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Metal-Catalyst-Free Growth of Single-Walled Carbon Nanotubes

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Single-walled carbon nanotubes (SWNTs) are attractive for vast potential applications in electronics, optical electronics, sensors, drug delivery, catalyst supports, composites, etc. Generally, metal catalysts, typically iron-group elements (Fe, Co, Ni) and their alloys, are indispensable for the growth of SWNTs. Recent experimental[1,2] and theoretical[3,4] studies show that the controllable synthesis of SWNTs, which is of vital importance, can be realized to some extent by the conscious selection of catalysts. Increasing attention is being paid toward exploring new catalysts for the controllable and efficient growth of SWNTs and for understanding their growth mechanism in-depth.[1,2,5−9] For these goals, a variety of metal catalysts, such as Au, Ag, Cu, Pt, Pd, Mn, Mo, Cr, Sn, Mg, and Al, have been newly developed for the synthesis of SWNTs.[5−9]

On the other hand, the unavoidable metal species remaining in the SWNT products would result in obvious disadvantages for both intrinsic property characterization (e.g., chemical, electronic and magnetic properties, thermal stability, and toxicity)[5,10,11] and application exploration (e.g., catalyst supports, biology, and medicine)[12,13] of SWNTs. Detriment effects of these metal particles to SWNT-based electronic devices are also of concern[13] because metal catalyst residues are incompatible with silicon semiconductor technology.[14] Despite sustained efforts, it has been until now an intractable problem to remove metal catalysts completely from SWNT samples without introducing defects and contaminations.

Very recently, Takagi et al. reported the growth of carbon nanotubes from ethanol by using epitaxial grown semiconductor nanoparticles as "templates".[15] However, their method suffers from shortcomings of the low yield and poor quality of the obtained samples, and the growth process is complex.[15]

In this communication, we present a simple and efficient method for realizing the growth of SWNTs with a metal-catalyst-free chemical vapor deposition (CVD) process. The details of our method are described in the Supporting Information (SI). Briefly, a 30-nm-thick SiO_2 film was first sputtering deposited onto a Si or Si/SiO_2 (1 μm thick thermally grown SiO_2 layer) wafer which serves as a substrate. The substrate was then put into a tube furnace and heated to growth temperature (900 °C) under the protection of 100 sccm Ar. When the temperature reached 900 °C, the synthesis was initiated by introduction of a flow of 500 sccm CH_4 and 500 sccm H_2 for 20 min. Dense and uniform SWNT networks were obtained on the surface of the substrate reproducibly.

Figure 1a and 1b are representative scanning electron microscopy (SEM) and atomic force microscopy (AFM) images of the as-grown SWNTs on the surface. As can be seen from Figure 1a (also see SI), a dense and large-area uniform SWNT thin film is obtained, indicating the effectiveness of our synthesis approach. The AFM image (Figure 1b) indicates a very high density (>100 tubes/μm^2) of the SWNTs grown. Moreover, almost no impurities were found in these observations. The surface resistance of the as-prepared

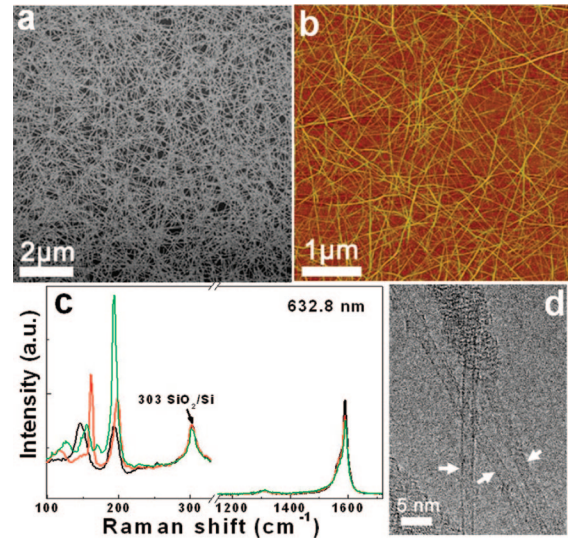


Figure 1. (a) Typical SEM and (b) AFM images of the as-grown SWNTs on Si/SiO_2 substrate covered with a 30-nm-thick sputtering deposited SiO_2 film. (c) Raman spectra of the same sample acquired at three positions, with the peaks at 303 cm^{-1} originating from Si/SiO_2 substrate and used for calibration. (d) HRTEM image of three individual SWNTs (indicated by arrows).

SWNT film was measured to be 3.8 kΩ/sq by using a four-probe method, confirming that a continuous SWNT network was formed. The presence of radial breathing modes (RBM) and the low intensity ratio of defect-induced D band to tangential G band (~0.04) in Figure 1c are indicative of the high quality of the SWNTs. We also conducted high-resolution transmission electron microscopy (HRTEM) observations on the as-grown sample. For TEM characterization, the specimens were prepared by utilizing a flexible poly(methyl methacrylate) (PMMA) film as a mediator to transfer the SWNTs from the source substrate to target Cu grid with the assistance of a hot KOH solution (see SI).[16] A typical HRTEM image is shown in Figure 1d, demonstrating the high quality and the individual nature of the obtained SWNTs. The amorphous covering on the SWNT surface is a PMMA residue, since it can not be removed completely by an acetone bath. We also observed that one end of the SWNTs is connected with nanoparticles (NPs) with a similar size (image not shown).

We performed synthesis experiments with varying parameters, and several interesting results were found. (i) The sputtering deposited SiO_2 film performs quite differently from the thermally grown one because the latter cannot grow SWNTs at all (see SI). (ii) The thickness of the SiO_2 layer is another key point for the efficient growth of SWNTs, and only very sparse SWNTs were obtained on a 10-nm-thick sputtering deposited SiO_2 film compared to 30-nm- and 100-nm-thick films (see SI). (iii) The pretreatment

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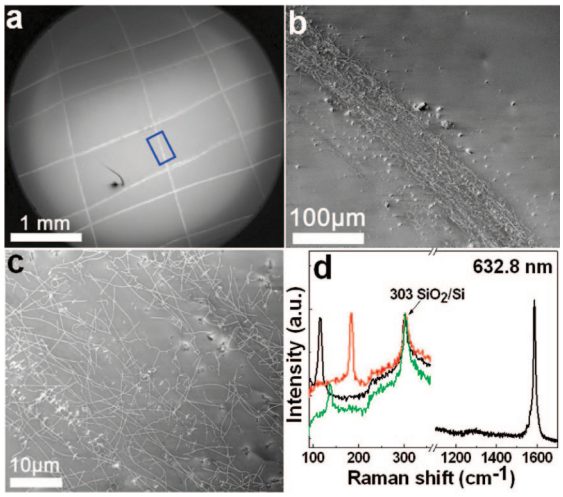


Figure 2. (a) SEM image of the SWNTs grown on a cross patterned Si/SiO_2 wafer. The cross pattern was made by scratching the wafer with another sharp Si/SiO_2 wafer. (b and c) Enlarged SEM images of the blue square area in image a, showing that SWNTs are grown at the scratched positions, while no SWNTs are found in the unscratched areas. (d) Raman spectra taken at three different positions in image c, showing the RBM peaks at 115 cm^{-1} (black), 137 cm^{-1} (green), and 184 cm^{-1} (red).

(oxidation and reduction) of the SiO_2 film deposited substrate is not absolutely necessary for SWNT growth since abundant SWNTs could also be obtained when the substrate underwent a higher temperature (850 °C) oxidation or reduction treatment before growth (see SI). This point is quite different from some newly established catalysts, where a high temperature oxidation (or oxygen plasma) and/or high temperature reduction treatment process is indispensable,[5−7,15] indicating that our approach is an easier process with a wide growth window. Note that a deposited SiO_2 film is used as a catalyst support layer (e.g., Fe) in the CVD growth of SWNTs,[17,18] while no special attention has been paid to the catalytic activity of the film itself previously. Our current findings of the excellent catalytic activity of the sputtering deposited SiO_2 film itself for SWNT growth urge us to reconsider the function of such a deposited film. AFM measurements on the deposited SiO_2 film reveal that many NPs with an average size of 1.9 nm were formed after H_2 treatment at 900 °C (see SI). We speculate that the formation of these NPs is essential for the high-efficiency growth of SWNTs. Studies on the detailed structure of these NPs and the function and catalytic mechanism of the deposited SiO_2 film are in progress.

We also found a simple method for patterned growth of SWNTs on a Si/SiO_2 wafer at any desired position via a similar metal-catalyst-free CVD process. In this case, a clean Si/SiO_2 wafer was scratched by another Si/SiO_2 wafer with a sharp tip to obtain a desired pattern (both wafers are Si covered with a 1 μm thick thermally grown SiO_2, but free of SiO_2 film deposition). Such a scratched Si/SiO_2 wafer was then directly subject to a CVD growth process in a tube furnace as described above (see SI). Typical results are presented in Figure 2. The white cross lines in Figure 2a are the scratched areas, and the enlarged images (Figure 2b and 2c) show that SWNTs are grown in the scratched area while no SWNTs can be found in unscratched areas. Raman spectra in Figure 2d confirm the growth of SWNTs. One should note that this process is essentially different from a recent report, in which SWNTs were pattern grown on a single-crystal quartz substrate scratched with blades containing Fe or Co.[8] In this study, one Si/SiO_2 wafer was used to scratch another Si/SiO_2 wafer to ensure a complete metal-free process. We speculate that the "scratching" between two Si/SiO_2 wafers will make the thermally grown SiO_2 layer crack and consequently generate some active sites, which have some similarities to the SiO_2 film by sputtering deposition, thus facilitating the growth of SWNTs. This "scratching growth" approach is quite simple without using any complex patterning process[8] and could be used for the growth of SWNTs at a precisely predefined position for device fabrication, e.g., by using a Si AFM tip to "write" a pattern onto a Si/SiO_2 wafer, because of the extremely tiny dimension of the AFM tip.

In summary, we proposed a simple and effective method for growing SWNTs via a metal-catalyst-free CVD process on a sputtering deposited SiO_2 film. Metal-free, pure, and dense SWNTs were obtained. A metal-catalyst-free "scratching growth" approach was also developed for the patterned growth of SWNTs. The successful growth of SWNTs using a nonmetal catalyst can provide valuable implications for understanding the growth mechanism of SWNTs in-depth, which accordingly will facilitate the controllable synthesis and applications of carbon nanotubes.

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Supporting Information Available: Synthesis details and characterization, XPS characterization of the substrate, the effect of substrate, substrate pretreatment and SiO_2 film thickness on the growth of SWNTs, and the formation of NPs from SiO_2 film. These materials are available free of charge via the Internet at http://pubs.acs.org.

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