Transfer and Alignment of Random Single-Walled Carbon Nanotube Films by Contact Printing

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ABSTRACT We present a simple method to transfer large-area random single-walled carbon nanotube (SWCNT) films grown on SiO_2 substrates onto another surface through a simple contact printing process. The transferred random SWCNT films can be assembled into highly ordered, dense regular arrays with high uniformity and reproducibility by sliding the growth substrate during the transfer process. The position of the transferred SWCNT film can be controlled by predefined patterns on the receiver substrates. The process is compatible with a variety of substrates, and even metal meshes for transmission electron microscopy (TEM) can be used as receiver substrates. Thus, suspended web-like SWCNT networks and aligned SWCNT arrays can be formed over the grids of TEM meshes, so that the structures of the transferred SWCNTs can be directly observed by TEM. This simple technique can be used to controllably transfer SWCNTs for property studies, for the fabrication of devices, or even as support films for TEM meshes.

KEYWORDS: carbon nanotubes · transfer manipulation · array

In recent years, single-walled carbon nanotubes (SWCNTs) have been actively explored as potential building blocks for various electronic applications, as they offer unique mechanical and electrical properties arising from their very small dimensions.[1] For example, they may assist the further scaling down of devices into the molecular regime, enabling enhanced performance and new functionality, leading to novel technological applications.[2−4] However, one of the most significant challenges for the integration of SWCNT-based devices is the controlled arrangement of SWCNTs with high scalability at well-defined locations on a substrate. So far, both direct-growth and post-growth approaches have been used to control the arrangement of carbon nanotubes (CNTs). The direct-growth approach, based on chemical vapor deposition, places catalysts at specific locations to control nanotube growth by gas flow,[5] electric field,[6] or crystal substrates.[7] In post-growth strategies, as-grown CNTs are transferred to a receiver substrate,[8−13] assembled by tweezers,[14] acoustics,[15] or microfluidics,[16] or positioned by a nanoprobe.[17,18] Among the above-mentioned post-growth strategies, the transfer of CNTs is one of the most versatile techniques because it enables the formation of large-scale complex layouts on various substrates ranging from silicon wafers to flat or curved glass plates or thin plastic sheets.[8−11] However, in previously reported transfer techniques, a mediator is usually required, or the receiver substrate or SWCNT film must be specially treated,[8−12] which both involve a complicated process. Recently, Im *et al.*[13] reported the successful preparation of laterally aligned thick CNT patterns on a SiO_2 substrate by the direct printing of aligned nanotube patterns, but this required the growth of vertically aligned SWCNT patterns before transfer manipulation. In all of the above transfer techniques, the transferred CNTs maintained their original geometric alignment during the transfer process. The aligned assembly of nanotubes by a transfer process has not yet been reported.

In this paper, we present a novel and simple method for the transfer and aligned assembly of large-area random SWCNT films. This method is based on a simple contact printing process that enables the direct transfer and positioning of SWCNTs from a growth substrate to a receiver substrate. More importantly, the transferred random SWCNTs can be assembled into high-density, horizontally aligned SWCNT arrays when the growth substrate is slid over the receiver substrate during the transfer process. The process is compatible with a wide range of receiver substrates, including non-flat-patterned substrates and metal transmission electron microscopy (TEM) meshes. The mechanism of this transfer and

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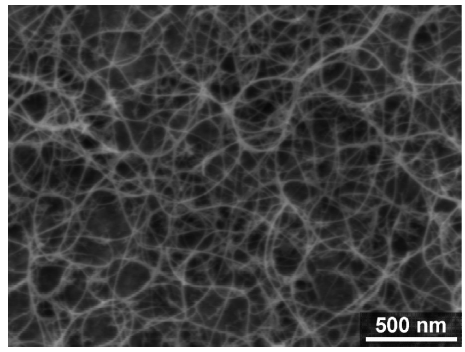

Figure 1. SEM image of as-grown SWCNTs on a SiO_2 substrate.

assembly process was explored through a series of systematic studies.

RESULTS AND DISCUSSION

A typical scanning electron microscopy (SEM) image of SWCNTs on a growth substrate (SiO_2/Si) before transfer manipulation is shown in Figure 1. The as-grown SWCNTs randomly distributed and entangled with each other, forming SWCNT networks. Two strategies for the transfer of SWCNT films are depicted in Figure 2a,b. As shown in Figure 2a, the first strategy uses a growth SiO_2 substrate (donor substrate) with an as-synthesized SWCNT film facing the target substrate (receiver substrate) with ~5 kPa of downward pressure applied by hand. Then, the donor substrate is removed. The other strategy is similar to the first strategy (as shown in Figure 2b), except that the donor substrate is slid ~1 mm in a specific direction along the receiver substrate during the contact process, under the same downward pressure.

In our experiments, we first employed a flat Si/SiO_2 (100 nm, thermally grown) wafer as the receiver substrate. After transfer manipulation, SEM was used to determine whether the nanotubes were successfully transferred to the receiver substrate. SEM images of SWCNT films transferred by the above two strategies are shown in Figure 3a−d. In both cases, high-density, uniform SWCNT films were observed on the receiver substrates, clearly demonstrating that the as-grown nanotube films were successfully transferred. As shown in Figure 3a,b, the random morphologies of the transferred SWCNT films were unaltered when there was no

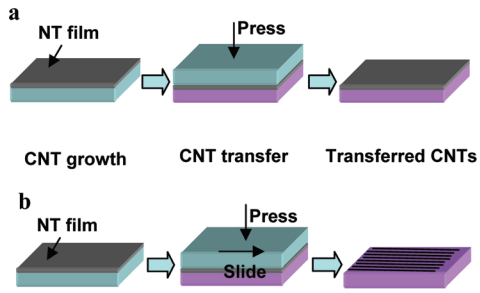

Figure 2. Schematic diagram of the transfer and assembly of SWCNTs.

sliding action of the donor substrate during transfer. In contrast, when the growth substrate was slid along the receiver substrate during transfer, the transferred SWCNTs were assembled into a high-density, well-aligned SWCNT array aligned in the sliding direction (Figure 3c,d). As indicated in Figure 3d, the highest aligned SWCNT density reached ~10 nanotubes per micrometer, assuming that all of the aligned SWCNTs were isolated. Note that some aligned SWCNTs overlapped or were close together, implying that SWCNT bundles were likely present. Therefore, the actual density of the aligned SWCNTs was probably higher than 10 nanotubes per micrometer, which is comparable to the density of horizontally aligned SWCNTs on crystal substrates obtained by CVD.[7] Compared to the density of aligned SWCNTs on SiO_2 substrates synthesized by a gas-flow-guided process, where a maximum density of ~0.6 nanotubes/μm was reported,[19] our contact printing method enables more than a 16-fold improvement in density. Such high-density aligned SWCNTs on SiO_2 substrates can easily be used in device applications.

It was possible that the transferred nanotubes were damaged by the physical friction between SWCNTs and substrates during transfer because the transfer of the SWCNT films was performed by direct physical contact without a mediator. To examine whether the transferred SWCNTs were damaged, we characterized SWCNT films before and after transfer manipulation by Raman spectroscopy. Raman spectra were measured at room temperature with a laser excitation wavelength of 785 nm and spot size of ~1 μm^2. It is well-known that the D-band (1300−1350 cm^{-1}) in the Raman spectra of SWCNTs derives from defects of nanotubes or other carbon materials. As shown in Figure 4a, before transfer, the Raman spectrum of as-grown SWCNTs on a SiO_2 substrate showed a clear D-band peak. However, after transfer manipulation, the D-bands in the Raman spectra of both the aligned and random SWCNTs on the receiver substrates (Si/SiO_2) became very weak or even disappeared (Figure 4b), indicating that the SWCNTs were not seriously damaged by the contact printing process. These results also indicate that the D-band peak in the spectrum of SWCNTs before transfer likely derived primarily from amorphous carbon deposited on the growth substrates. During the transfer process, most of the amorphous carbon was not transferred onto the receiver substrates. Therefore, the transfer process purified the transferred SWCNT films to some extent. On the other hand, multiple radial breathing mode (RBM) peaks (Figure 4b) were usually detected from the aligned SWCNTs, indicating that several nanotubes in the spot size of ~1 μm^2 were simultaneously resonating with the laser wavelength. These findings further demonstrate that high-density horizontally aligned SWCNTs were transferred onto the receiver substrates, which is consistent with the SEM observations.

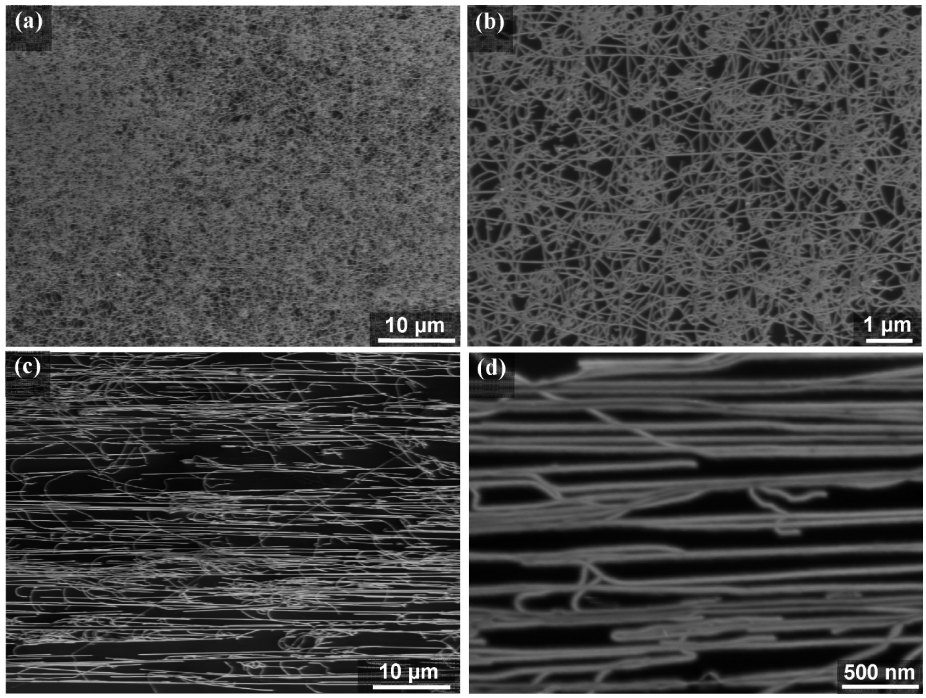

Figure 3. SEM images of the transferred SWCNT films on SiO_2 substrates. (a,b) Random SWCNT films, (c,d) aligned SWCNT arrays. (b) High-magnification image of panel a, (d) high-magnification image of panel c.

Since the transfer of the SWCNTs was performed by a simple contact process, the position of the transferred SWCNTs on the receiver substrates could be controlled by employing a patterned receiver substrate. We believe that, with this transfer technique, SWCNT films could be printed in predefined patterns on the receiver substrate, while other parts of the substrate remain clean. To implement this idea, we employed patterned Si receiver substrates for the transfer and alignment of SWCNT films. As shown in Figure 5, dense SWCNT films were transferred onto the patterns, and aligned SWCNT arrays were suspended over the trenches. From Figure 5b, most of the suspended SWCNTs had Y-shaped features at one of their ends, indicating that they were bundles. If these patterns were metal electrodes, the transport properties of the aligned suspended SWCNTs could be easily measured. Therefore, the capability of the contact printing process was further demonstrated by the successful transfer and assembly of SWCNTs onto predefined patterns on the receiver substrates. In other words, precisely defined patterns on a receiver substrate have the controllability of positioning and alignment of nanotubes.

The same transfer procedure is compatible with metal Ni meshes (3 mm diameter, 1500 grids, grid size $10 \times 10\ \mu m^2$), which are commonly used to support samples for transmission electron microscopy (TEM) observation. Transferred SWCNT films on Ni mesh substrates are shown in Figure 6. When transferred without sliding action, the transferred SWCNT films retained their original random morphologies (Figure 6a,b), forming large-area dense suspended SWCNT networks over the mesh. These transferred SWCNTs can be aligned on the Ni meshes by sliding the substrates during transfer (as shown in Figure 6c,d), leading to the formation of aligned suspended SWCNT arrays over the wide (about 10 μm) grids.

The successful transfer of SWCNTs onto Ni meshes enables the direct observation of the structures of transferred SWCNTs by TEM. As shown in Figure 7, most of

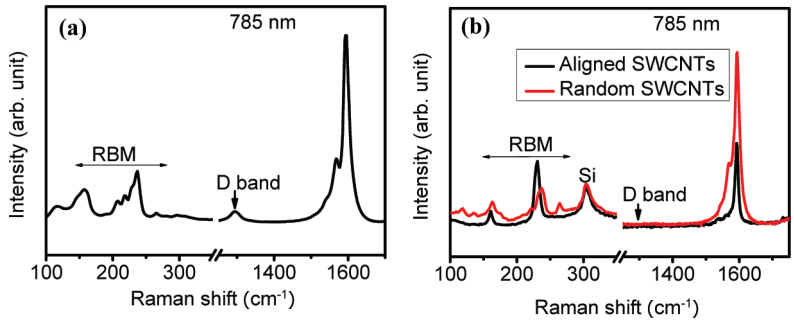

Figure 4. (a) Raman spectrum of as-synthesized SWCNTs on growth substrates (SiO_2), (b) Raman spectra of transferred SWCNTs on SiO_2 substrates.

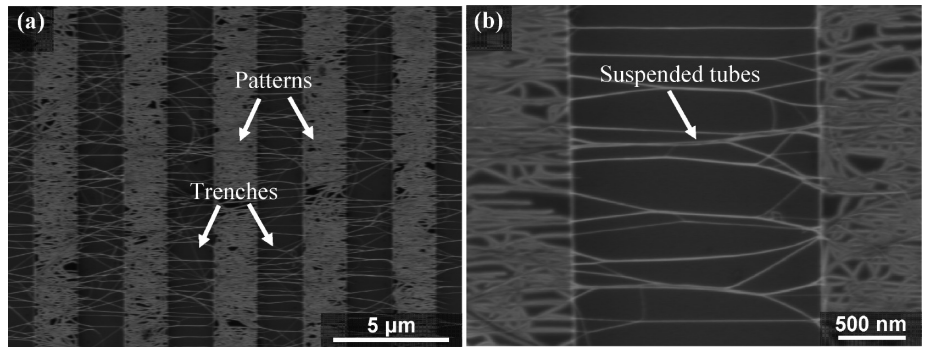

Figure 5. SEM images of transferred SWCNTs on patterned Si substrates. (a) Low-magnification image; (b) high-magnification image.

the transferred SWCNTs were in the form of bundles. These bundles consisted of various numbers of SWCNTs, ranging from 2 to about 10. Interestingly, small bundles consisting of two or three nanotubes were often observed (Figure 7a,b). The presence of a large number of SWCNT bundles further demonstrates that the density of the aligned SWCNT arrays on Si/SiO_2 substrates obtained by our contact printing process is much higher than 10 nanotubes per micrometer (Figure 3). Such highly dense aligned SWCNT films have great potential for the fabrication of high-power and high-current devices. In addition, multiwalled CNTs have recently been used to fabricate supporting films for TEM grids,[20,21] which enabled a higher performance in the observation of samples than a conventional amorphous carbon supporting film, particularly for par-

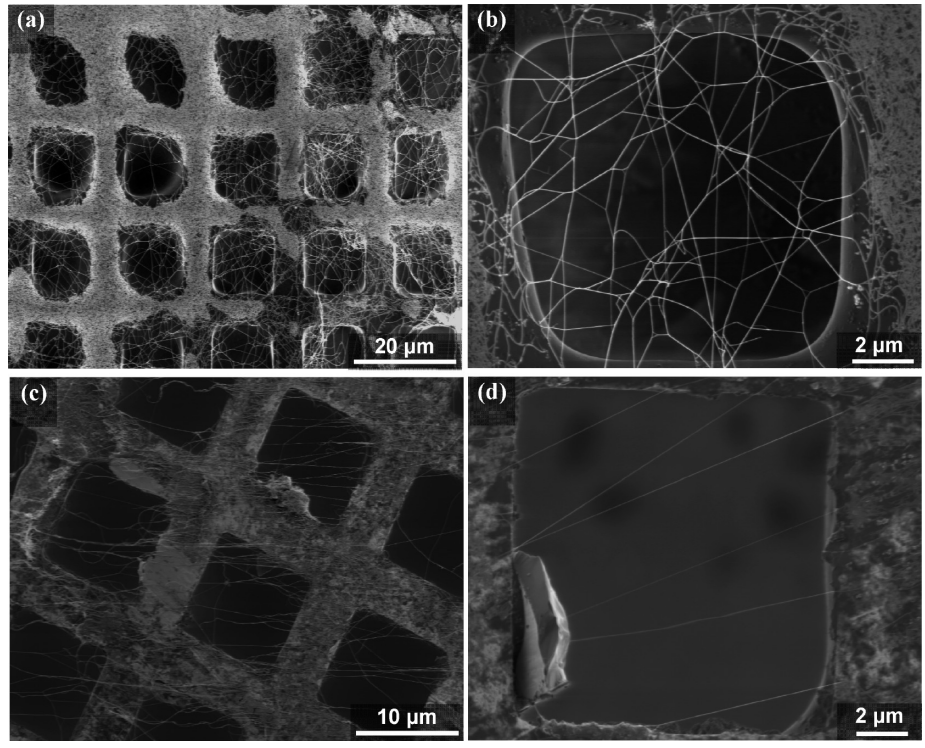

Figure 6. SEM images of transferred SWCNTs on Ni mesh substrates. (a,b) Random SWCNT films on a mesh, (b,d) aligned SWCNT arrays on a mesh. (a,c) Low-magnification images; (b,d) high-magnification images.

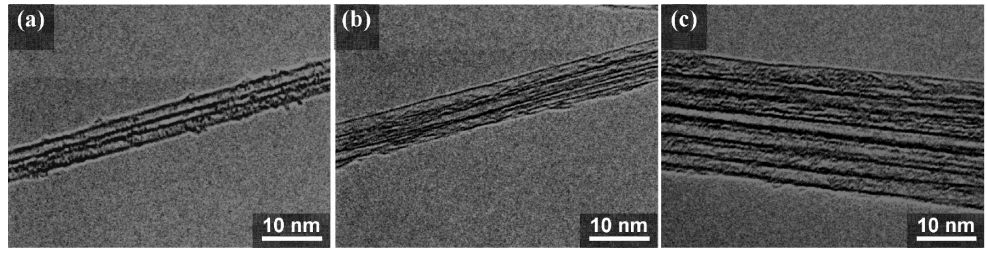

Figure 7. TEM images of transferred SWCNTs at different positions on a Ni mesh.

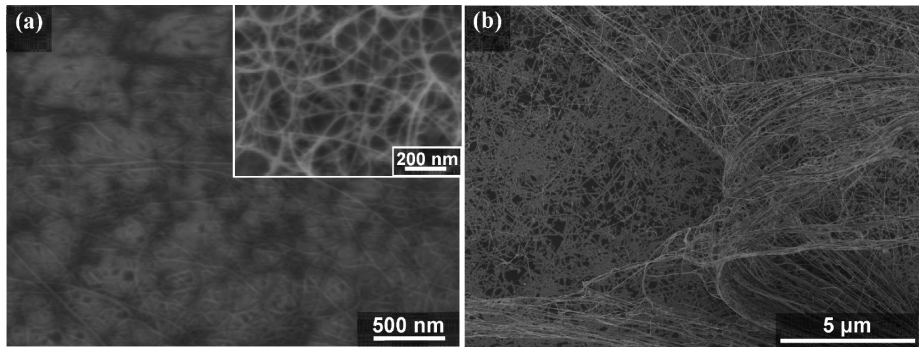

Figure 8. SEM images of (a) the remaining SWCNTs on a growth substrate after transfer and (b) SWCNT films manipulated with a ceramic tweezers tip. The inset in (a) is the corresponding morphology of the nanotubes on the growth substrate before transfer manipulation.

ticles less than 5 nm in diameter. The successful transfer of high-density SWCNTs onto TEM meshes by our simple printing process provides the possibility of the application of transferred SWCNTs as supporting films on TEM meshes. Moreover, SWCNT support films should have a higher performance than multiwalled CNTs because of their smaller diameter and single-layer graphitic structure.

Finally, we discuss the transfer mechanism of SWCNT films. As shown in Figure 8a, after transfer, an untransferred SWCNT film remained on the growth substrates. Compared to the original morphology of the nanotubes (the inset in Figure 8a) before transfer, these remaining nanotubes strongly adhered to the substrates, and an amorphous carbon layer seemed to cover them. These results indicate that the as-synthesized SWCNT films included two sublayers: a top sublayer consisting of a random SWCNT network, and a bottom sublayer of SWCNT film, which contacts the substrate surface. During the transfer process, most of the SWCNTs in the top sublayer were transferred. The bottom layer remained on the growth substrate because of a strong interaction between the nanotubes and the substrate. These results clearly indicate that the adhesion forces between SWCNTs and substrates are stronger than those between SWCNTs.

In order to examine the strong adhesion forces between substrates and nanotubes, we used tweezers to manipulate the as-synthesized SWCNT film. The detailed manipulation process was reported previously.[14] To perform this manipulation, we pressed a ceramic tweezer tip onto the growth substrate with a loading force of less than 10^{-3} N, and then slowly moved the tweezer tip along a certain direction. As shown in Figure 8b, the top sublayer of the synthesized SWCNT films peeled off. However, the bottom sublayer remained strongly adhered to the substrate. These results are consistent with those of the contact printing, further demonstrating that the adhesive interaction between nanotubes is smaller than that between nanotubes and substrates, which is likely essential to the successful transfer of SWCNTs.

We also investigated the effect of downward pressure on the growth substrate on the transfer of SWCNT films. When the downward pressure was less than 4 kPa, almost no nanotubes were transferred. With an increase in the downward pressure, the amount of transferred SWCNTs increased greatly. As shown in Figure 3, high-density, large-area SWCNT films were transferred at a downward pressure of ~5 kPa. On the basis of the above results, we believe that the high pressure between the two substrates caused the nanotubes to make sufficient contact with the receiver substrate surface to strongly interact with it, eventually resulting in detachment of the nanotubes from the donor substrate and their direct transfer to the receiver substrate. When the contact process included directed sliding of the growth substrate over the receiver substrate, the SWCNTs were aligned by a similar mechanism as in the tweezers-driven alignment.[14] While the suspended portions of the SWCNT film detached from the donor substrate and became anchored by van der Waals interactions to the receiver substrate surface, the nanotubes still in contact with the donor substrate remained pinned on the surface. With the movement of the receiver substrate, the originally curved nanotubes became straightened. Finally, the dragged nanotubes detached from the donor substrate, or broke at defects, and thus became aligned on the receiver substrate surface.

CONCLUSIONS

An approach was developed to directly transfer random SWCNT films from a growth substrate to a receiver substrate by a simple contact printing process. The transferred SWCNT films can be assembled into highly ordered, aligned SWCNT arrays on the receiver substrate. Precisely defined patterns on the receiver substrates enable control of the location of the transferred nanotubes. Another interesting feature of this printing process is its compatibility with metal substrates such as metal TEM meshes, which enables the direct observation of the structure of transferred SWCNTs by TEM. With this simple contact printing process, the ability to

uniformly transfer and assemble random SWCNT films of large area should be of interest for various applications of SWCNTs in electronic devices and support films for TEM meshes.

METHODS

Growth of Single-Walled Carbon Nanotubes. The SWCNT films used for transfer were prepared by catalytic CVD, using ethanol as the carbon source. A submonolayer of Fe catalyst film with a nominal thickness of 0.02 nm was thermally evaporated onto a SiO_2/Si (100 nm, thermally grown) substrate at a background pressure of 2×10^{-3} Pa. Nanotube growth was initiated by introducing 70 sccm Ar/H_2 (3% volume) through ethanol solution and 840 sccm Ar/H_2 through another gas line at 950 °C. Before nanotube growth, the as-prepared catalyst was annealed at 750 °C in air for 5 min, and subsequently at 950 °C in Ar/H_2 for 10 min. After CVD growth for 30 min, the samples were cooled in Ar to room temperature. The entire CVD process was done at atmospheric pressure.

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