

LETTERS

Chemical Alignment of Oxidatively Shortened Single-Walled Carbon Nanotubes on Silver Surface

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We propose here a simple technique for the assembly of oxidatively shortened single-walled carbon nanotubes (SWNTs) on silver surface. This technique is based on the spontaneous adsorption (self-assembly) of the $-\text{COOH}$ groups at the open ends of carbon nanotubes onto silver surface. Raman spectroscopy, tapping mode atomic force microscopy (TM-AFM), and transmission electron microscopy (TEM) results have shown that the oxidatively shortened SWNTs assemblies have been formed on the silver surface, with the nanotubes perpendicular to the surface. Moreover, TEM studies also revealed that most of the SWNTs (ca. 80%) assembled on silver surface have a bundle size of 6.5 ± 0.5 nm, possibly suggesting the selective adsorption of SWNTs on silver.

The discovery of carbon nanotubes,¹ has shown them to be promising materials for a variety of applications: for example, nanopores for scanning probe microscopy,² nanotweezers,³ batteries,⁴ chemical sensors,⁵ nanoelectronic devices,⁶ and flat panel field emission displays.⁷ For most of these applications, it is highly desirable to prepare aligned nanotubes. Although the aligned carbon nanotubes have been prepared either by postsynthesis manipulation or by synthesis-induced alignment,^{8–11} it still remains a great challenge for scientists to get the carbon nanotubes organized in a controlled way. Immobilizing the randomly shortened tangled single-walled carbon nanotubes (SWNTs) into a controlled orientation would be an extremely important step for the real device application of the nanotubes.

In our previous work,¹² we developed a wet chemical approach for organizing randomly tangled SWNTs into well-ordered arrays on gold surface using a self-assembly technique. This wet chemical method allowed us to immobilize the thiol-derivatized SWNTs on gold surface and to generate a highly

organized self-assembled monolayer (SAM) with the nanotubes oriented perpendicular to the gold surface. This achievement is an important step in the direction toward the construction of nanodevice using carbon nanotubes.

In this paper, we report an alternative method for immobilizing the randomly tangled SWNTs on silver surface, forming an organizing nanotube assembly. The as-prepared long and randomly tangled SWNTs were cut into short pipes by chemical oxidation, which produced $-\text{COOH}$ groups at the open end of the tubes.¹³ On the basis of the fact that spontaneous adsorption (self-assembly) of long chain *n*-alkanoic acids can occur via the carboxyl groups on various metal native-oxide surfaces,^{14,15,16} we expect that such oxidatively shortened SWNTs would be immobilized on the silver surface. Raman spectroscopy, tapping mode atomic force microscopy (TM-AFM), and transmission electron microscopy (TEM) have been used to characterize the formation and structure of such shortened SWNTs assemblies on silver surface.

Scheme 1 illustrates the basic method for immobilizing the SWNTs on silver surface using the self-assembly technique.

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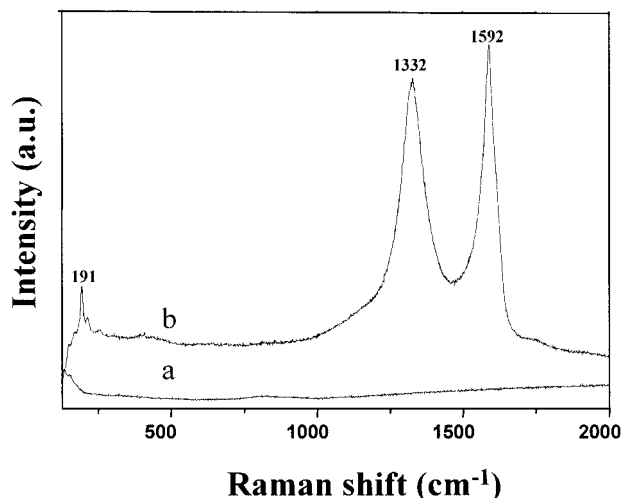


Figure 1. Raman spectra of bare silver surface (a) and SWNTs assembled on silver surface (b).

Following the conventional method, SWNTs were synthesized by chemical vapor deposition (CVD) using Fe–Mo catalyst on MgO support.¹⁷ The chemical shortening of these long SWNTs was performed by oxidation in a mixture of concentrated sulfuric and nitric acids (3:1, 98% and 70%, respectively) under ultrasonication for 8 h at 0 °C, which resulted in the shortened SWNTs having terminal carboxyl functionalities.¹³ Such shortened SWNTs can be dispersed in water, ethanol, and other polar solvents using ultrasonication. This procedure actually forms stable colloidal SWNTs suspensions without the aid of surfactants. These colloidal SWNT suspensions contain various lengths of SWNTs ranging from several tens of nanometers to several hundreds of nanometers, as confirmed by AFM investigations (data not shown).¹⁸

Carboxylic acids can be deprotonated by various metal oxides such as silver, aluminum, or copper, forming monolayers in which the carboxylate anion headgroups are bound by Coulombic forces to the metal oxide substrates. Using this method, we attempted to immobilize the oxidatively shortened SWNTs on silver surface in a controlled fashion. Silver films on silicon wafer substrates were prepared by thermal evaporation of silver in a vacuum chamber (pressure, $\sim 3 \times 10^{-7}$ Pa). The self-assembly of SWNTs on silver surface was performed by dipping silver coated silicon wafers into the colloidal SWNTs suspension for a certain time, followed by thorough rinsing with ultrapure water and drying in a stream of nitrogen prior to use.

Raman spectroscopy has been shown to be a powerful tool in characterizing SWNTs because of a unique Raman band around 200 cm^{-1} which arises from the radial breathing mode (RBM). This is directly related to the diameter of the tube by the relation, $d = 223.75/\omega$, where d is the tube diameter in nanometer and ω is the RBM in wavenumber. Typical Raman spectra¹⁹ are shown in Figure 1a,b of silver surface before and after coating with the SWNTs. No obvious Raman bands are observed with bare silver surface. After coating with SWNTs, however, the characteristic bands of SWNTs centered around 191 cm^{-1} and 1592 cm^{-1} which can be assigned to the RBM peak and G band of the SWNTs were seen in the Raman spectrum. This shows that the SWNTs have been deposited on the silver substrate in the self-assembly process.

We noted that there was also an intense band located around 1332 cm^{-1} in Figure 1b. The Raman band in this region is usually assigned to ill-organized graphite, the so-called D-line, which has been used for estimation of sample purity.²⁰ One possible explanation for this observed band is that it originates

from the nanotubes themselves due to an increased contribution of sp^3 carbons in the oxidatively shortened nanotubes.²¹ At the present, however, it is also difficult to rule out the possibility of some amorphous carbon impurity, possibly arising from the oxidative cutting process attached to silver surface as well as to the nanotubes. In addition, reflection absorption infrared spectroscopy (RA-IR) was performed to follow the salt formation of Ag and $-\text{COOH}$ groups during self-assembly on the silver (data not shown). The absence of a $\nu(\text{C}=\text{O})$ peak and appearance of a new peak of $\nu_{\text{as}}(\text{COO}^-)$ in RA-IR^{22,23} showed that the oxidatively shortened SWNTs were being adsorbed on silver surface through $-\text{COOH}$ groups by releasing its proton, forming a chemical bond between SWNTs and the silver/silver oxide.²⁴

From the above results, we can draw a preliminary conclusion that the oxidatively shortened SWNTs have been immobilized on silver surface via spontaneous chemical adsorption through terminal carboxyl groups. However, as yet, the orientation of such assemblies is unknown.

Tapping mode atomic force microscopy (TM-AFM, Nanoscope IIIa, Digital Instruments) was exploited to obtain structural information of such SWNTs assemblies on silver surface. A typical TM-AFM image of the shortened SWNTs assemblies immobilized on silver surface by the self-assembly technique is shown in Figure 2a. For comparison, a TM-AFM image of a bare silver surface is also provided in Figure 2b. The fine structure of the assemblies in Figure 2a can also be observed from the cross sectional analysis, as shown in Figure 2c. This sawtooth structure suggests the perpendicular orientation¹² of SWNTs because otherwise we would observe a flat cross section for the stacked nanotubes along the long-axis direction. In addition, the nanotubes may tilt some degree from normal to the surface, depending on how many carboxylic groups are present at the tube end (typically not one). The cutting angle²⁵ during oxidative shortening process may also affect its tilt angle on surface.

Unlike conventional “small” organic molecule self-assembly on solid surface (e.g., alkanethiols on gold), the assembly of shortened SWNTs on silver surface is a very complicated system. This is due to the fact that chemically shortened SWNTs have structures of different lengths, possibly different cutting angles²⁵ and degrees of oxidation (i.e., variations in the number of carboxylic groups at the tube end). From the histograms of the heights and the lateral dimensions of the SWNTs assemblies on AFM images ($4 \times 4 \mu\text{m}^2$), we found that the height of such SWNT assemblies falls into a range of 10–100 nm, mostly within 20–60 nm (84.5%) and the observed lateral dimensions fall into a range of 80–300 nm. Inevitably, this estimation is complicated by the convolution of AFM tip geometry.

In addition, we also observed some nanotubes which are lying down on substrate surface. Most of them are relatively longer tubes, having a length of more than 200 nm. It seems that shorter tubes (e.g., < 150 nm, see below) tend to stand on the surface but longer tubes lie down on the surface. A detailed investigation is underway.

To further investigate the orientation of SWNTs on silver surface, we employed transmission electron microscopy in this study. The samples for TEM observation were prepared by immersing a short silver wire 99.99% pure silver into the SWNTs suspension prepared by the same self-assembly process as that above. The images of the SWNTs assemblies were obtained from the edge of the silver wire surface. Three typical TEM images about the orientation of SWNTs on silver surface are shown respectively in Figure 3a–c. The SWNTs were

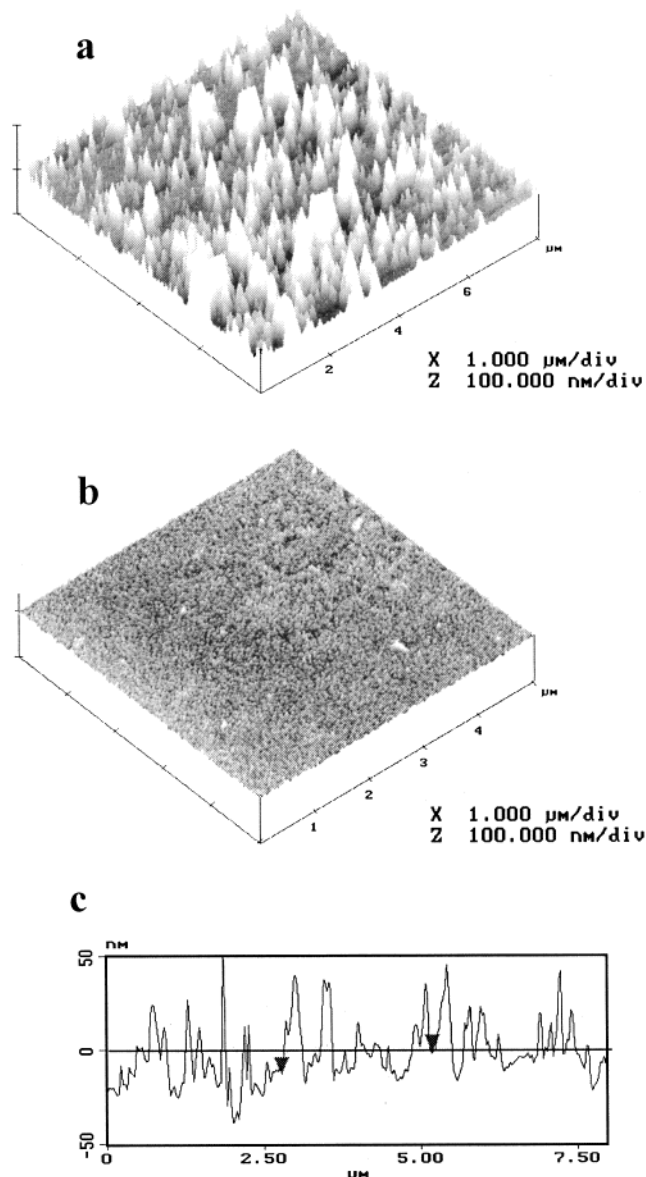


Figure 2. Tapping mode AFM images of the assembly of single-walled carbon nanotubes on silver (a) and bare silver surface (b). Typical cross section of the nanotube AFM image, showing the sawtooth structure of nanotube bundles (c).

clearly standing more or less perpendicular to the silver surface, but with different lengths and tilt angles.

The shortened SWNTs on silver surface have typical lengths of 60–150 nm in TEM images (Figure 3), which is longer than that obtained from AFM image. The diameters of the tubes fall

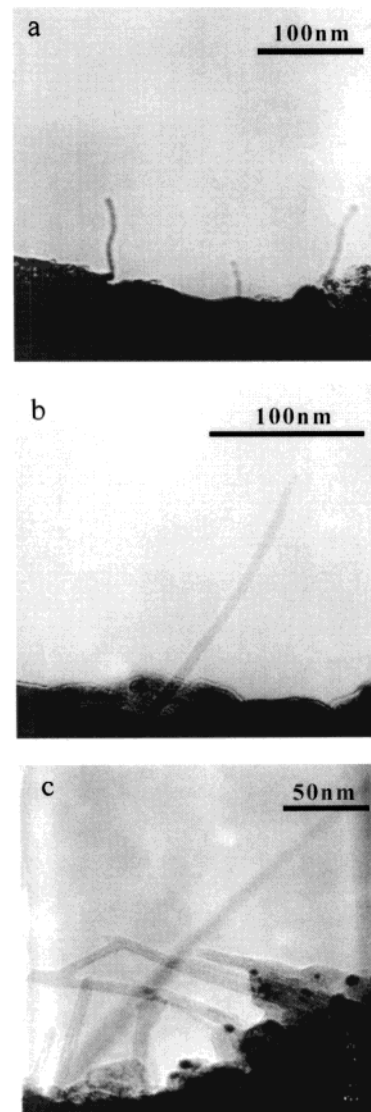
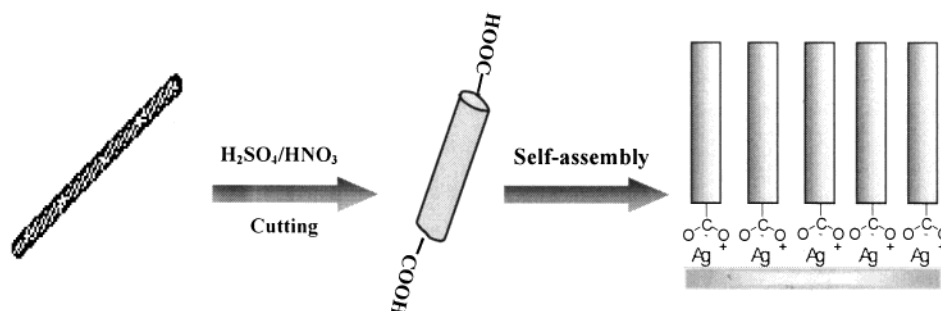


Figure 3. TEM images of the shortened SWNTs standing on silver surface with different tilt angles.

into a range of 2–15 nm from TEM images, showing that most of the shortened SWNTs existed in bundles. We noticed most (80%) SWNTs on silver surface had a similar bundle size (6.5 ± 0.5 nm). Only 15% showed a smaller bundle size (~ 2.5 nm) (or individual SWNTs). And also, less than 5% of SWNTs with the bundle sizes more than 7 nm were found in our experiment, which might be produced by the graphite fragments adhering to the SWNTs. In addition, we also found some nanotubes with



SCHEME 1: Schematic Illustration of the Self-Assembly Process for Fabricating Aligned Single-Walled Carbon Nanotubes on Silver

longer lengths (more than 200 nm) (Figure 3b), and some of them cross together (Figure 3c).

From the above, the typical size of one bundle was found to be about 6.5 ± 0.5 nm, 10–50 times smaller than the measured width of the observed SWNTs bundles from AFM images. We believe that the AFM tip-broadening effect, the lateral elastic deformation²⁶ of the SWNTs during the AFM imaging process, may distort the image, leading to the increasing of apparent larger bundle size. This lateral elastic deformation may also explain why tubes found in TEM appear longer than that obtained from AFM imaging. Moreover, the crossed tubes on silver surface (Figure 3c) will give out a bump-like topography several times wider than that of the bundle size of SWNTs.

SWNTs are rarely seen as individual entities but tend to form bundles in the solid state or in “colloidal suspension” due to the strong hydrophobic interactions between the sidewalls of nanotubes. Previous investigations on the bundles of SWNTs by TEM, AFM, and STM showed that generally bundle sizes range from less than 10 nm to more than 100 nm, with typical sizes between 10 and 20 nm.²⁷ Generally, the oxidation process reduces the cross-sectional diameter of the bundles.^{13,25} It is very interesting, however, that in our experiment most of the SWNTs (80%) perpendicular to the silver surface have a similar bundle size (6.5 ± 0.5 nm). This was very different from the height dimension when SWNTs are lying flatly on mica, which ranged from 1 nm to several tens of nanometers.¹⁸ These results suggest that the silver surface can selectively immobilize the shortened SWNTs into specific bundle sizes possibly related to the silver lattice structure. This substrate selectivity for bundle size offers insight into the formation mechanism of SWNTs on silver. The first possibility is a “nucleation growth” model proposed in our previous work.¹² A single nanotube or a single small bundle with active ends will adhere to the surface and form a “nucleation” center for the further incoming nanotubes, which will attach initially by hydrophobic interaction. New centers would form when old centers reach a certain size. The second possibility is that the shortened SWNTs may directly adsorb on to silver with the original bundle in solution but with a selectivity of bundles size. While at this current stage it is hard to say which mechanism works, further work is underway in order to explore the assembly mechanism.

In summary, we have shown that SWNTs undergo spontaneous adsorption (self-assembly) on silver surface via oxidatively produced carboxylic end groups. The self-assembled oxidatively shortened SWNTs occur more or less perpendicular to the silver surface at a specific bundle sizes (6.5 ± 0.5 nm).

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- (18) Before AFM measurement, 1 mg of shortened SWNTs were dispersed in 1 mL of DMF solvent by ultrasonication for 30 min to form a black transparent suspension. A drop of 1 μ L suspension was added on mica. After the solvent had evaporated, TM-AFM was performed on nanoscope IIIa (Digital Instrument).
- (19) Renishaw System 1000 Raman imaging System (Renishaw plc, UK), equipped with a 632.8 nm, 25mW He–Ne laser (Spectra Physics, USA) and a BH-2 microscope (Olympus, Japan). The incident light was introduced to the sample through a $50^\circ \times$ objective as a spot less than 2 μ m in diameter, with the power no more than 5 mW. The backscattered light from the sample was collected through the same objective. The spectrum was the sum of at least 10 spectra at different spots.
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