly grown by CVD method have higher alignment and purity because of the interaction between the SWNTs and the substrate [12] and the avoidance of using solutions and surfactant. However, the density of SWNT arrays obtained by CVD so far can't meet the requirements for high-performance devices [1,9].

Many efforts have been made to directly grow high-density SWNT arrays. For CVD growth methods, strategies like multiple

loading [13], multi-cycle growth [14], gradually release of catalysts [15], reactivation of catalysts [16] and periodic growth [17], have been developed. However, it is still hard to prepare uniform high-density horizontal SWNT arrays on quartz in large area. Actually, in CVD method, the density of SWNTs can be described as below:

$$D = \eta \times N$$

In the above equation, D means the density of SWNT arrays; η means the catalysts' efficiency to grow SWNT arrays; N means the number of times of multi-loading and growth, which is proportional to the amount of catalysts used in SWNTs growth. Therefore, the key to improve the density of SWNT arrays is to enhance catalysts η . On this basis, if active catalysts can be loaded onto the substrate repeatedly, the density of SWNT will increase with the increasing growing times. η of catalysts is determined by the preparation method of catalysts, and usually, catalysts or their precursors were pre-positioned on substrate before SNWTs growth. The air, humidity, and oxidation state of catalysts all affect the activity of catalysts [18,19]. Therefore, improving and maintaining the activity of catalysts is an effective way to increase the density of SWNT arrays.

Herein, a new strategy of multi-cycle in-situ loading of catalysts

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is developed to prepare high-density horizontal SWNT arrays [20–22]. Copper is one of most used catalyst to grow horizontal aligned SWNT array. As designed in Fig. 1, Cu catalysts in-situ formed on quartz substrate through condensation of Cu vapor, which was produced by hot copper mesh. Because of avoiding the influence of the air and humidity etc., Cu catalysts directly formed by Cu atom or clusters will present much higher and stable efficiency to grow SWNTs than traditional methods. And the density and size of copper catalysts can be controlled by the in-situ loading conditions, such as depositing temperature and time. Moreover, after one cycle of growth, the fresh catalysts reloaded in-situ still possess a high activity of growing SWNT array. As a result, the density of SWNT array can keep increasing with the increasing cycles of loading and growth.

2. Experimental

2.1. Synthesis of horizontal SWNT array on the ST-cut quartz substrate using multi-cycle in-situ loading Cu method

In particular, ST-cut quartz substrates (single side polished, miscut angle 0.5°, surface roughness <math><5 \text{ \AA}</math>) were purchased from Hefei Kejing Materials Technology Co., China. After cleaning, the quartz substrates must undergo a necessary annealing process (at 900°C in air for 8 h) for a better crystallization. The quartz substrate was placed at $\Delta x = 7 \text{ cm}$ from the center of furnace (950°C). After the system was purged with 300 sccm Ar and 100 sccm H_2 , copper mesh was sent to the center of furnace by a quartz tube with magnet for 5 min. When the deposition ended, the copper mesh was pulled out and ethanol was introduced through an ethanol bubbler by 10 sccm argon. After 10 min, the ethanol was shut off. The substrate then underwent a 20 min annealing at 950°C with 300 sccm Ar and 100 sccm H_2 . After that, the next deposition and growth of SWNT could begin.

3. Results and discussion

In specific experiments, to realize the in-situ loading of catalysts, the copper mesh was put at the highest temperature (950°C) area in the furnace to produce copper vapor, and quartz substrate was put at relatively lower temperature ($800\text{--}900^\circ\text{C}$) area to receive copper vapor to form Cu catalysts, as shown in Supplementary Fig. 1. By controlling deposition conditions, such as temperature of the substrate, deposition time, rate of flow, temperature gradient and so on, the density of catalysts particles, with diameters between 1.5 and 2.5 nm can be tuned. Substrate's temperature and

deposition time are two essential factors because substrate temperature would influence the deposition of catalysts [23] and time would change the diameter distribution of catalysts by sintering [24].

The substrate temperature could be directly controlled by the distance (Δx) between the copper mesh and quartz substrate, because of the temperature distribution in the furnace, as shown in Supplementary Fig. 2. For example, SWNTs had been grown at locations with different Δx after 5 min deposition and SEM images of SWNT arrays are shown in Fig. 2a and b. The density of SWNT array grown at $\Delta x = 7 \text{ cm}$ is obviously higher than that obtained at $\Delta x = 5 \text{ cm}$. Through comparing the AFM inserted in Fig. 2a and b, the result can be explained by the difference of the density and average diameter of catalysts. The catalysts obtained at $\Delta x = 5 \text{ cm}$ were smaller and fewer than those obtained at $\Delta x = 7 \text{ cm}$. The average diameter and density of catalysts nanoparticles on the quartz with different Δx , and the results is shown in Fig. 2c. When Δx is small, the temperature difference between the copper mesh and the substrate is small. As a result, the density of nanoparticles is relatively low and diameter distribution is relatively large. This phenomenon can be caused by different degree of oversaturation of copper vapor. When Δx gradually increases, the degree of oversaturation increases, which leads to a large amount of crystallization [25,26]. However, it has also been shown in Fig. 2c that when $\Delta x > 7 \text{ cm}$, the density of catalysts becomes less. This can be attributed to the low amount of copper in gas phase at low temperature. The fitted curve of $\Delta x - T$ (substrate temperature), $\Delta x - p$ (vapor pressure of copper) and $\Delta x - dp/dx$ are shown in Supplementary Fig. 2. The dp/dx is smallest at $\Delta x = 8 \text{ cm}$, which means the deposition rate of copper is the most. This is nearly the same as our experiment results ($\Delta x = 7 \text{ cm}$).

Besides, the deposition time is also an essential factor in loading catalysts, and scanning electron microscope (SEM) images of the growth results with $t = 5 \text{ min}$ and 15 min are shown in Fig. 2d and e. The difference in density of SWNT array can result from the different average diameter of catalysts. It has been reported that nanoparticles will sinter quickly at high temperature and form nanoparticles with larger diameter. Therefore, the densities and the average diameters of the nanoparticles with different deposition time have been counted by atomic force microscope (AFM), and the results are shown in Fig. 2f. It is hard to find nanoparticles with diameter larger than 2 nm on the substrate, when the deposition time is below 5 min. The average diameter of the nanoparticles on quartz gradually increases with the increasing time, which indicates the sintering of catalysts on substrate [26]. When the time is over 15 min, the density of catalysts is much higher than those deposited in 5 min and the average diameter is more than 4 nm. X-ray photoelectron spectroscopy (XPS) results of substrates after different deposition time are given in Supplementary Fig. 4, and the amount of copper increases with the growing deposition time indeed. However, although the density has been improved, the diameter of nanoparticles is too large to grow SWNT on substrate. Although the density of nanoparticles increases, the density of SWNT arrays decreases at last. Finally, we consider the whole deposition procedure as a process of gradually forming nanoparticles and the density and average diameter of nanoparticles can be controlled by adjusting the deposition temperature and time.

Via this in-situ loading method, large-area, highly dispersed Cu nanoparticles have been prepared on quartz. The growth results of in-situ loading method and the traditional spin-coating method are shown in Fig. 3a–d. The details of preparing catalysts and growth conditions are described in Supplementary Information. The density of SWNT array grown by in-situ loading method is around 10 SWNTs/ μm , while the density by spin-coating is only around 2 SWNTs/ μm . However, the difference in density of SWNT array

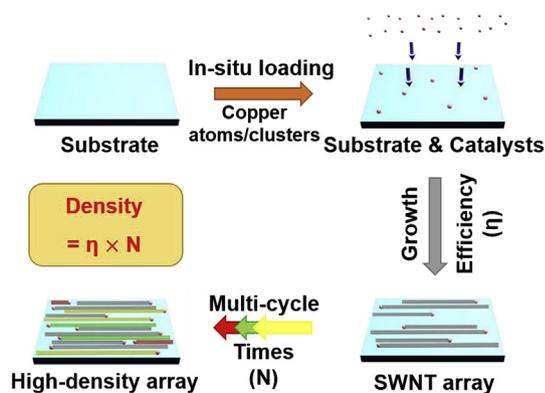


Fig. 1. Schematic illustration of the growth of high-density horizontally aligned SWNT arrays using multi-cycle in-situ loading catalysts.

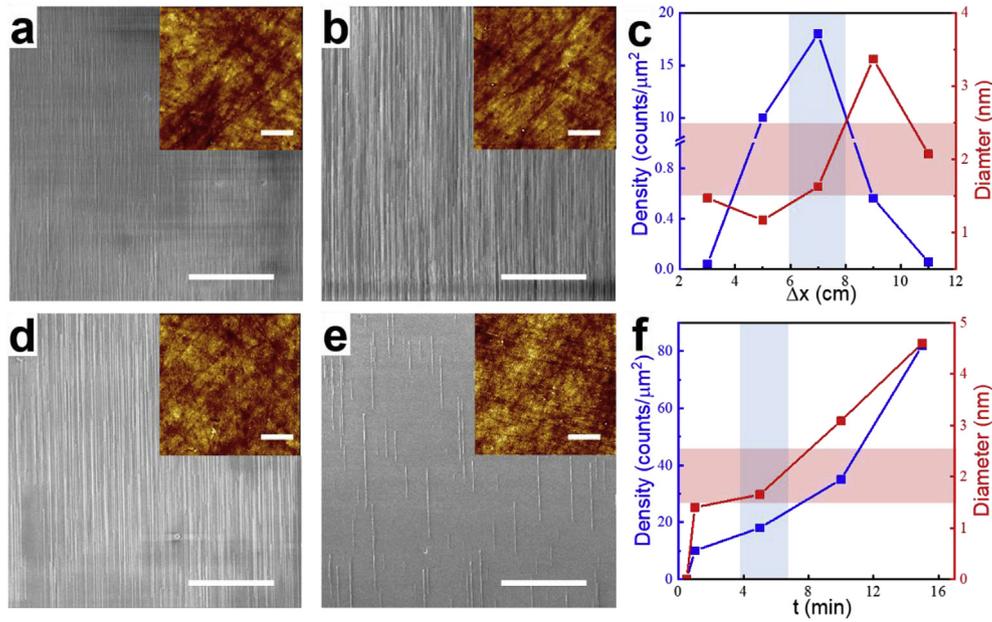


Fig. 2. The influence of substrate's temperature and deposition time on the efficiency of catalysts' deposition and SWNT arrays' growth. (a–b) SEM images of SWNT arrays with different Δx , $\Delta x = 5$ cm (a) and $\Delta x = 7$ cm (b) (insets: AFM images of catalysts after 5 min deposition). (c) The statistics of density and average diameter of catalysts with different Δx after 5 min deposition. (d–e) SEM images of SWNT arrays with different deposition time, $t = 5$ min (d) and $t = 15$ min (e) (insets: AFM images of catalysts with $\Delta x = 7$ cm). (f) The statistics of density and average diameter of catalysts with different t with $\Delta x = 7$ cm. Scale bar, $40 \mu\text{m}$ (a, b, d, e) (scale bar is 500 nm for the insets in a, b, d and $1 \mu\text{m}$ for inset in e). Scale bar of height is $-2 \text{ nm}-2 \text{ nm}$ for the insets in a, b, d and e. (A colour version of this figure can be viewed online.)

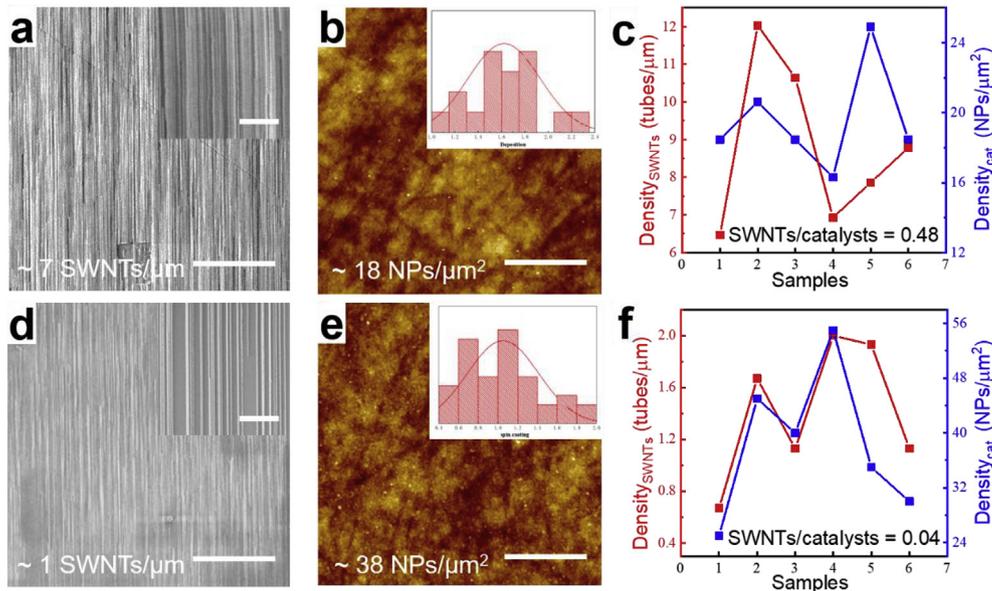


Fig. 3. Difference in efficiency of growing SWNTs by in-situ loading method and spin-coating method. (a, d) SEM images of SWNT arrays after growth by in-situ loading method (a) and spin-coating method (d) (insets: high magnification SEM images). (b, e) AFM images of catalysts prepared by in-situ loading method (b) and spin-coating (e). (insets: density and size distribution of NPs on substrate). (c, f) The statistics of density of SWNT arrays and catalysts on substrate at different locations by in-situ loading method (c) and spin-coating method (f). Scale bar, $40 \mu\text{m}$ (a, d) (scale bar, $6 \mu\text{m}$ for the insets in a, d). Scale bar, 750 nm (b, e). Scale bar of height is $-2 \text{ nm}-2 \text{ nm}$ for the b, e. (A colour version of this figure can be viewed online.)

cannot be attributed to the density or average diameter of catalysts. AFM images of substrate after loading catalysts by two methods are shown in Fig. 3b–e. The density of copper catalysts by spin-coating method is actually higher than that by in-situ loading, and the diameter distribution of catalysts is both under 2.5 nm , which is considered suitable for growing SWNT arrays. The density of catalysts and the density of as-grown SWNT arrays extracted from 7 samples by these two methods are shown in Fig. 2c and f

respectively. The ratio of SWNTs/NPs could be used to reflect the average length of SWNT grown by each catalyst. The ratio of SWNTs/NPs is nearly 0.48 in in-situ loading, while the ratio is only 0.04 by spin-coating, which means the catalysts' efficiency of growing SWNTs by in-situ loading is ten times higher than that by spin-coating. The difference in efficiency may be caused by the assisted catalyzing of the copper in the gas phase [27,28]. In our system, the required rate of flow of carbon sources by in-situ

loading is much lower than that by spin-coating, which may reflect the difference in efficiency of dissociation of carbon sources. However, if the same rate of carbon sources is used to grow SWNT arrays by spin-coating method, there is no SWNTs grown on the substrate. Besides, we also try to add an additional huge rate of flow of argon to remove the copper in the gas phase, and the growth efficiency decreases indeed, as shown in [Supplementary Fig. 9](#).

After one cycle of growth, copper nanoparticles were deposited in-situ again and SWNT array was prepared in the same method. The details of growth procedure are in [Supplementary Information](#). AFM images of SWNT array obtained with $N = 2, 4$ and 6 are shown in [Fig. 4a–c](#). Different from other methods, we find that the density of SWNT array obviously increases with the number of growth (N). The average density of SWNT array and the corresponding cycle times are shown in [Fig. 4d](#). The density of SWNT arrays increases nearly linearly with the increasing N . AFM and SEM images of SWNT array by more N are shown in [Supplementary Figs. 10 and 11](#), which also supports the conclusion. When $N = 6$, the average density was around 60 SWNTs/ μm and the highest density is as high as 70 SWNTs/ μm . The diameter distribution of SWNT arrays is shown in [Fig. 4e](#), and the average diameter of SWNTs is 1.37 nm. Furthermore, AFM measurements show that diameters of some SWNTs could be more than 3 nm. This could be explained by the forming of some bundles during the growth. [Fig. 4f](#) shows the Raman spectra of the high-density SWNT arrays with 514 nm and 633 nm with a barely noticeable D band, which indicates the high quality of SWNT arrays [29].

In order to figure out the key factor which makes multi-cycle growth work, catalysts were reloaded in-situ after 1st growth of SWNTs, and AFM images and diameter distribution of catalysts are shown in [Supplementary Fig. 12](#). The catalysts on quartz were obviously larger and fewer and the direct growth results are undesirable because there were many unaligned SWNTs grown on

substrate. The difference in diameter of catalysts can result from the catalysts residue on substrate. As a result, an evaporation procedure is essential to the multiple-cycle growth. In [Supplementary Fig. 13](#), when the evaporation time varies from 0 min to 20 min, the unaligned SWNTs decreased obviously while the density of aligned SWNTs increased, and AFM shows that after 20 min evaporation, most of catalysts residue had been removed. This phenomenon can be attributed to the competition of nucleation and growth of nanoparticles during the deposition [26,30]. The copper atoms or clusters prefer to deposit on the pre-existing nanoparticles than the surface of substrate because the surface energy of bigger nanoparticles is less than smaller one. As a result, if the catalysts residue had been removed in-situ, the behavior of catalysts' deposition would be similar. Besides, SWNT arrays with different N by traditional spin-coating method have been prepared (details see [supplementary Information](#)), and the density didn't increase with N obviously (SEM images shown in [Supplementary Fig. 14](#)). Even after 4 cycles of growth, the density of SWNT arrays is still below 10 SWNTs/ μm . Moreover, there are many small tubes with a shape like plants' tendril, and they are not defined as SWNTs because of bad alignment and morphology. This phenomenon could be considered as the relatively stronger interaction between the catalysts and the substrate. Because the catalysts loading by spin-coating would be normally oxidized in air at high temperature [14,31], the interaction between catalysts and substrate may be stronger than that deposited from gas phase.

What's more, it is found that when N is more than 7, the density would still increase, but there are some new problems. From [Fig. 4d](#), when $N = 1$ to 5, the linear relationship between the density and the N is pretty good. However, it is obvious that when the $N = 6$, the density of SWNT array shows more deviation from linear relations than others, and this deviation also exists when N is larger than six. As shown in [Supplementary Fig. 13](#), when N increases to 7,

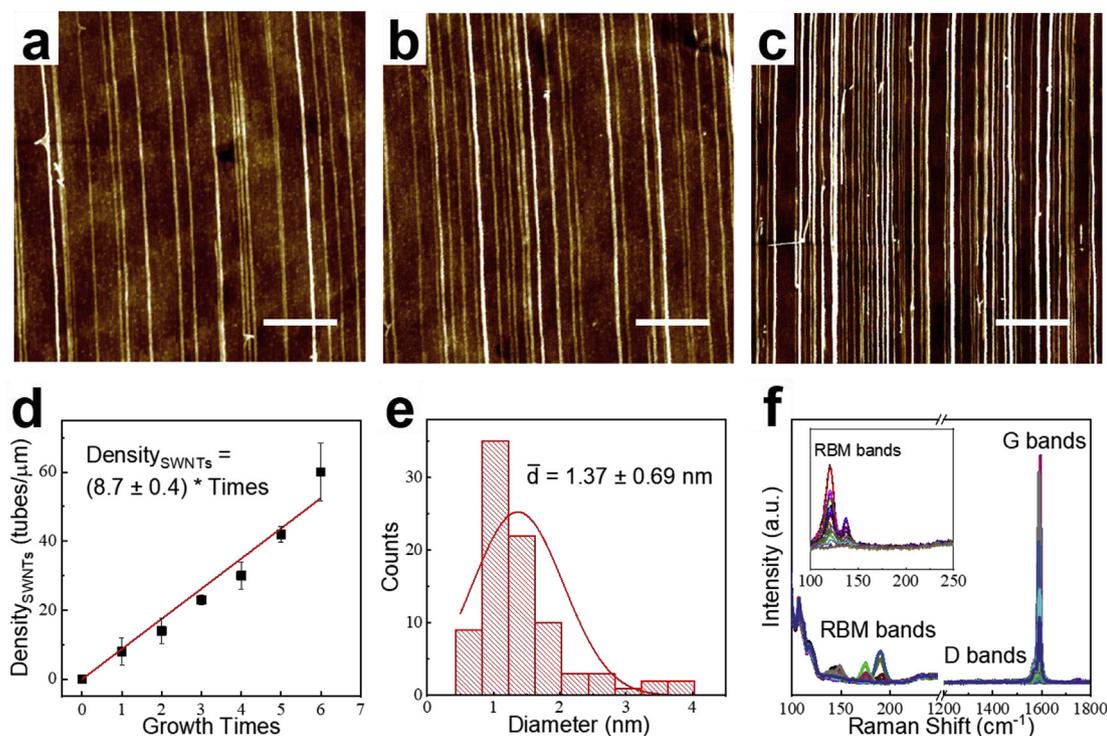


Fig. 4. SWNT array obtained by using multi-cycle in-situ loading catalysts with different N . (a–c) AFM images of SWNT arrays obtained by different growth times. $N = 2$ (a), 4 (b), 6 (c). (d) The growth times and the corresponding density of SWNT array. (e) The diameter distribution of as-grown SWNT array, when $N = 6$. (f) Raman spectra of as-grown SWNT array with 514 nm excitation. (insets: 633 nm). Scale bar, 200 nm (a, b, c). (A colour version of this figure can be viewed online.)

the density of SWNT array is more than 70 SWNTs/ μm , even nearly 90 SWNTs/ μm at some place, while the alignment of SWNT array becomes lower, as shown in Supplementary 15. There are some SWNTs which are not perfectly aligned by the quartz, because some catalysts are deposited on SWNTs rather than quartz [32], when coverage of SWNTs on quartz becomes high (SEM and AFM images are shown in Supplementary Fig. 16). When the catalysts are attached to the SWNTs, the SWNTs may not be aligned by the crystal lattice. As a result, although the density of SWNT arrays still keep increasing, the alignment of SWNT arrays becomes worse. This problem might be solved by decreasing the deposition amount of catalysts when N is above 6.

4. Conclusion

In summary, a method of multi-cycle in-situ loading catalysts to grow high-density horizontal SWNT array has been developed. In this method, Cu catalysts in-situ formed on quartz substrate through condensation of Cu vapor, which was produced by hot copper foil. Because of avoiding the influence of the air and humidity etc., Cu catalysts directly formed by Cu atom or clusters will present much higher and stable efficiency to grow SWNTs than traditional methods. Moreover, density and size of Cu catalysts can be controlled by adjusting the substrate's temperature and the deposition time. Besides, by multi-loading catalysts in-situ, SWNTs could be grown more than once. Horizontal SWNT array with ultra-high-density of 70 SWNTs/ μm has been obtained, and the density of SWNT array increases nearly linearly with the increasing cycle times. In this system, the high density results from the combination of high growth efficiency (η) and large number of catalysts realized by multi-cycle loading (N). This work provides a new method to obtain high-density horizontal SWNT arrays and shows potential for application in nanotube-based nanoelectronics.

Declaration of competing interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.carbon.2019.10.002>.

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