

# Selective Coating of Single Wall Carbon Nanotubes with Thin SiO<sub>2</sub> Layer

Qiang Fu, Chenguang Lu, and Jie Liu\*

Gross Chemistry Laboratory, Duke University, Box 90354,  
Durham, North Carolina 27708

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## ABSTRACT

Single walled carbon nanotubes (SWNTs) have been shown to be highly sensitive gas sensors. However, attaching functional groups with selective sensing functions on nanotubes without destroying the intrinsic electronic property of the nanotubes is still challenging. Here, we report a new method of coating SWNTs with a thin layer of SiO<sub>2</sub> using 3-aminopropyltriethoxysilane as coupling layers. The thickness of the SiO<sub>2</sub> could be controlled at about 1 nm. The coating of SiO<sub>2</sub> on SWNTs was confirmed by burning the SWNTs in air. The effect of 3-aminopropyltriethoxysilane was also discussed.

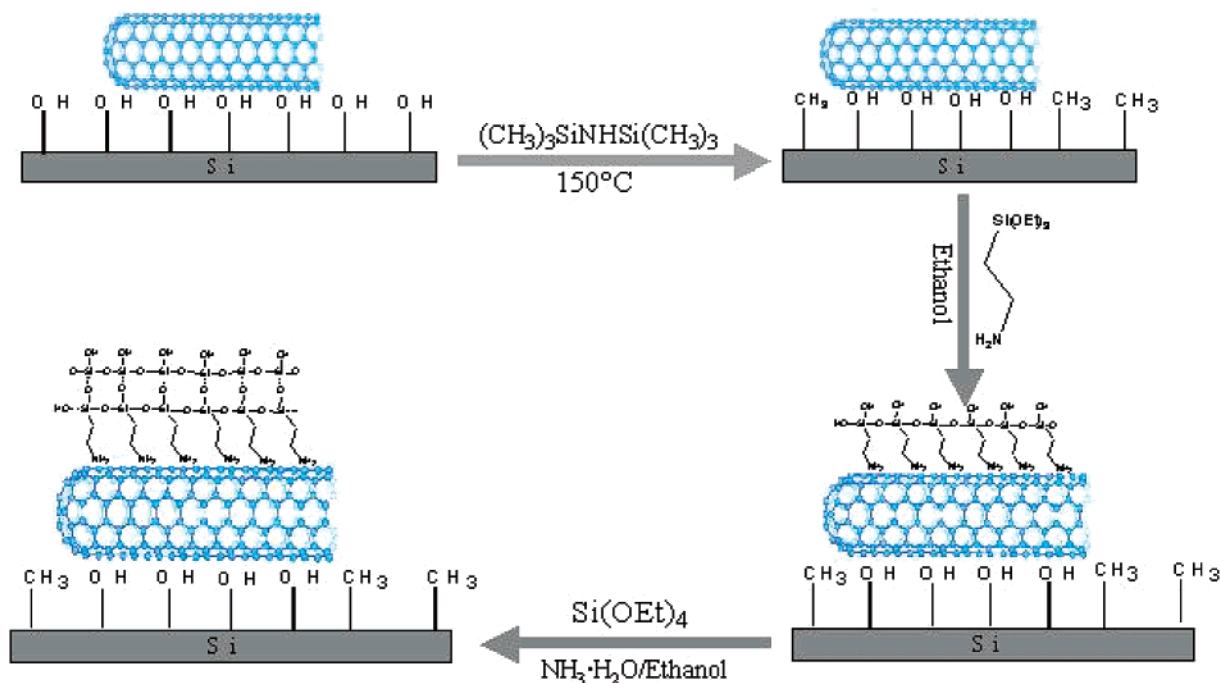
Carbon nanotubes have been the most actively studied materials in the past few years due to their unique electronic and mechanical properties.<sup>1,2</sup> Carbon nanotubes can be either metallic or semiconductive, depending on their helicity and diameter. More importantly, it was observed that the electronic properties of nanotubes, especially semiconducting carbon nanotubes, are very sensitive to the surrounding environments. The presence of oxygen, NH<sub>3</sub> and many other molecules that can either donate or remove electrons from the nanotubes can significantly alter the overall conductivity of the nanotubes.<sup>3–5</sup> Such properties make carbon nanotubes ideal candidates for nanoscale sensing materials. Actually, it was reported that nanotubes FETs can function as gas sensors.<sup>3,4</sup> However, to introduce selectivity to nanotube-based sensors, certain functional groups that can selectively bind to specific target molecules needs to be anchored on the nanotube surface. Unfortunately, the sidewall of carbon nanotubes is chemically stable, making the functionalization of the nanotubes with sensing molecules a challenge. Moreover, covalent modification of the nanotube sidewalls could totally change the electronic properties of the nanotubes, making them insulators rather than semiconductors. So, a reliable, noncovalent modification of the sidewall of carbon nanotubes is required for the development of carbon nanotube based nanosensors. Functionalization of carbon nanotubes with different functional groups have been reported by several groups in the past: 1-pyrenebutanoic acid, succinimidyl ester has been used as anchored molecular for immobilizations of bimolecular;<sup>5,6</sup> and anti-Fullerence IgG monoclonal antibody has been bound to SWNTs.<sup>7</sup> Certain proteins and DNA have also been demonstrated to modify multiwall carbon nanotubes (MWNTs).<sup>8–11</sup> In addition, wrap-

ping and coating by polymers and surfactants were reported.<sup>13–15</sup> More recently, coating with thick layer of SiO<sub>2</sub> on MWNTs for composite applications have been reported.<sup>12</sup> However, so far, there is no flexible method that could functionalize SWNTs with a broad variety of functionalities. Here, we report a new method to selectively functionalize SWNTs sidewalls with a thin layer of SiO<sub>2</sub>, which could offer flexible ways for further modification by utilizing the rich chemistry available for silica surface. Our approach involves the use of a promoter, 3-aminopropyltriethoxysilane (APTES), which could be absorbed on the sidewalls of SWNT by the interaction between amine groups and SWNTs sidewalls, and could be polymerized by simply heating to make the coating irreversible. Then a thin SiO<sub>2</sub> layer is subsequently grown on the polymerized APTES layer through a modified Stöber method.<sup>16</sup> The thickness of the layer can be controlled by the adjusting the growth conditions of SiO<sub>2</sub>. Using this process, SWNTs sidewall could be converted into a silica surface, which could be further functionalized with a large variety of functional groups by utilizing the chemistry of SiO<sub>2</sub> surface. Because the coating of SiO<sub>2</sub> is not covalent, the electronic structure of SWNTs will not be altered significantly (Scheme 1). In addition, because that SiO<sub>2</sub> layer is very thin, it is reasonable to assume that the chemical process caused by the binding of target molecules will still have a strong effect on the nanotubes underneath.

In our experiments, SWNTs were directly grown on silica surface by chemical vapor decomposition using catalytic Fe/Mo nanoparticles as described previously.<sup>17</sup> Silicon wafer (MEMC Electronic Materials) was cleaned by isopropyl alcohol and annealed in air at 1200 °C for more than 12 hours prior to use. A drop of diluted hexane solutions of

\* To whom should be corresponded. E-mail: jliu@chem.duke.edu.

**Scheme 1.** SiO<sub>2</sub> Growing on SWNTs Sidewalls using 3-Aminopropyltriethoxysilane as Primer Layer



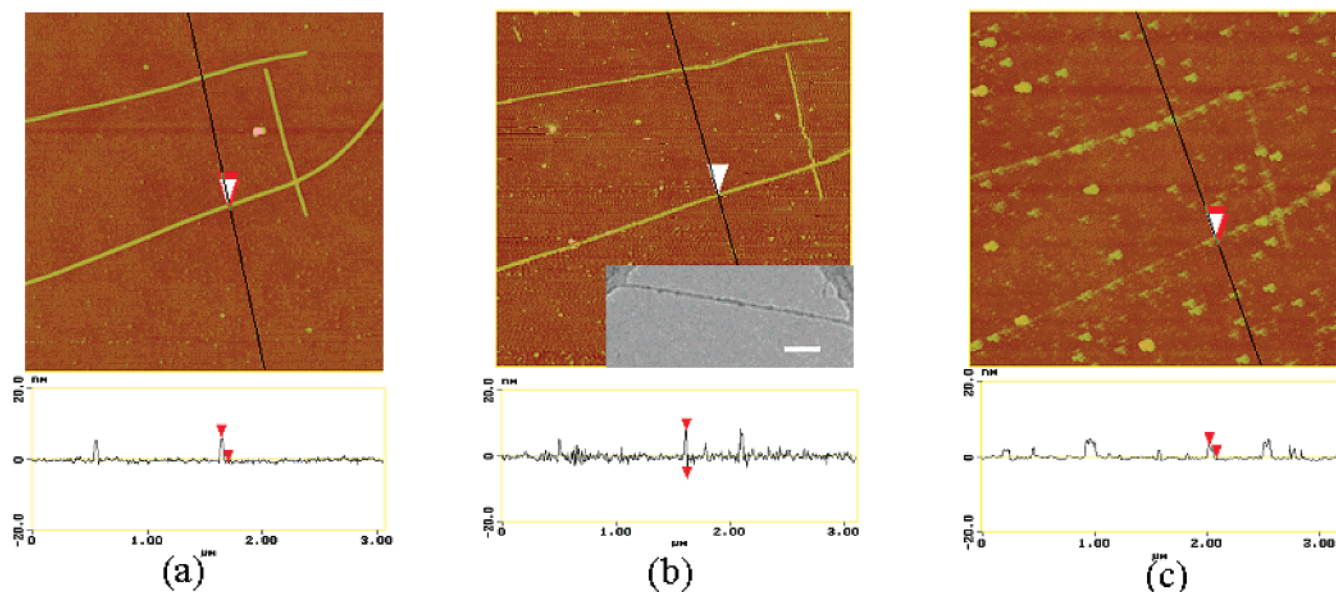
Fe/Mo nanoparticles with diameters  $\sim 4$  nm was then directly dropped on the Si wafers. After the solvent was evaporated, the dried wafer was put into an alumina boat and then put in a quartz tube; a small amount of Fe/Mo catalysts supported on alumina aerogel<sup>18</sup> was placed in the front parts of boat as promoter for growth of SWNTs. The quartz tube was then put in a furnace and first heated to  $700^\circ\text{C}$  and maintained for 5 min in air to remove organic coating on the nanoparticles. Then the argon flow (500 sccm flowrate) switched on and temperature was raised to  $900^\circ\text{C}$ . After 5 min, argon flow was switched to methane (1000 sccm flowrate) and maintained for 30 min. The methane flow was then turned off and the furnace was cooled to room temperature under the protection of argon. AFM image shows that SWNT grown on surface with length ranging from 500 nm to 10  $\mu\text{m}$  and height range from 1 nm to 5 nm. The use of nanotubes directly grown on surfaces have many advantages than using bulk nanotubes. First, it avoided all the purification process, which may create defects on the nanotubes;<sup>19,20</sup> Second, the majority of nanotubes directly grown on surfaces are individual nanotubes while bulk samples of nanotubes are bundles of nanotubes. For electronic application, individual nanotubes are desired. Previously, separation of nanotube bundles is achieved by long time ultrasonication, which is also a process that creates defects within the nanotubes.<sup>21</sup>

As shown in Scheme 1, to selectively coat nanotubes with a thin layer of SiO<sub>2</sub>, we first coated the substrate surface that is not covered by nanotubes with a methyl terminated self-assembled monolayer (SAM) by sealing the sample with a drop of 1,1,1,3,3,3-Hexamethyldisilazane (98%, Acros) in a steel chamber ( $\sim 200$  mL in volume) and heated at  $150^\circ\text{C}$  overnight. After thorough rinsing with ethanol and blown dry with fluorocarbon gas, The wafer was put in 5mM

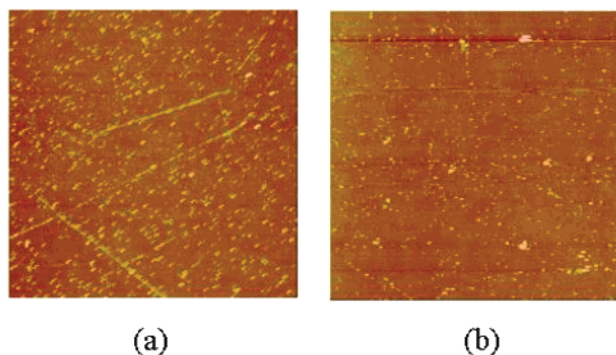
3-aminopropyltriethoxysilane (APTES, 99%, Aldrich) ethanol solution under stirring for 30 min, and then rinsed with ethanol and blown with fluorocarbon gas. The dried wafer was then put in oven at  $120^\circ\text{C}$  for 30 min to cross-link the absorbed APTES. In a typical experiment, after cooling to room temperature, the wafer was put into solution with 10 mL ethanol, 50  $\mu\text{l}$  Tetraethyl Orthosilicate (TEOS, 98%, Aldrich) and 100  $\mu\text{l}$  concentrated ammonia solution under stirring for 90 min to form desired SiO<sub>2</sub> coating on nanotubes. The thickness of the coating can be adjusted by changing the reaction time and the concentration of TEOS.

AFM image (Figure 1) shows that the changes on SWNTs before and after silica coating. Before the coating process, the average height of SWNTs was about 4 nm. After coating with SiO<sub>2</sub>, the height increased to about 5 nm, which means there could be a SiO<sub>2</sub> layer about 1 nm thick on SWNTs. To confirm the existence of SiO<sub>2</sub> on SWNTs, the wafer was brought to a furnace and heated at  $900^\circ\text{C}$  in air for 1 h. Under such conditions, SWNTs on surface should be burned out and SiO<sub>2</sub> on them should remain on the surface at the same positions. AFM image of the same area reveals linear features formed at the positions of SWNTs after the wafer was burned. Alternatively, TEM images of SiO<sub>2</sub> coated nanotubes treated using the same procedure (insert in Figure 1b) also showed the coating of nanotubes with a thin layer of amorphous materials. Those images clearly show that silica was selectively deposited on SWNTs in our samples.

We have also found that the use of APTES as promoter is an important factor for the selective coating of SiO<sub>2</sub>. In a control experiment to grow SiO<sub>2</sub> on SWNTs without APTES as coupling layer, the wafer coated with methyl groups was directly put into solutions of TEOS for 90 min under the same conditions. AFM image shows that there were no obvious changes in height. After burning nanotubes away



**Figure 1.** (a) AFM image of SWNTs on Silicon surface. (b) AFM image of SWNTs coated with SiO<sub>2</sub> (Inset: A TEM image of SWNTs coated with SiO<sub>2</sub>, scale bar 20 nm) (c) AFM image of SWNTs coated with SiO<sub>2</sub> burned at 900 °C for an hour. Linear features are the SiO<sub>2</sub> left after SWNTs was burned out. All images are  $3 \times 3 \mu\text{m}$ .



**Figure 2.** (a) AFM image of SWNTs with APTES as coupling layers incubated in TEOS solutions for 90 min and then burned at 900 °C for 1 h. (b) An AFM image of SWNTs without APTES as coupling layers incubated in TEOS solutions for 90 min and then burned at 900 °C for 1 h. Both images are  $7.5 \times 7.5 \mu\text{m}$ .

in air under the same conditions, we did not observe linear SiO<sub>2</sub> structures as before. Figure 2 shows the contrast of samples with APTES and without APTES as coupling layer. For samples with APTES as coupling layer, after burned, linear residuals of SiO<sub>2</sub> could be clearly seen on the position of SWNTs. However, for samples without APTES as coupling layers, the surface was very clean after burning and there were no similar feature as samples with APTES on surface. Those results show that APTES play an important role in the coating process. It is well-known that APTES interact with the sidewall of nanotubes strongly.<sup>13,22</sup> We believe that the APTES molecules in our system were absorbed on SWNTs sidewalls first. After polymerization, the surface would become more hydrophilic than pristine SWNTs because of the  $-\text{OH}$  and  $-\text{NH}_2$  functional groups available in the polymer, which favor the growth of SiO<sub>2</sub> by the hydrolysis of TEOS.

In summary, we have developed a flexible method to form a thin layer of SiO<sub>2</sub> on SWNTs, which could be used for

further immobilizations of biomolecules or other functional materials. We have clearly showed the selective deposition of SiO<sub>2</sub> on the nanotubes and the importance of using APTES as promoter. More works are under way to explore the further functionalization of the SiO<sub>2</sub> coating. In addition, the versatility of this method could be extended to other oxides and might be used to build other functional nanocomposites. Combined with the CVD methods that grow individual nanotubes on surfaces, this method might be used to build new types of electronic units and sensors in nanoscale.

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