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Microwave-Assisted Regeneration of Single-Walled Carbon Nanotubes from Carbon Fragments

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Direct growth of chirality-controlled single-walled carbon nanotubes (SWNTs) with metal catalyst free strategy, like cloning or epitaxial growth, has suffered from the low efficiency. The underlying problem is the activation of seed edge. Here an unexpectedly efficient microwave-assisted pathway to regenerate SWNTs from carbon fragments on SiO_2/Si substrate is demonstrated via Raman spectroscopy and atomic force microscope (AFM) characterization. In this attempt, microwave irradiation provides fast heating to remove polar groups bonded to carbon nanotubes and reduce the spontaneous closure of tubes' open ends. The survived SWNT and carbon fragments connected to it after plasma treatment are simply microwaved and then they serve as the template for regeneration. Scanning electron microscope and AFM characterizations indicate that the efficiency of the regeneration can reach 100%. And the regenerated SWNT has been proved without any change in chirality compared to the original SWNT. Electrical measurements on regenerated carbon nanotube films indicate 1 and 2 times increase in on/off ratio and on-state current respectively than original carbon nanotube films obtained from solution-phase separation, confirming the improvement of SWNT's quality. The microwave-assisted regeneration is found to be highly effective and would be applied to improve the cloning efficiency of carbon nanotubes potentially.

Single-walled carbon nanotubes (SWNTs) have been extensively studied during the last few decades due to their unique atomic and electronic structures, and ensuing promising applications in electronic[1–4] or other areas.[5,6] Thus, the mass production of single-chiral SWNTs has yet been regarded as the "holy grail," and tremendous efforts have been done to chase this goal. To date, SWNTs with high purity of electronic type, or even predominantly single chirality, can be enriched through solution-phase separation.[7–9] Despite of the fascinating developments with SWNT separation, this approach is still limited by the low yield and poor quality due to the harsh treatment during separation. At the same time, catalytic chemical vapor deposition (CVD), in which metal particles are generally taken as the catalysts, has shown advances of scale-up potential and high quality.[10–15] Since the chirality of an SWNT is considered to be determined at the nucleation stage of catalytic CVD process, the catalyst structures turn out to play the deterministic role on diameter and chirality control. Very recently, a symmetry matching theory has described an attractive prospect toward the controlling of SWNTs structures.[16] Unfortunately, single-chirality control of SWNTs is now still like an unreachable distance due to the inevitable thermal vibration in catalyst engineering. Recent work has reported that cloning strategies[17–19] or end-cap engineering[20–22] should provide a route to achieve truly single-chirality control when the SWNT segments, carbon nanorings, and end cap are precisely prepared as the template for SWNTs growth. However, an effective pathway to improve the growth efficiency of those metal catalyst free strategies remains elusive, even various complicated treatments are applied to activate the seed template, such as high temperature annealing for long duration,[23] air oxidation, and water treatment.[19]

It is widely known that oxygen functional groups are easy to bond with the end of SWNTs' seed covalently, forming highly stable ether and hydroxyl groups, which should account for the frustration of those cloning strategies. Microwave annealing reduction of SWNTs has been reported previously.[24,25] Comparing to traditional chemical or thermal method, microwave irradiation will introduce no impurity and achieve a rapid increase of temperature.[20] As the microwave irradiation is carried out under noble gas, oxygen functional groups on SWNTs turn to be efficiently removed,[26] and preventing the formation of H-terminated tubes' ends which may be too stable to participate in growth.[18] Furthermore, microwave induced fast annealing accomplishes in very short duration and will somewhat reduce the closure possibility of tubes' open-ends, which prefer to be closed in traditional long-duration annealing process.[27,28]

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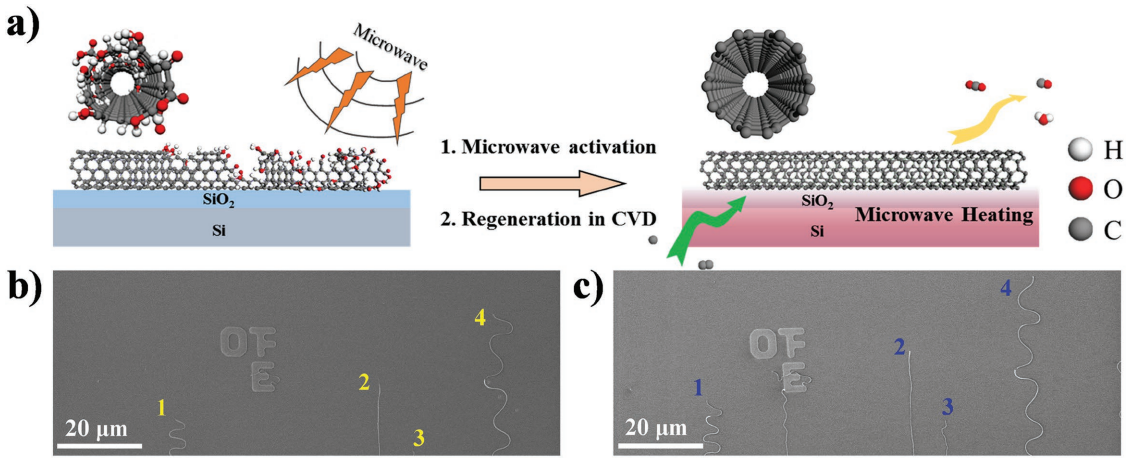

Figure 1. Regeneration process of an individual carbon nanotube with the assistance of microwave. a) Schematic showing the microwave-assisted regeneration of SWNTs. Typical SEM images of SWNTs after b) weak air plasma treatment and c) microwave-assisted regeneration.

Herein, we first report an unexpectedly efficient regeneration of SWNTs from carbon fragment. Our strategy is to combine microwave induced fast heating with subsequent CVD growth process to achieve the impressive improvement of such metal catalyst free regeneration. SWNT connected with carbon fragments were prepared from a long SWNT based on SiO_2/Si substrate by air plasma exposure treatment. When microwave field was applied under argon, the SWNT and connected carbon fragment reached to a high temperature together with SiO_2/Si substrate rapidly, so that the growth activity of end-bonded carbon atoms got recovered due to the desorption of oxygen functional groups, and the short duration, which was the advantage over other traditional methods, would benefit the reserve of SWNTs' open ends as well. Finally, ends of survived SWNTs and edges of connected carbon fragment were highly activated and served as the template for growth later in CVD synthesis, resulting in the 100% efficiency of regeneration.

Figure 1a schematically illustrated the process of microwave-assisted regeneration of SWNTs from carbon fragment. Details of regeneration process are described in the Experimental Section. In brief, an individual SWNT connected with carbon fragment was prepared by relatively weak air plasma treatment from the preliminary SWNT directly grown on SiO_2/Si substrate with 300 nm SiO_2 dielectrics. And the as-prepared SWNT connected with plasma-induced carbon fragment was put into a modified household microwave oven with the protection of Ar. Because of the absorption of microwave by SiO_2/Si substrate, an extremely high local temperature around substrate could be achieved in a few seconds. This step contributed to remove polar oxygen-containing groups bonded to the edges of carbon fragment and resulted in active edges. As such SWNT companied by plasma-induced carbon fragment with active edges was delivered to the CVD furnace, a general alcohol CVD process was performed immediately and even micrometer-scale carbon fragment would get regenerated to intact carbon nanotube without disturbance in chirality. It was believed that the active end of SWNT and edges of residual connected carbon fragment served as the template for the regeneration growth. Upon the test of different microwave times and CVD parameters, optimized growth condition was identified with 5 min microwave radiation. Figure 1b showed the representative scanning electron microscope (SEM) image of four long and separated SWNTs after relatively weak air plasma treatment. Using the markers in SEM images such as "OFE," we could accurately locate each ends of these four tubes. Since optimized microwave treatment and subsequent regeneration process in CVD system were carried out, all these four carbon nanotubes got regenerated and led to the elongation of micrometers as shown in Figure 1c.

To confirm our hypothesis of the process of regeneration, atomic force microscope (AFM) was employed to characterize the residual carbon fragment and the diameter variety along an individual SWNT which had gone through the microwave-assisted regeneration. **Figure 2**a showed one intact SWNT near the marker of substrate, and the diameter of this preliminary carbon nanotube turned out to be uniform (1.57 nm) according to the AFM characterization in Figure 2d. Then relatively weak air plasma was applied to break the SWNT at an accurate position near the marker "UF9." Figure 2b indicated that the top part of SWNT exposing to the plasma was etched away. However the corresponding AFM characterization offered more information, the end of SWNT produced by air plasma was not sharp but gradual (see Figure S1, Supporting Information) which meant a length of carbon fragment connected to the protected part of SWNT survived. Microwave-assisted regeneration was then carried out for this as-prepared SWNT and carbon fragment connected to it. As shown in Figure 2c, the length of SWNT was apodictically extended following the left "trace" which was believed to be the survived carbon fragment. The diameter of regenerated SWNT returned back to original value (1.59 nm). As such microwave-assisted regeneration was applied for more carbon tubes, the statistic results in Figure 2g indicated that SWNTs after regeneration would be elongated for tens of micrometers which depended on the etching degree by air plasma. Moreover, Figure 2h about the statistic height demonstrated that the residual carbon fragments were indispensable for regeneration, and the increase of height value after regeneration suggested the recovery of tubes diameter. Thus, the process of microwave-assisted regeneration with 100% efficiency was revealed.

To further investigate the SWNT regeneration process as a function of time, we collected the SEM images of the same one

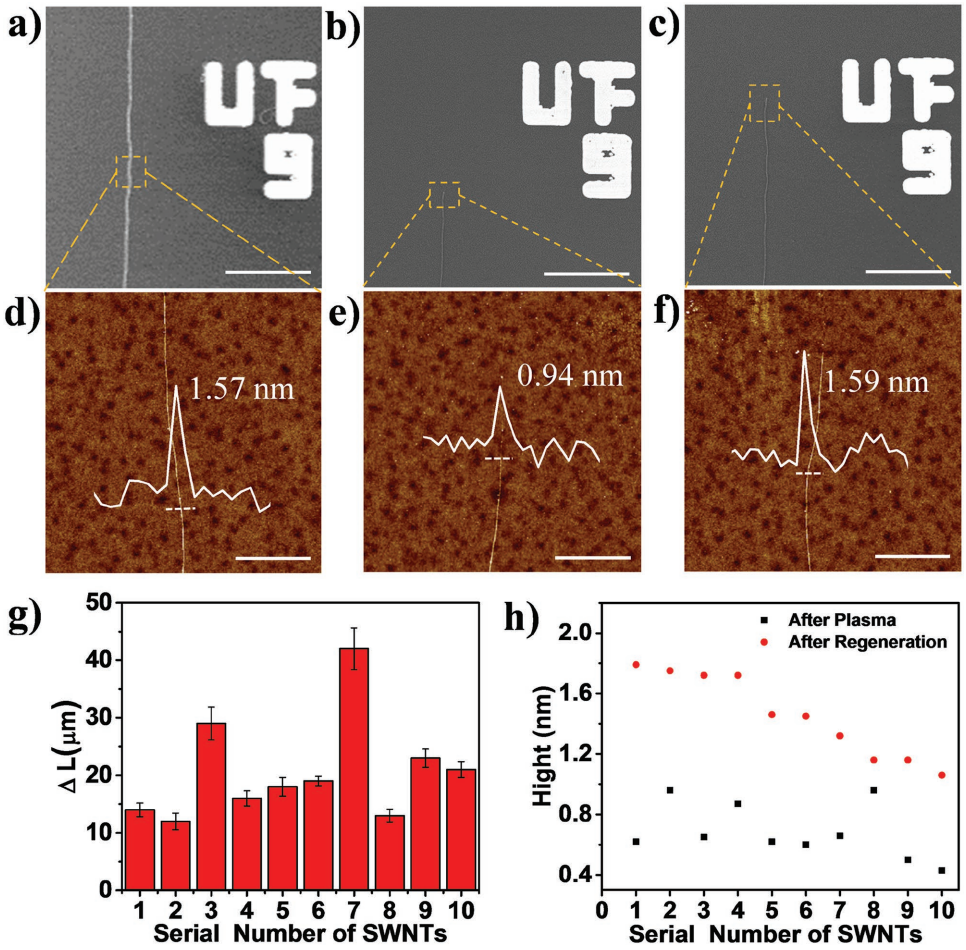

Figure 2. Characterization of the carbon nanotubes regeneration process. SEM and AFM images of the individual SWNT at different treating stages: a,d) the original individual SWNT; b,e) the SWNT after plasma treating; c,f) the SWNT after microwave-assisted regeneration. g) The statistics elongated length of SWNTs after regeneration. h) The statistic height of SWNTs after plasma treatment (black square) and regeneration (red dot). Scale bar: a–c) 20 μm and d–f) 2 μm.

SWNT of different time for regeneration (see Figure S2, Supporting Information). When it took only a few time (5 min) for regeneration in CVD system, the SWNT got lengthened right begin at the end of unbroken part as shown in Figure S2c (Supporting Information). Then a repeating microwave-assisted regeneration was carried out for the second time (see Figure S2d, Supporting Information), this SWNT continued to extend for more than 20 μm in 30 min. According to these morphology and structural characterization, microwave radiation annealing and subsequent alcohol CVD regeneration growth were able to regenerate the broken SWNTs with the exact template of SWNT end and connected carbon fragment, and the regenerate process developed gradually from the near end to the distance.

The resonance Raman data of individual SWNT were collected using a confocal imaging microscope combined with micro-Raman spectroscope to verify that the regenerated part of SWNT has the same predetermined chirality as the template one, the excitation spot size was about 1 μm in diameter. **Figure 3**c indicated a typical Raman spectroscope characterization of the SWNT in Figure 3b, microwave-assisted regenerated from the SWNT in Figure 3a, showing a same radial breathing mode (RBM) shift at 257.4 cm^{-1}. Since the RBM frequency is inversely proportional to the diameter of SWNT, the diameter was unambiguously preserved in the regenerated part of SWNT, which coincided with the AFM characterization, and confirming that the regeneration process was accurately induced by the template.

Microwave annealing treatment is the most critical factor to determine whether the carbon fragment can regenerate or not. As the usual regeneration growth except microwave annealing treatment was carried out, no phenomenon about regeneration of the SWNTs was observed (see Figure S3, Supporting Information). It suggested that microwave radiation indeed helped activate the end of SWNT and edge of connected carbon fragment, therefore, this microwave heating method possessed the potential to develop cloning efficiency in the cloning of SWNTs in future. Due to the extreme condition under microwave radiation, the annealing atmosphere in furnace should be carefully selected so that the as-prepared SWNTs could be activated rather than destroyed. Annealing in vacuum or under Argon is wildly approved effective for removing polar groups on SWNTs, and hydrogen-terminated sp^2 carbon edges have been reported

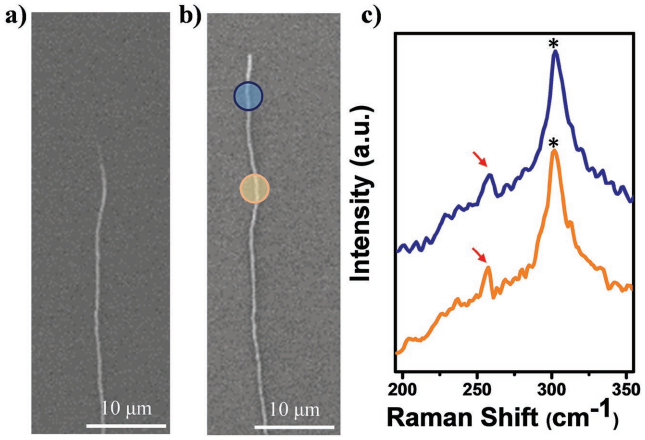

Figure 3. Raman characterizations along an individual SWNT after microwave-assisted regeneration. a) SEM image of the air plasma treated SWNT before regeneration. b) SEM image of regenerated SWNT from the nanotube in (a). c) Typical RBM peaks of the specific SWNT with different positions in (b). The same Raman shift at 257.4 cm^{-1} confirming that the chirality is preserved after the regeneration process using the laser wavelength, 633 nm.

being active for regrowth. Therefore, the optimized gas atmosphere during microwave radiation was revealed by a series of control experiments as shown in the Supporting Information (Figure S4, Supporting Information). As the quartz tube was purged with Argon, there was no structural damage about the SWNT after microwave radiation when compared with the sample after air plasma treatment (see Figure S4g, Supporting Information). While an Ar/H_2 (300 sccm/10 sccm) mixture gas was introduced, the SWNT was partly etched under microwave treatment as shown in Figure S4h (Supporting Information). This might be attributed to the hydrogen etching during fast heating. While all the gas were pumped out and the SWNT on SiO_2/Si substrate was microwaved in vacuum (≈0.5 Pa), the obvious glow discharge phenomenon was observed and no SWNT survived (see Figure S4i, Supporting Information) due to the etching by glow discharge induced plasma. Thus, microwave treatment under Argon was demonstrated indispensable.

Noting that the microwave radiation was essential for the regeneration of SWNTs, we further investigated what role the microwave played and how it worked during radiation. The microwave response of carbon nanotubes has been reported widely as the carbon nanotubes were prepared in great amount. However, the microwave abosrbance of a single SWNTs is not clear yet. As shown in Figure S5 (Supporting Information), the aligned SWNTs based on quartz substrate were used for microwave-assisted regeneration, but no phenomenon of regeneration was observed. Thus, the microwave absorption of SiO_2/Si substrate induced heating was believed as the principal pathway to provide heat supply and activate the ends of SWNTs and edges of connected carbon fragments in a short duration sequentially. Semiconductor silicon would absorb the energy of microwave

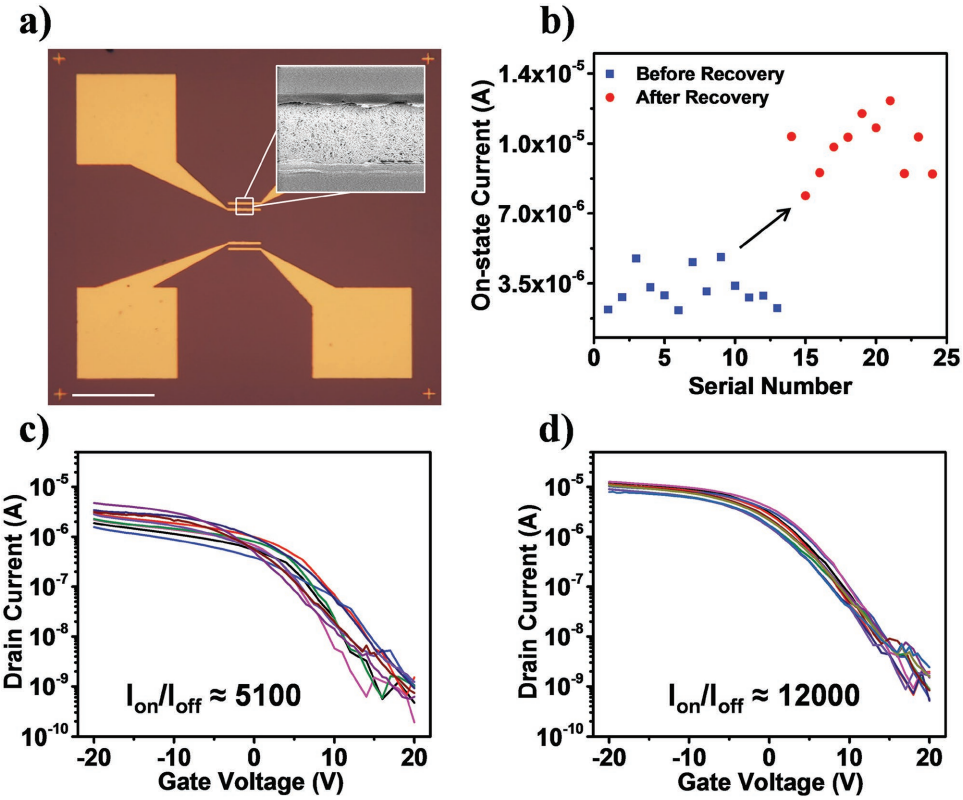

Figure 4. a) The optical and SEM (inset) images of typical FET devices fabricated on solution-dispersed semiconducting SWNTs, scale bar, 50 μm. b) The statistics of the on-state current of regenerated (red circle) and original (blue square) nanotube films. Transfer characteristics of c) original and d) regenerated nanotube films.

and generate a lot of heat because of the intrinsic higher complex permittivity around 2.45 GHz compared to quartz substrate.

Finally, to further evaluate the achievement of microwave-assisted regeneration about SWNTs, the electrical measurements of back-gated field-effect transistor (FETs) fabricated on solution-dispersed semiconducting SWNTs normally with defects were performed. The optical and SEM (inset) images of typical FET device were shown in **Figure 4**a. In brief, the solution-dispersed semiconducting SWNTs were deposited on SiO_2/Si substrates with 300 nm SiO_2. Half of them were followed by formation of Cr/Au (5/60 nm) metal contact using photoetching and lift-off techniques, while the others had gone through the microwave-assisted regeneration in advance of preparing metal electrodes (for details see the Supporting Information) as the control group. The electron transfer characterizations (I_D–V_G) of SWNTs film without and with microwave-assisted regeneration are provided in Figure 4c,d, respectively. The average on/off ratio of original nanotube films appeared to be about 5100 while the regenerated nanotube films were increased to about 12 000. In addition, statistics of the on-state current for both regenerated and original nanotube films was shown in Figure 4b. It was obviously that the on-state current increased by 2 times from 3.3 to around 10 μA, which was consistent with the result of Raman characterization (see Figure S6, Supporting Information). The average ratio of G peak intensity divided by D peak intensity (G/D) increased from ≈8.1 to ≈12.4 as microwave-assisted regeneration was carried out, suggesting the great quality improvement of solution-dispersed SWNTs.

In summary, we put forward an unexpectedly efficient microwave-assisted method to regenerate SWNTs from carbon fragments on SiO_2/Si substrate. In this attempt, microwave irradiation provided fast heating to remove polar groups bonded to carbon nanotubes and reduce the spontaneous closure of tubes' open ends. The survived SWNT and carbon fragments connected to it after plasma treatment were simply microwaved and served as the template for regeneration. SEM and AFM characterizations revealed the process of microwave-assisted regeneration with 100% efficiency. Finally, the FET devices were fabricated on regenerated solution-dispersed SWNTs as well as original ones and the transfer characteristics confirmed that the SWNTs possessed higher quality after microwave-assisted regeneration. Nevertheless, exploration of the underlying mechanism of activation during microwave radiation still needs to be done henceforward.

Experimental Section

Microwave-Assisted Regeneration Process: The carbon fragments were prepared by air plasma treatment of long SWNTs. Then the whole as-prepared SWNTs connected with carbon fragment were delivered into a 1 inch quartz tube combined with a household microwave oven as well as a tube furnace. After the whole system was purged with 300 sccm argon, samples on SiO_2/Si substrate were microwaved for 5 min. No obvious arcing was observed around substrate during the microwave radiation. Subsequently, the microwaved samples were moved to the heating zone of furnace and kept for 20 min at 400 °C with the flow of an Ar/H_2 (300 sccm/50 sccm) gas mixture. For alcohol-based CVD regeneration, the temperature was increased to 900 °C and 80 sccm argon through an ethanol bubbler was introduced. For all experiments, the regeneration of carbon fragments was carried out for 30 min.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

carbon nanotubes, chirality, efficiency, microwaves, regeneration

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