

## Plasma Etching for Purification and Controlled Opening of Aligned Carbon Nanotubes

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Plasma etching was applied for removal of the amorphous carbon layer that covers *aligned* carbon nanotube films produced by pyrolysis of metal-containing organometallic precursors. Microscopic and kinetic studies showed that amorphous carbon could be easily removed by H<sub>2</sub>O-plasma etching while carbon nanotubes remain largely unchanged under relatively mild plasma conditions. Prolonged plasma treatment, however, was found to cause a controllable disintegration of the graphitic structure, leading to a region-selective opening of the aligned carbon nanotubes (e.g., the removal of one end-cap only). Metal-filling was demonstrated to be also possible even with the resultant *one-end* opened nanotubes.

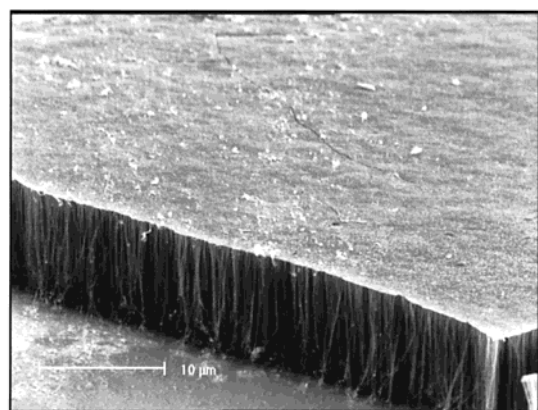
We have previously developed a technique for large-scale synthesis of carbon nanotubes aligned in the direction normal to the substrate surface (typically, quartz glass plates) by pyrolysis of iron(II) phthalocyanine (FePc) at 800–1100 °C under Ar/H<sub>2</sub>.<sup>1</sup> The aligned carbon nanotubes thus prepared are ideal for the use as, for example, electron field emitters in panel displays.<sup>2</sup> As is the case in many other systems, however, the concomitant formation of amorphous carbon cannot be fully avoided. In particular, we occasionally observed that our aligned nanotube films were covered by a thin layer (ca. 0.1–0.5 μm) of amorphous carbon film, which has been an impediment for the above-mentioned, and many other applications. It is necessary, therefore, to devise a selective and effective technique to remove the amorphous carbon layer. Several methods, including the gas oxidation in air or oxygen,<sup>3</sup> dispersion filtration,<sup>4,5</sup> and chemical oxidation in solution,<sup>6</sup> have been developed for the purification of carbon nanotubes prepared either by arc discharge or chemical vapor decomposition. Many of them involve a tedious procedure with a very low yield of pure nanotubes.<sup>7</sup> Simple adoption of these methods to the present study could also damage or even destroy the highly desirable *vertical alignment*. The unique layered structure of the amorphous carbon film formed on the top of the aligned nanotubes makes the radio frequency glow-discharge plasma etching the method of choice for purification.

We have previously reported that H<sub>2</sub>O-plasma can be used to effectively etch many substrates including mica sheets.<sup>8</sup> In the present study, we found that the amorphous carbon layer on the aligned carbon nanotube arrays can be easily removed by the H<sub>2</sub>O-plasma etching. As we shall see later, the plasma etching causes no observable structural damage to the nanotubes in most cases. When particularly severe conditions are used for the plasma etching, however, the aligned carbon nanotube tips exposed to the plasma vapor can be selectively removed. This is because the amorphous carbon layer is more susceptible to the plasma etching than the carbon nanotubes, while the tips of nanotubes are known to be more reactive, and hence be more easily etched off, than the cylindrical nanotube walls.<sup>9</sup>

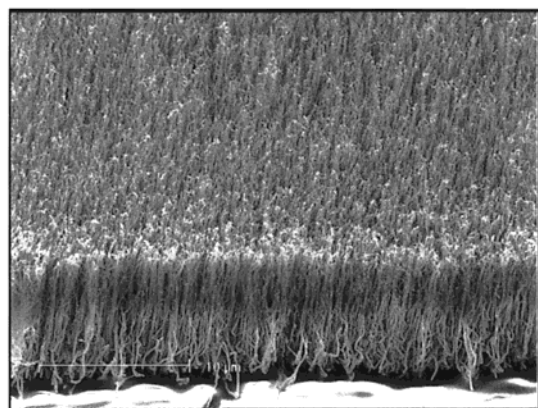
The synthesis of aligned carbon nanotube films on quartz glass plates by pyrolysis of FePc has been described in detail elsewhere.<sup>1</sup> The plasma treatment was performed using a custom built reactor,<sup>8</sup> powered by a commercial radio frequency generator operating at 250 kHz, 30 W, and  $P_{\text{H}_2\text{O}} = 0.62$  Torr. For the metal encapsulation work, the tip-opened nanotube film was gently washed with HCl (37%) to remove the Fe catalyst residues, if any, followed by drying in a vacuum oven at 150 °C, and then soaking in a AgNO<sub>3</sub>/CH<sub>3</sub>COCH<sub>3</sub> (1:1 v/v) aqueous solution (0.2 M) for 24 h under magnetic stirring. Finally, the reaction mixture was centrifuged and the resultant nanotubes filled with the metal salt were thoroughly washed with deionized water, followed by drying under vacuum (10<sup>−4</sup> Torr) at room temperature. The impregnated AgNO<sub>3</sub> was then decomposed to Ag by heating the metal-salt-filled nanotubes at 300 °C in air for 2 h.<sup>10</sup> All of the samples were checked on a field emission scanning electron microscopy (SEM, Philips XL-30 FEG). Transmission electron microscopic (TEM) images were taken on a JEOL 200 after the sample was dispersed in acetone by sonication and transferred onto a carbon-coated grid. The plasma-etching kinetics was characterized by weight loss of the amorphous carbon recorded at intervals during the plasma treatment.

Figure 1a shows a typical layered structure of the aligned carbon nanotubes covered by a thin layer (typically, 0.1–0.5 μm) of amorphous carbon. We have tried to remove the amorphous carbon layer with a minimized undesirable effect on the vertical alignment of the carbon nanotubes by using the air-oxidation method.<sup>3</sup> However, it was found to be ineffective in this case, most probably, because the amorphous carbon layer is so densely packed that oxygen molecules can hardly diffuse through. As an alternative, we used the more effective etching technique based on the H<sub>2</sub>O-plasma treatment under relatively high plasma-vapor pressures<sup>8</sup> to remove the densely packed amorphous carbon layer. The aligned carbon nanotube film was examined on SEM after the H<sub>2</sub>O-plasma etching. As can be seen in Figure 1b, the amorphous carbon layer was removed almost completely by water plasma etching for 30 min at 250 kHz, 30 W, and  $P_{\text{H}_2\text{O}} = 0.62$  Torr. Figure 2 shows the weight loss as a function of the etching time, which indicates that the loss of the amorphous carbon is characterized by fast kinetics with a quasi-linear relationship at the initial stage (<15 min).

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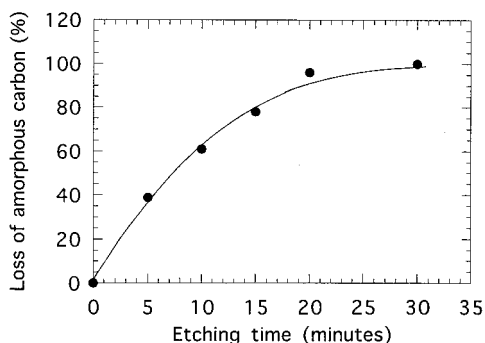


(a)



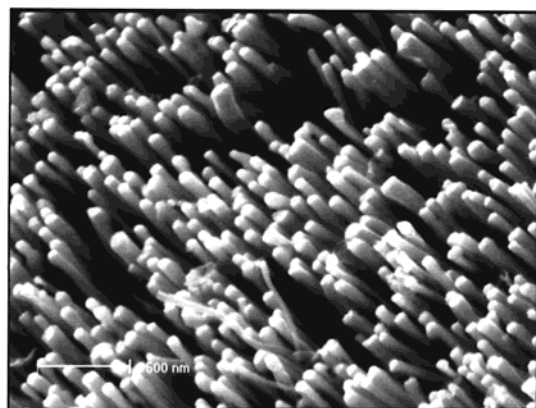
(b)

**Figure 1.** SEM images of an aligned nanotube film before and after H<sub>2</sub>O-plasma etching (a) a large area aligned nanotube film covered by a thin amorphous carbon layer on a quartz glass plate before plasma treatment, (b) the same nanotube film as (a) after the H<sub>2</sub>O-plasma etching for 30 min at 250 kHz, 30 W, and 0.62 Torr. Note that the micrographs shown in (a) and (b) were not taken from the same spot due to technical difficulties.

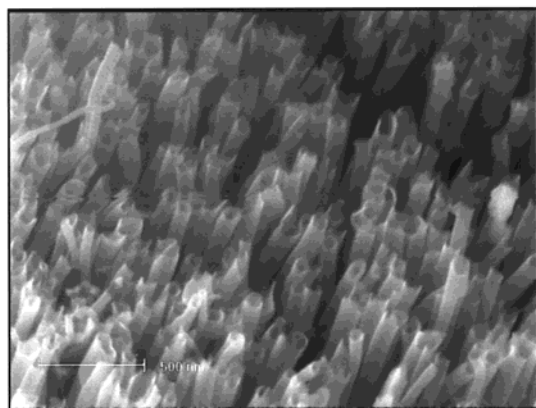


**Figure 2.** The percentage weight loss of amorphous carbon as a function of the H<sub>2</sub>O-plasma etching time. The H<sub>2</sub>O-plasma etching was performed at 250 kHz, 30 W, and 0.62 Torr.

Then, the curve levels off. In most cases, more than 95% amorphous carbon was removed after the plasma etching for 20 min, as confirmed by SEM examination. Under these conditions, there was no damage seen on the integrity of the carbon nanotubes. Prolonged etching, however, could partially remove graphitic sheets from the carbon nanotube structure. Since the nanotube tips are more reactive than tube walls,<sup>9</sup> the end-caps exposed to the plasma vapor were found to be opened after the plasma etching of the perpendicularly aligned nanotubes for about 80 min (Figure 3), whereas their bottom counterparts were effectively protected by interfacing with the substrate. This



(a)



(b)

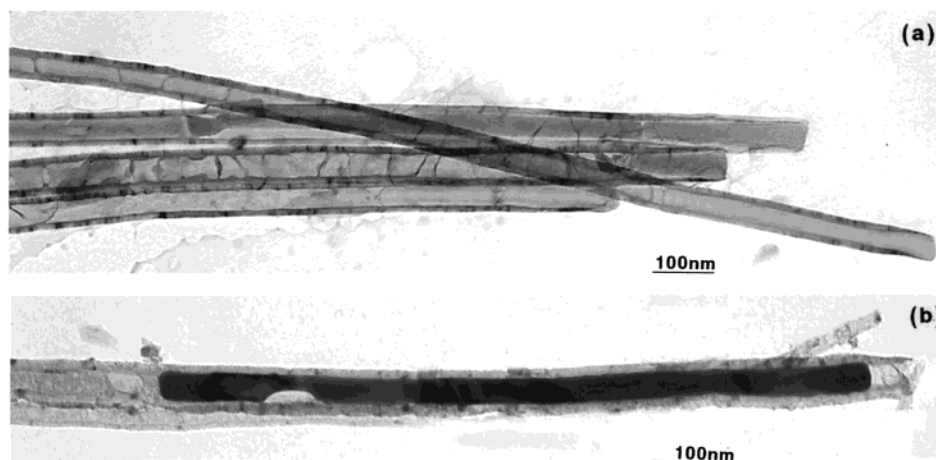
**Figure 3.** SEM images of the aligned nanotubes (a) before and (b) after the plasma-treatment for 80 min, followed by a gentle wash with HCl (37%) to remove the Fe catalyst residues, if any (see text). Note that the micrographs shown in (a) and (b) were not taken from the same spot due to technical difficulties.

observation implies that the plasma-etching technique can be used to produce *one-end* uncapped carbon nanotubes.

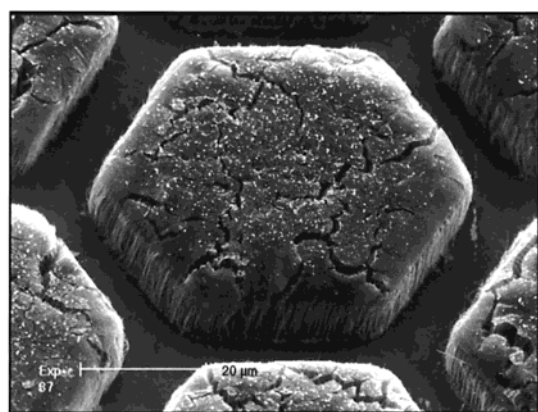
Unlike most of the *both-end* opened nanotubes produced by more conventional chemical oxidation methods,<sup>11</sup> the *one-end* uncapped carbon nanotubes prepared with the plasma etching technique provide truly miniaturized “test tubes” for the investigation of various physicochemical processes at the nanometer scale. For instance, our preliminary results indicated that the inclusion of foreign materials is also possible with the one-end uncapped carbon nanotubes. Figure 4 shows a typical TEM image of the one-end uncapped nanotubes filled with Ag nanorods prepared according to the procedures described above.

Furthermore, we have also demonstrated the use of plasma etching technique for removing the amorphous carbon layer on micropatterns of aligned carbon nanotubes prepared by our previously reported microfabrication methods<sup>1</sup> (Figure 5). Comparing Figure 5b with Figure 5a clearly shows that the amorphous carbon layer can be fully removed with no change in the integrity of the nanotube patterns.

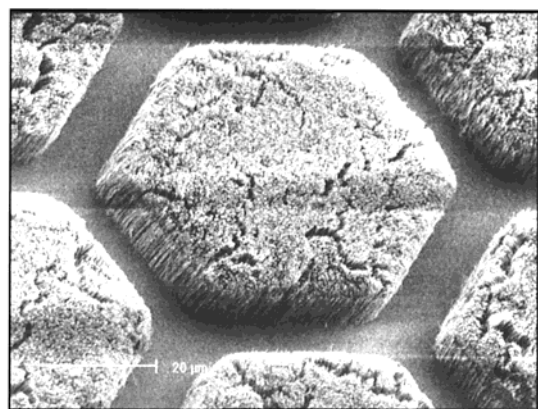
In summary, we have applied the plasma etching technique to the purification of aligned carbon nanotube films and micropatterns. Microscopic and kinetic studies show that the amorphous carbon layer can be removed by H<sub>2</sub>O-plasma etching in a controllable fashion without much undesirable effect on the nanotube structure or aligned/micropatterned arrangement. Under appropriate conditions, however, the plasma etching technique could be used to produce one-end uncapped carbon nanotubes, which can be used as nanoscale test tubes. These



**Figure 4.** TEM images of the opened carbon nanotubes (a) before and (b) after filling with the Ag nanorod. Note that the micrographs shown in (a) and (b) were not taken from the same nanotubes due to technical difficulties.



(a)



(b)

**Figure 5.** SEM images of the micropatterns of aligned carbon nanotubes before (a) and after (b) the  $\text{H}_2\text{O}$ -plasma etching for 30 min at 250 kHz, 30 W, and 0.62 Torr.

results, together with the patterned plasma etching methodology previously reported,<sup>8</sup> should not only have important implica-

tions for the use of plasma techniques in purification/modification of carbon nanotubes, but also facilitate the preparation of aligned carbon nanotube micropatterns with region-specific features for a wide range of applications including electron-emitting displays, laboratory-on-a-chip systems, and sensing arrays.

## References and Notes

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