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Ultralow Feeding Gas Flow Guiding Growth of Large-Scale Horizontally Aligned Single-Walled Carbon Nanotube Arrays

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ABSTRACT

On the basis of the rational analysis about the fluidic property of the system, an ultralow gas flow chemical vapor deposition (CVD) strategy was designed to prepare large-scale horizontally aligned ultralong single-walled carbon nanotube (SWNT) arrays. SWNT arrays could be well obtained under extremely low feeding flow of 1.5 sccm in a 1 in. quartz tube reactor. It was confirmed that the tubes grew floatingly and could cross microtrenches or climb over micro-obstacles in ultraslow gas flow. SWNTs arrays also could be formed no matter the substrate was placed vertically or upside down. The growth mechanism was discussed. Both the buoyancy effect induced by gas temperature/density difference and gas flow stability played dominant roles. More attractively, simultaneous batch-scale preparation of SWNT arrays was realized by the ultralow gas flow strategy. This new strategy turns to be more abstemious, efficient, promising, and flexible compared with the high gas flow rate fast-heating CVD processes.

The preparation of horizontally aligned single-walled carbon nanotube (SWNT) arrays on flat surfaces is attracting intensive attentions for the prospect of SWNT-based integrated nanodevices. In recent years, several strategies based on chemical vapor deposition (CVD) have been developed to guide the growth direction of SWNTs by external electric field,[1,2] special substrates,[3−6] or gas flow.[7−11] Substrate-lattice-induced alignment of SWNT arrays has shown to be a very efficient way. For instance, well-aligned very dense (∼10 SWNTs/μm) SWNT arrays were obtained on quartz substrate by Rogers et al.[6] Such SWNT arrays were used for high-performance thin-film transistors. The gas-flow-guided process often obtained less dense SWNT arrays, but it is still of particular interest. The substrates used in this method are very flexible. Especially, it can be applied in growing ultralong SWNT arrays on commercial silicon wafer substrates,[7−11] which is more compatible with current silicon-based microelectronics technology, and the tubes obtained can be as long as millimeters to centimeters.[12] In addition, it can be used to grow SWNTs on a patterned surface[8] and obtain crossed SWNTs.[9]

In the reported CVD methods, high flow rate feeding gas of hundreds to thousands sccm were usually required. Especially, in the gas flow guided "fast-heating" strategy developed by Liu et al.,[7,10] "fast-heating" and high feeding gas flow rate (∼1000 sccm) were required to lift up the catalyst particles together with the growing SWNTs away from the substrate surface and pilot their growth direction (so-called "kite-mechanism"). It was supposed that low gas flow rate will cause "skidding" of the catalyst particles on the substrate surface, and the frictional force between the substrate and the catalyst particles on SWNT tips will cause wavy SWNTs and the eventual growth termination of long SWNTs.[12]

There is a question herein, is high feeding flow really essential in the process? Therefore, it is interesting both theoretically and technically to explore the undermost flow rate limit for guiding the growth direction of SWNTs. However, such attempt has never been reported. On the basis of the rational analysis on the fluidic property of the gas flow in CVD system, we designed ultralow flow rate CVD process and successfully achieved the growth of high-quality

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centimeter-scaled parallel SWNT arrays under extremely low feeding flow of several sccm without fast heating. Moreover, the batch-scale preparation of ultralong SWNT arrays could be realized by relying on this low flow rate strategy. Compared with the substrate lattice-induced method, this strategy is more flexible in substrates, the tubes obtained are much longer, and suspended SWNTs can be prepared. Compared with the high flow rate gas flow-guided method, this strategy is more controllable and economical.

Let us first briefly discuss about the theoretical possibility of growing horizontally aligned SWNT arrays under low flow rate condition. The furnace tube used for CVD processes can be considered as a strong heated aclinic pipe. When gas flow reaches the center region of the tube from the relatively cool front region, owing to the direct conduction heat transfer and especially radiant heat transfer from the heavily heated tube wall to the substrate, the temperature difference between substrate surface and nearby gas flow will generate a vertical gas density difference. The buoyant effect of convection flow induced by such gas density gradient can help to lift the carbon nanotubes up, and the growth direction of carbon nanotubes is guided by the shear flow near the substrate. The buoyancy-to-inertia ratio of mixed convective gas flow may be characterized by Richardson number $Ri = \Delta\rho gh/\rho v^2$, where $\Delta\rho/\rho$ is the density difference between a vertical length scale h in a flow of velocity v. When the gas velocity is low enough, the buoyant force will become dominant.[13,14]

Besides the magnitude of the buoyancy, the stability and laminar property of the gas flow also should be taken into account. The gas flow stability and laminar feature can be evaluated by Reynolds number $Re = \rho vd/\mu$, where d is the tube inner diameter and μ is the gas viscosity. It is obvious that more stable laminar flows will be obtained when decreasing the gas flow velocity and inner diameter of the furnace tube, thus more favorable for growing ordered SWNT arrays.[15]

Moreover, in the strongly heated tube, the hotter gas near the tube wall would levitate along the tube wall at the same time the cooler gas at the center of the tube descend down, thus forming a symmetrical gas circulation called secondary flow.[16,17] The existence of such lateral vortex flow will distort the laminar flow and decrease the buoyancy effect that uplifts the growing SWNTs and also may be harmful for the SWNTs growing straightly along the axial direction of furnace tube. However, in ultralow flow rate CVD process, slow velocity feeding gas can be heated more gently and equably before reaching the tube center, and the secondary flow is much weaker and thus has little disturbing to the nanotube growth. On the basis of the above analyses, a normal heating low gas flow rate CVD strategy was designed and performed.

Fe−Mo nanoparticles with average diameter of 6.1 nm were prepared by the method similar to our former article[18] and used as the catalyst for SWNTs' growth. Typically, diluted Fe−Mo nanoparticle solution was applied on the front margin of a piece of silicon wafer (with ~400 nm of silica layers) using a syringe. Then the silicon wafer was directly placed at the center of a quartz tube furnace (Lindberg/Blue M tube furnace, quartz tube inner diameter 22.0 mm, outer diameter 25.4 mm). The CVD reaction system was kept at ambient pressure. The catalysts were heated to 900 °C in Ar atmosphere and treated in 100 sccm H_2 for 20 min. Then the furnace temperature was increased to 970 °C and the H_2 flow was reduced to low flow rate. Three minutes later, after the furnace temperature and gas flow was surely stabilized, CH_4 gas flow was introduced into the system for the growth of SWNT arrays. The volume flow rate ratio of CH_4:H_2 for SWNT growth was maintained at 1:2. While in ultralow flow rate conditions, the CH_4 and H_2 flow was respectively controlled by precisely adjusting the mass flow controllers (Beijing Qixinghuachuang Electronics Co., Ltd, China). The accuracy was ±0.05 sccm and the measurement range was 0−10.00 sccm. After 30 min of growth, CH_4 and H_2 flow was shut down and the furnace was cooled down under ~10 sccm Ar. Low- and high-resolution SEM images of SWNTs were respectively obtained on a Quanta 200FEG SEM and a START DB235 SEM operated both at an accelerating voltage of 1.0 kV. HRTEM images were obtained on a Hitachi 9000 TEM. Raman spectra were measured with a Renishaw 2000 micro-Raman with the excitation wavelength of 632.8 nm and spot size of 1 μm. AFM measurement was achieved on a SPI3800 SPM operated at tapping mode.

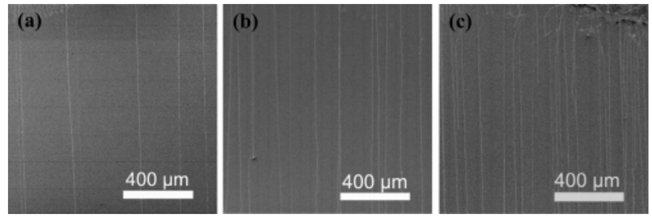

Figure 1. SWNT arrays obtained with 0.5 sccm of CH_4 and 1.0 sccm of H_2 at 930 °C (a), 950 °C (b), and 970 °C (c), respectively. The upper margin of each SEM image just starts from the edge of catalyst region.

The horizontally aligned SWNT arrays can be obtained with feeding flow as low as 0.5 sccm CH_4 and 1.0 sccm H_2 (Figure 1). Relatively higher CVD temperature is beneficial for the SWNT growth in this extreme condition because higher temperature is propitious to accelerate the decomposition of CH_4 and increase the activity of catalyst particles. Comparing with SWNT arrays grown at lower temperature, the arrays grown at 970 °C are more dense and straight. But when the reaction temperature was further increased to higher than 990 °C, amorphous carbon adhered on carbon nanotube walls and substrate surface increased. It was confirmed that gas flow rates of 1.5−150 sccm are all suitable for SWNT arrays' growth as long as the CH_4:H_2 ratio is fixed to 1:2 and the temperature is suitable (see Supporting Information Figures S2−S4).

Considering the straightness and density of SWNTs, an optimal growth condition of 2.0 sccm CH_4 and 4.0 sccm H_2 at 970 °C was set. A typical SWNT array grown under this condition is shown in Figure 2. As-grown straight nanotubes stretched from the catalyst area to the end of the silica substrate after 30 min of growth (Figure 2a, also see Figure S1 (JPG) in Supporting Information). When the catalysts were patterned in the middle of the silicon wafer, the SWNTs

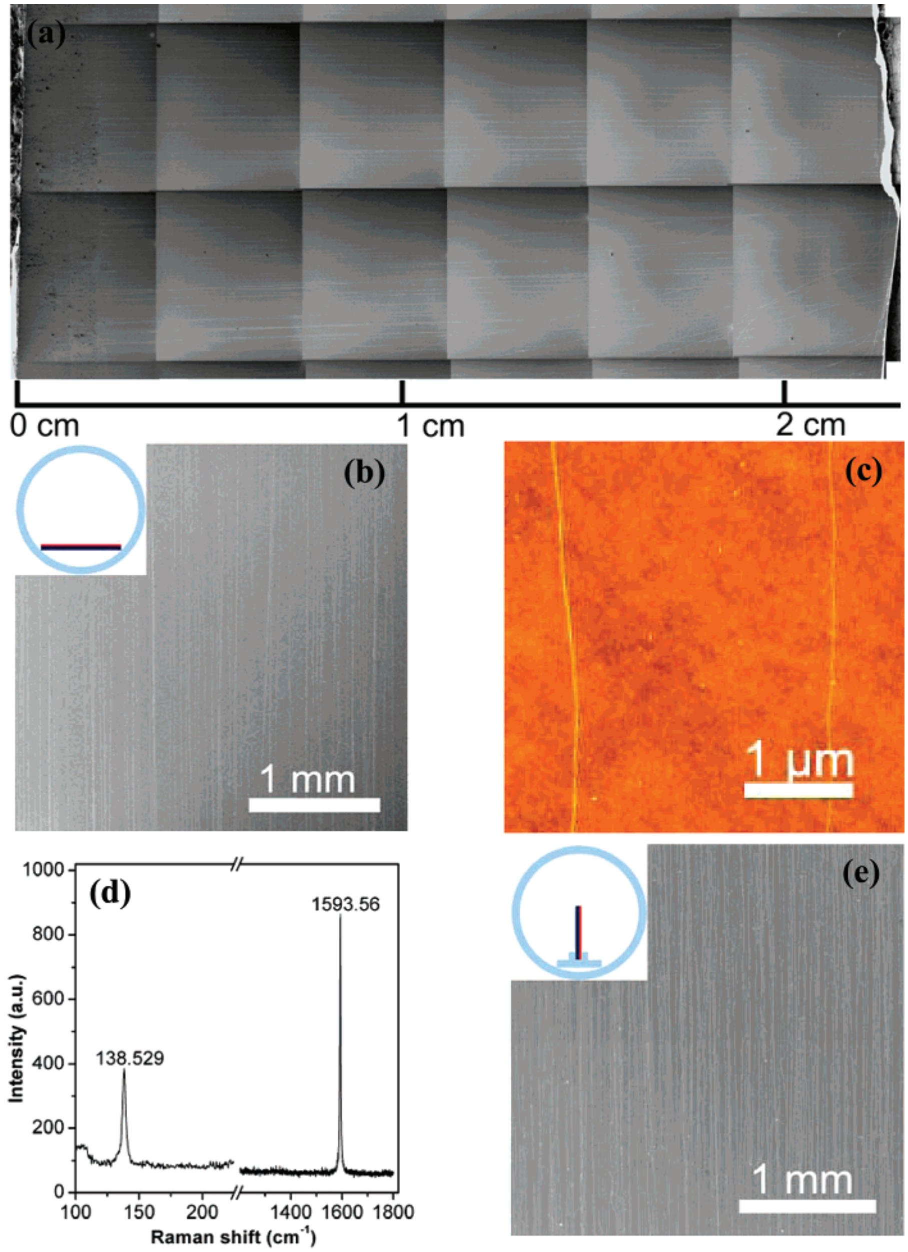

Figure 2. (a) Picture merged by SEM images shows SWNT array obtained on a piece of silicon wafer. (b) A partial magnified image of (a). (c) AFM image of as-grown SWNTs with diameters of 1.9 and 1.4 nm, respectively. (d) A typical Raman spectrum obtained from the as-grown sample. (e) SEM image of SWNT arrays grown on vertical-placed silicon wafer. In (b) and (e), schemes showing the placement of silicon wafers were inserted, in which upper surface of silicon wafers with catalyst was highlighted using red color. Both samples were obtained with 2.0 sccm of CH_4 and 4.0 sccm of H_2 at 970 °C.

still stretched from the catalysts area and went down along the flow direction, and no SWNTs grew from the front margin of the substrate (see Figure S5 in Supporting Information). The diameter distribution of nanotubes measured by AFM is 0.9−3.3 nm with the mean value of 2.0 nm. Figure 2c shows an AFM image of two parallel SWNTs with diameters of 1.9 and 1.4 nm, respectively. The Raman spectra of the samples all show a distinct RBM band and an extremely weak D band, which indicates that the products were made of high-quality single-walled carbon nanotubes. A typical Raman spectrum was shown in Figure 2d, which hints at a semiconductor SWNT of 1.8 nm in diameter.

To confirm the buoyancy effect, the substrates were also placed vertically on a quartz holder (Figure 2e). We found that oriented SWNT arrays can also be obtained under the same CVD conditions. The growth angles of these SWNTs were nearly aclinic, without obvious obliquities to the horizontal direction. It reveals that the SWNTs were lifted up and blown along the gas flow direction while growing. The gravity is not a key factor to the growth of SWNT array under low gas flow rate conditions.

To further make sure whether the nanotubes were grown floatingly, substrates with microtrenches and micro-obstacles was used for SWNT growth.[10,19] The results are shown in Figure 3. The microtrenches on silicon wafers were fabricated by traditional photolithography technique with ~3 μm in width and ~0.5 μm in depth. SWNTs could all grow across the microtrenches under ultralow flow rate conditions (Figure

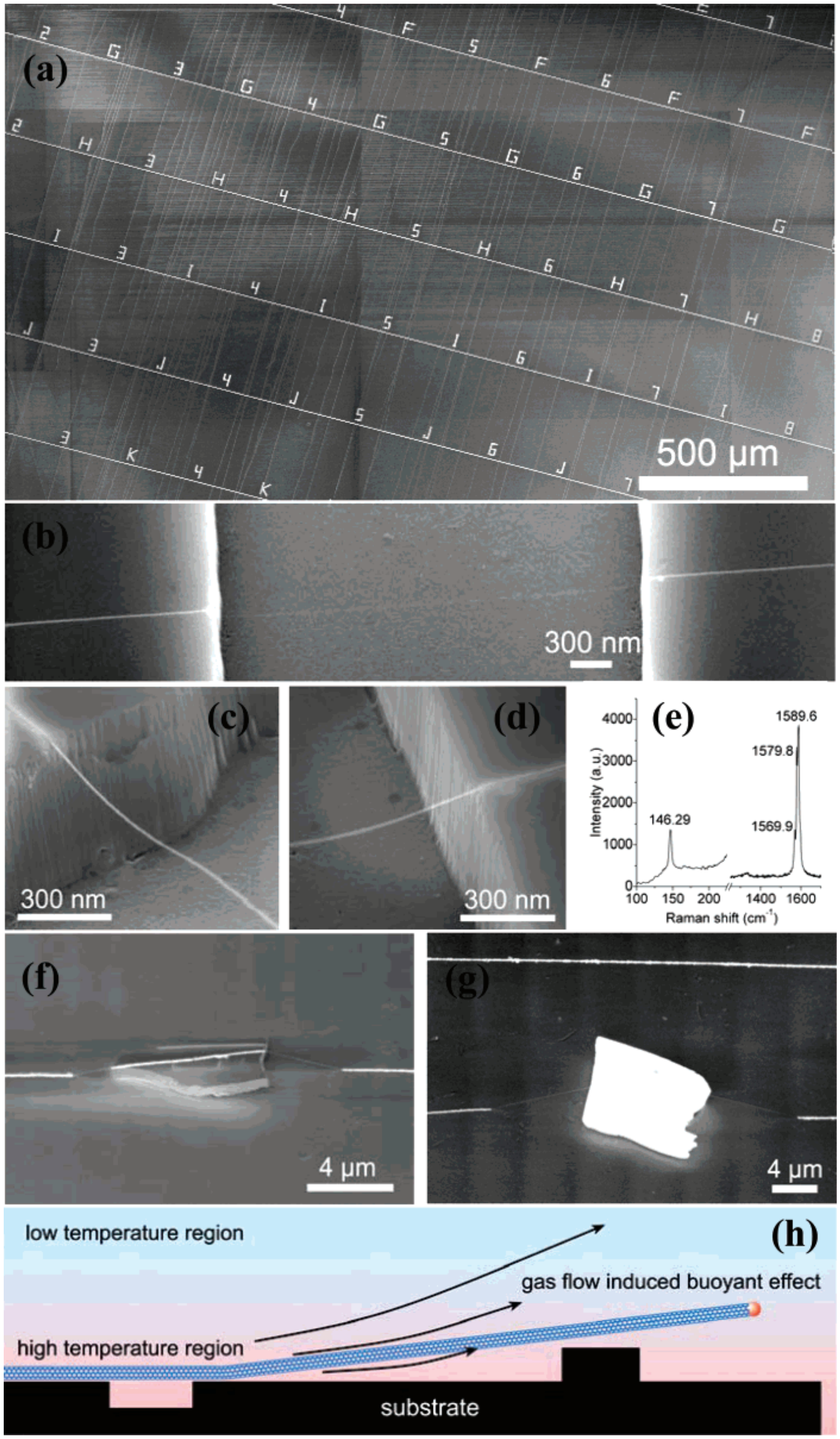

Figure 3. (a) SEM image of SWNT arrays grown across microtrenches. (b) A suspended SWNT crossing over a microtrench, the two ends of this SWNT "rope bridge" are shown in (c) and (d), respectively. (e) Raman spectrum measured from the center part of the suspended SWNT. (f,g) SEM images of SWNTs grown over micro-obstacles. (h) Schematic drawing of the growth mechanism. The front section of a growing SWNT floats in low rate gas flow relying on the buoyant effect induced by gas density/temperature gradient (shown as the gradual change of background color) and shear flow near the substrate surface. All samples were obtained with 2.0 sccm of CH_4 and 4.0 sccm of H_2 at 970 °C.

3a, more examples are shown in Figure S6 of Supporting Information). The SWNTs diving from one edge of the trench can climb up to the other edge again, forming suspended SWNT "rope bridges" (Figure 3b−d). Raman spectrum (Figure 3e) taken at the center of the microtrench reveals that this SWNT is a semiconductor SWNT with diameter of 1.7 nm. The D band of the suspended SWNT is also extremely weak. Similar to a previous report,[20] Raman signals

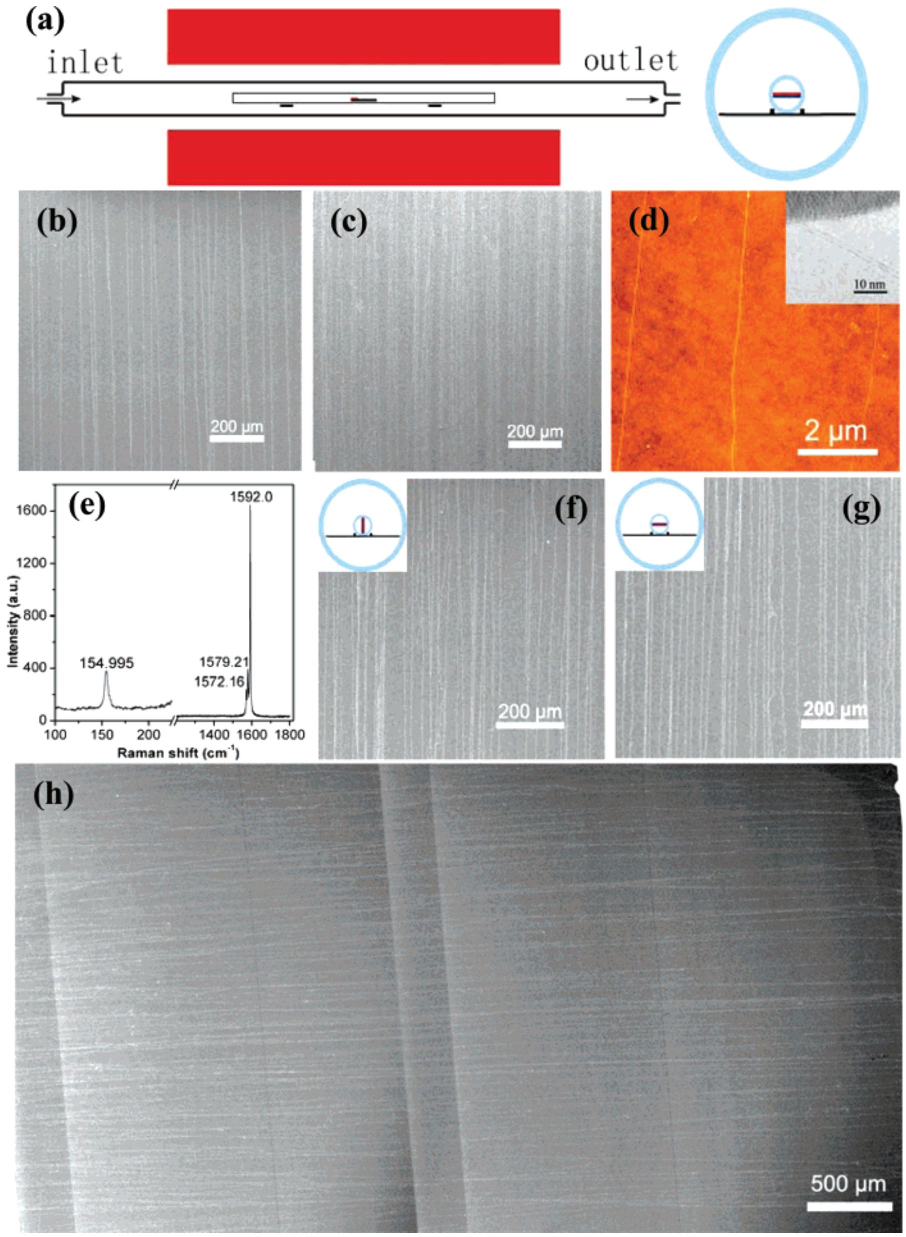

Figure 4. (a) Side view (left) and cross section (right) of the setup for SWNT array growth with an inserted small quartz tube. (b,c) SEM images of SWNTs grown on silicon wafer and quartz glass substrate, respectively. (d) AFM image of three parallel SWNTs on silicon substrate with the diameters of 1.2, 1.7, and 1.1 nm, respectively. Insert shows a typical HRTEM image of a 1.6 nm diameter SWNT grown on TEM grid coated with a thin layer of silica. (e) The Raman spectrum of a SWNT. (f) SEM images of SWNTs grown on vertically placed silicon wafer. (g) SEM images of SWNTs grown on inversely placed silicon wafer. (h) A full view of horizontal SWNT arrays grown in an inserted small quartz tube. All samples were obtained with 2.0 sccm of CH_4 and 4.0 sccm of H_2 at 985 °C.

from suspended parts of SWNTs are more intensive than that from the part lying on flat surface. Moreover, by placing silicon fragments on the substrate surface, SWNTs were proved to be able to grow over small obstacles with the height of about 10 μm (Figure 3f,g). These results indicated that the growing tubes still floated along the gas flow in the low feeding gas flow rate process, as shown in Figure 3h.

Besides Fe−Mo nanoparticles, SWNT arrays can also be obtained by using Fe−Mo nanolusters[21] or $FeCl_3$ ethanol solution as catalyst precursors at similar conditions. It shows the low flow rate strategy is universal and facile.

The above experimental results confirmed that normal heating low feeding flow rate CVD is very compatible for the growth of ultralong paralleled SWNT arrays. It proved that SWNT arrays also can grow floatingly in gas flow with extremely slow velocity (0.3 and 1.2 mm/s when the total gas flow rate is 1.5 and 6.0 sccm, respectively). Neither high velocity gas flow nor fasting heating is necessary. Different from the “kite-mechanism” based on a large flow rate growth method, our ultralow flow rate strategy shows its own traits. First, it revealed that the buoyant effect of convection flow induced by the vertical gradient of gas temperature and density can lift the carbon nanotubes up sufficiently, as described in Figure 3h. A large gas flow rate is not a decisive factor for the growth of SWNT arrays, whereas the intensity of vertical gas convection in the boundary layer near the substrate surface seems more important. Besides, stable low velocity laminar flow was also proved beneficial for growing straight SWNTs. In our process, the simply calculated Reynolds number inside the CVD reaction system is merely about 2.1 at room temperature and 0.76 at 970 °C (see Supporting Information), which means the gas flow is highly laminar and very stable.

For further decreasing the Reynolds number of the gas flow, we also tried decreasing the diameter (d) of the furnace tube[15] by inserting small quartz tubes into the CVD system (Figure 4a). The catalyst-loaded substrates were put horizontally into a small quartz tube with an inner diameter of 4.0 mm, outer diameter of 6.0 mm, and length of 20 cm, as shown in Figure 3a. The inserted small tube was lifted up to the center of quartz tube furnace on a holder. The CVD condition is the same as aforementioned, except the optimal growth temperature was increased to ~985 °C, for the inserted small tube wall is slightly unfavorable to heat transfer. Within the inserted small tube, horizontal straight SWNT arrays can also be obtained on a silicon wafer (Figure 4b) and quartz glass wafer (Figure 4c), and the array obtained is very uniform (Figure 4h). Figure 4d shows an AFM image of three parallel SWNTs grown on silicon wafer with the diameters of 1.2, 1.7, and 1.1 nm, respectively. For HRTEM observation, suspended SWNTs were also grown under the same CVD conditions on TEM grids coated with a thin layer of silica. SWNT bundles and multiwalled carbon nanotubes were rarely found under HRTEM observation. A typical HRTEM image of a 1.6 nm diameter SWNT is inserted in Figure 4d.

It was also confirmed that no matter whether the substrates were placed vertically (Figure 4e) or upside down (Figure 4f), SWNT arrays were well obtained inside the inserted small tube. The nanotubes could still float along the gas flow direction while growing and then attached to substrates in these situations. It was demonstrated in our previous work that the Van der Waals interaction between SWNTs and silica substrates is very strong.[22] The strong interaction can overcome the influence of gravity and eventually positioned the SWNTs to the substrate even when the silicon wafer is placed upside down.

Attractively, when several small tubes were mounted side by side in the furnace tube, SWNT arrays can be obtained similarly on each piece of silicon wafer in the small tubes simultaneously. Figure 5 shows an example. The SWNT arrays grown in different small tubes in such a way have no notable distinction, no matter whether the inserted small tubes were placed adjacent to the outer tube wall or at the center of the outer tube. This result is important for it gives us an approach toward batch scale preparation of ultralong horizontally aligned SWNT arrays, which has never been attempted in previous studies. The ultralow gas flow rate condition makes this strategy possible. Under high feeding gas flow, the inserted inner tubes may cause turbulence and thus cannot obtain straight long tubes. Moreover, compared with the method reported before, this kind of strategy working together with the low feeding gas flow of the process can effectively make use of the feeding stocks and greatly reduce the prodigality.

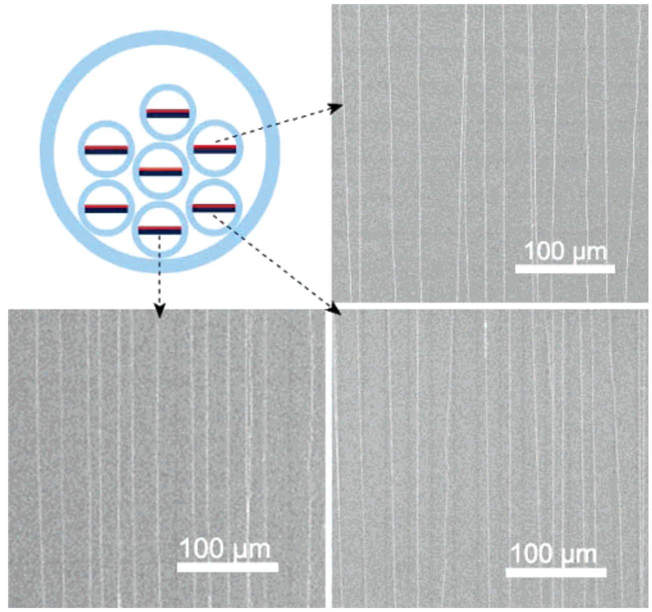

Figure 5. SEM images of SWNT arrays grown simultaneously in different small tubes inserted side by side into the outer furnace tube.

In summary, we have demonstrated that normal heating ultralow feeding gas flow rate CVD process is very promising and facile for guiding the growth of horizontally aligned ultralong SWNT arrays without the use of any other external driving force or special substrates. High-quality SWNT arrays can be obtained with several sccm of feeding gas. By mounting small tubes containing silicon wafers side-by-side into the quartz tube of the CVD system, batch scale preparation was achieved under low gas feeding flow rate. From the experiments of SWNT arrays growing across microtrenches and micro-obstacles as well as on silicon substrates with different obliquities, it was deduced that, in the ultralow flow rate process, the growing SWNTs can still be lifted up from the substrates and navigated by the gas flow. Here the temperature/density gradient induced buoyancy effect plays an important role, and the steady and highly laminar gas flow is very suitable for piloting the growth of paralleled long tubes. This strategy applies to different catalysts and substrates. It should be a promising and prospective method due to its efficiency, flexibility, and economizing for the batch production of large-scale SWNT arrays.

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Supporting Information Available: More CVD experimental details and results, the systematical investigation on the effects of growth temperature and gas flow rate, and the calculation of Reynolds numbers. This material is available free of charge via the Internet at http://pubs.acs.org.

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