

Synthesis and mechanical properties of carbon nanotubes produced by the water assisted CVD process

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Catalyst activity during the carbon nanotubes (CNTs) growth by chemical vapor deposition (CVD) is enhanced when water, a weak oxidizer, is introduced together with the carbon source. The height as well as the CNTs density can be controlled by fine-tuning the water content. The characterization of the

mechanical properties of CNTs produced by the water assisted CVD process clearly indicates that high quality materials are produced. CNTs with diameter smaller than 12 nm exhibit Young's modulus higher than 400 GPa.

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1 Introduction In 2004, Hata et al. [1] discovered that carbon nanotubes (CNTs) growth, by chemical vapor deposition (CVD), can be dramatically enhanced by introducing traces of water together with the carbon source. Water is believed to extend the catalyst lifetime by etching the amorphous carbon deposit on the surface of the catalyst. In the optimum growth conditions, more than 85% of the catalyst nanoparticles are active [2]. The growth kinetics is strongly extended as well such as millimeter height carpet, made of vertically aligned CNTs can be grown in few minutes [3]. Consequently, the water assisted method is named as “Super growth CVD process.”

By patterning the catalyst on silicon wafer, large scale structures with complex shape can be produced using classical e-beam lithography [1, 4]. The CNTs density within these structures can be as high as 10^{12} tubes/cm² being very suitable building blocks for electronics as interconnects that can drive high current density. Recently, nanoelectromechanical relays based on CNTs produced by the “Super growth CVD process” have been demonstrated [4]. The mechanical properties of the CNTs-based cantilever have been derived from the electromechanical characteristics of the relay. The Young's modulus of the cantilever was estimated to be in the range of only few hundreds of MPa [4]. Therefore, the device does not take the full advantage of the superior mechanical properties of the CNTs. One possible

cause for this flaw is the weakness of the van der Waals forces that bind the CNTs together within the cantilever structure. If inter-tube sliding is allowed, cantilever will behave as loose CNTs agglomerate rather than a homogeneous, stiff and strong structure. On the other hand, the low mechanical properties of the cantilever can be ascribed to a poor structural quality of CNTs. Nevertheless, the mechanical properties of individual CNTs produced by the “Super growth CVD process” have not yet been measured.

In this paper, we present the synthesis of millimeter height carpet of CNTs by a water assisted CVD process in conditions similar to the “Super growth CVD process.” In the second part, we will report on the measurement of the mechanical properties of individual CNTs. This study was performed by the “Swiss cheese method” developed in our group which is based on AFM measurement [5, 6].

2 Experimental

2.1 Water assisted CVD growth of CNT forest

Carbon nanotube forests were synthesized in a horizontally mounted quartz tube furnace by water assisted CVD process. Ethylene (50–400 sccm) as the carbon source was diluted with argon (100–300 sccm) previously mixed with hydrogen (40–150 sccm). Water was continuously introduced in the reaction chamber by fluxing Ar (5–50 sccm) through a water bubbler. The water content was calibrated by quadrupolar

mass spectrometry. Catalyst Al_2O_3 (10 nm) and Fe (1 nm) is deposited on a silicon substrate with 500 nm oxide layer. Furnace temperature was raised to 750 °C prior to the growth. One square centimeter pieces of substrate were used for the growth of CNTs carpets.

For the realization of large scale organized structures of CNTs, catalyst layers made of Al_2O_3 and Fe were patterned by optical photolithography and lift-off technique.

2.2 Elastic modulus measurement For direct measurements of the elastic properties of individual CNTs produced by the water assisted CVD process, raw CNTs were dispersed in ethanol or water, and a droplet was deposited on a polished alumina ultrafiltration membrane (Whatman Anodisc, with 200 nm pores). Nanotubes occasionally lie over pores with most of their length in contact with the membrane surface, producing a double clamped beam configuration at nanoscale. An atomic force microscope (AFM) operating in air was used to apply a load to the nanobeams and to determine directly the resulting deflection.

3 Results and discussion

3.1 Water assisted CVD growth of CNTs Figure 1a shows that nanotube carpet of an average height of 950 μm can be produced in 30 min. These results, being in perfect agreement with previous reports of the “Super growth CVD process” have been obtained in slightly different growth conditions than in Refs. [1–4]. In particular, gas phase composition within the reactor is enriched with ethylene and water while keeping other growth parameters similar to the ones found in previous reports [1–4]. We subsequently produced large scale structures with desired shapes on catalyst patterned surfaces. For instance, pillars and sheets of CNTs can be produced from, respectively, squares or lines of

catalyst particles (Fig. 1b). Unexpectedly, the height of such structures depends on the size and form of the catalyst patterns from which the CNTs growth stems. This effect could be related to the catalyst homogeneity. Larger patterns provide more homogeneous, and consequently more active, catalyst particles resulting a more efficient CNTs growth. Additional studies are in progress to better understand this effect.

TEM studies of the as grown CNTs reveal that the forest and the large scale structures are composed of narrow diameter CNTs. Single walled as well as multi-walled CNTs with small number of walls (two to five walls) can be found in the deposits. The average outer diameter is about 7–8 nm. CNTs are clean, free of amorphous carbon, and catalytic particles (Fig. 1c and d). This shows that high purity materials can be produced by the CVD growth process. Furthermore, the absence of amorphous carbon substantiates the cleansing role of water during the CNTs growth.

We further studied the role of water by varying the gas phase composition during the CVD process. Figure 2 demonstrates that a CNT forest with maximum height can be obtained when 800 ppm of water is introduced. This corresponds to a $\text{H}_2\text{O}/\text{C}_2\text{H}_4$ ratio of about 1/1000. This value fits very well with the general trend previously established by the group of Hata [3].

Any deviation from this value dramatically decreases the carpet height. This clearly shows that the ethylene/water ratio is a critical parameter to be fine tuned for taking a full advantage of the water assisted CVD process in producing high CNTs-based objects. In addition, SEM micrographs of carpets produced with different water content clearly point out that CNTs alignment depends as much as the forest height on the $\text{H}_2\text{O}/\text{C}_2\text{H}_4$ ratio. Raising the $\text{H}_2\text{O}/\text{C}_2\text{H}_4$ ratio from 0.62/1000 to 1.5/1000 increases the number of active

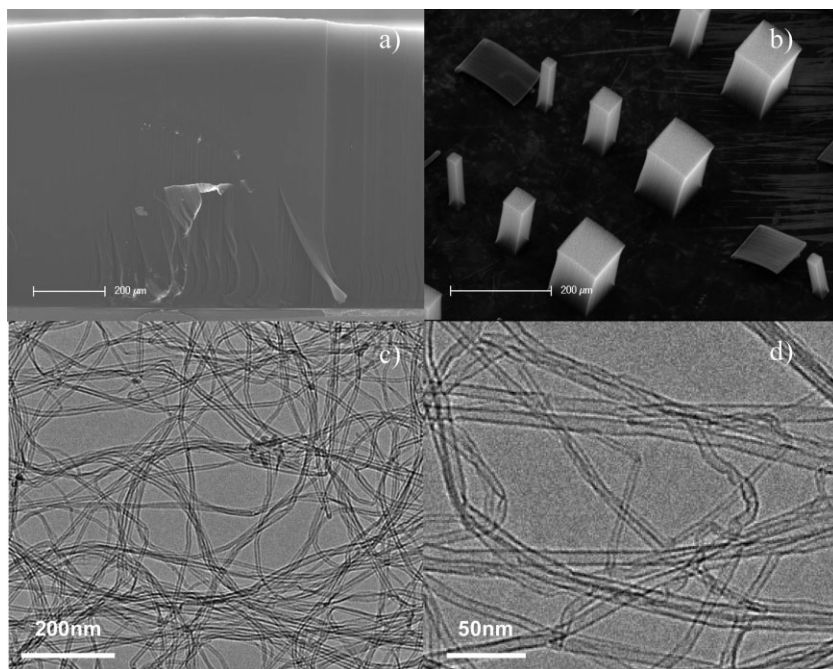


Figure 1 CNTs forest with a height of about 1 mm has been produced by the water assisted CVD growth process (a). Large scale structure with well-defined shape can be produced on catalyst patterned surfaces (b). TEM micrographs of CNTs produced at 750 °C (c and d).

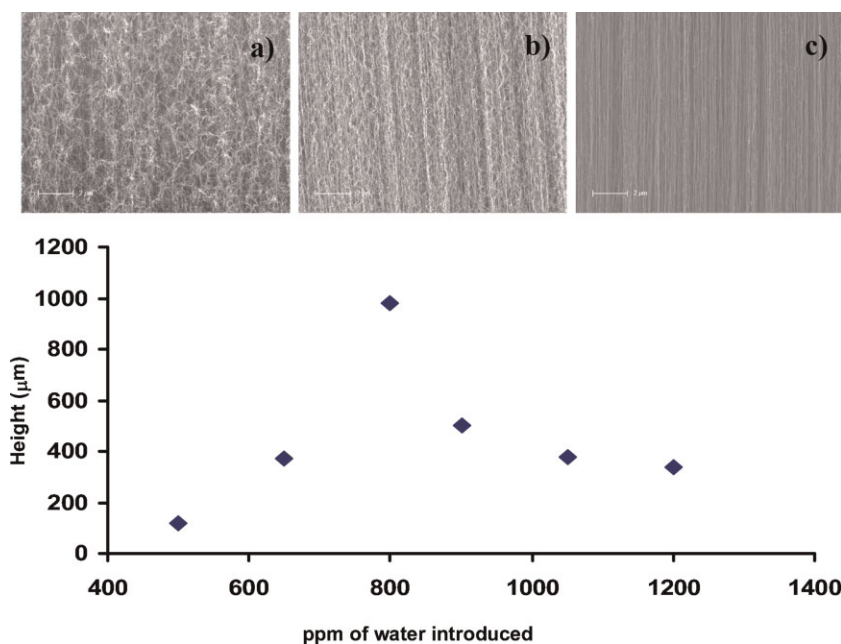


Figure 2 (online color at: www.pss-b.com) The height of CNT forest plotted as a function of water content introduced in the reactor. CNTs alignment within the forest is also influenced by the water content. SEM micrographs of carpet produced with 500 ppm (a), 800 ppm (b) and 1200 ppm (c).

catalytic particles and consequently the density of the carpet. It is known that CNTs alignment in forest, like in ropes or bundles is caused by the strong van der Waals interaction between tubes. When CNTs density is too low, they grow randomly and the carpet height does not reflect the actual CNTs length (Fig. 2a). When the water content is raised to 800 ppm, alignment is improved and the carpet keeps some porosity for ethylene to be continuously provided to the catalytic particles. The growth duration is extended and millimeter height carpet is obtained (Fig. 2b). When water content is raised further, all catalytic particles are activated and very dense mat with almost perfectly aligned CNTs are produced. However, ethylene penetration through the carpet is reduced and therefore ethylene molecules can hardly reach the catalyst. The CNTs growth stops at early stages. Carpet height is consequently reduced (Fig. 2c).

In conclusion, we have produced dense carpet of CNTs by the water assisted CVD process. We have shown that carpet height as well as CNTs density drastically depends on the gas phase composition and in particular on the water to ethylene ratio.

3.2 Mechanical properties of individual CNTs produced by the water assisted CVD process

Carbon nanotubes produced by the water assisted CVD process can be easily removed from the substrate and dispersed in a solvent. Once deposited on the alumina porous membrane, part of the CNTs can lie over a hole. The adhesion of a CNT on the flat parts of the substrate is usually much stronger than the normal force applicable by the AFM cantilever, so that we modeled the suspended nanotube as a doubly clamped beam (see Fig. 3). We also assumed that the beam has a uniform and circular cross-section. The midpoint of a doubly clamped beam deflects by δ when loaded with a force F , and the bending modulus E_b can be derived from

the F - δ graph using the equation:

$$E_b = \left(\frac{L^3}{192I} \right) \left(\frac{dF}{d\delta} \right) \quad (1)$$

where L is the suspended length and I is the second moment of area of the beam, which for a filled cylinder is $\pi D^4/64$. D is the outer diameter of the nanotube. We consider shear to be negligible for the suspended CNTs, as in the case of long thin beams, and take the bending modulus to be the Young's modulus.

To measure the stiffness of a suspended nanotube, we applied a force at its midpoint with an AFM cantilever, acquiring force-displacement data. The F - δ curves were then obtained by subtracting a reference force-displacement curve taken on a flat substrate. Young's moduli are obtained by fitting lines through these curves (see Fig. 4).

Carbon nanotubes are known to exhibit exceptional mechanical properties. Very high Young's moduli of about

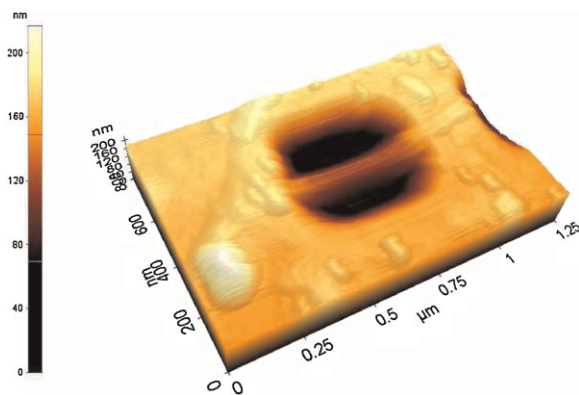


Figure 3 (online color at: www.pss-b.com) Typical AFM image of CNT partly suspended over a hole of the alumina membrane.

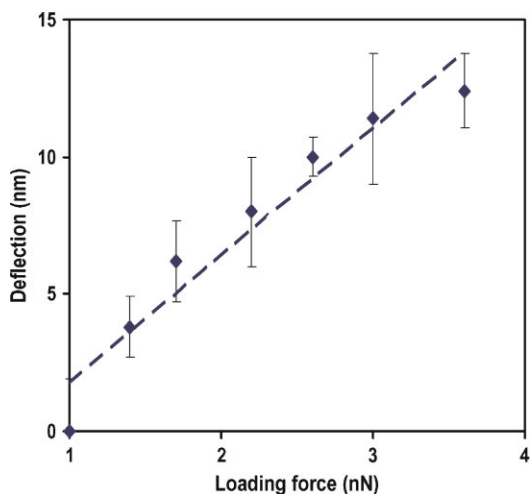


Figure 4 (online color at: www.pss-b.com) F - δ curve obtained for a CNT of a diameter of $10 (\pm 1)$ nm and of a suspended length of $580 (\pm 10)$ nm. The calculated Young's modulus of the CNT is $393 (\pm 247)$ GPa.

1 TPa have been obtained for CNTs produced by high temperature process like arc discharge or laser ablation [5, 6]. On the other hand, the graphitic structure of CNTs produced by CVD, usually below 1000°C , contains a large defect density. Therefore, CVD grown CNTs are regarded as materials with very poor mechanical properties. However, we have recently shown that the Young's modulus of CNTs with diameter below 20 nm exhibit clear diameter dependence (Fig. 5) [7, 8]. CNTs with smaller diameter have better structure quality and consequently mechanical properties similar to high temperature grown CNTs.

In this study, we have measured the bending modulus of CNTs with diameter spanning a 7–12 nm range and produced

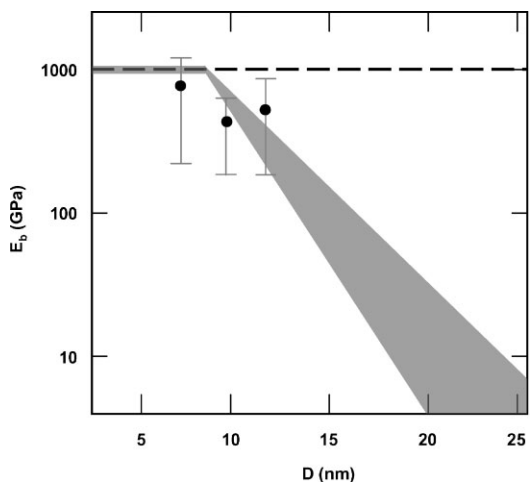


Figure 5 Bending modulus of CNTs produced by the water assisted growth process (\bullet). Data obtained for CNTs produced by the standard CVD processes are reported (gray area) for comparison [7]. They show a strong diameter dependence due to the low structural quality. Dash line stands for the bending moduli, close to the ideal value of 1 TPa, for CNTs produced by high temperature processes.

with various $\text{H}_2\text{O}/\text{C}_2\text{H}_4$ ratios. Young's modulus of CNTs with 7, 10, and 12 nm diameter are $631 (\pm 389)$, $393 (\pm 247)$, $477 (\pm 326)$ GPa, respectively. Despite no clear diameter dependence of the CNTs Young's modulus can be drawn from these measurements, these values are close to the ones obtained for the best CVD grown CNTs measured. Consequently, very high quality CNTs are produced by the water assisted CVD process. Hence, this is a clear indication that the presence of water, as a weak oxidizer preventing amorphous carbon deposition, does not produce extended damages in the graphitic structure of the CNTs, even when water concentration as high as 1200 ppm is used. This notion is supported by the results of oxidation experiments of CNTs using water vapor which concluded that CNTs oxidation is limited at temperature below 900°C [1].

4 Conclusion The introduction of water together with the carbon source enhances the efficiency of the catalyst during the CVD process such as millimeter height carpet of CNTs can be grown in few minutes. Moreover, the density of active catalytic particles increases by raising the water content. This yields an improvement of the CNTs alignment within the carpet. The CNTs structure is not damaged by the presence of water, being a weak oxidizer. CNTs with diameter smaller than 12 nm exhibit Young's modulus higher than 400 GPa. This is a clear indication that high quality materials are produced by the water assisted CVD process.

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References

- [1] K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, and S. Iijima, *Science* **306**, 1362–1365 (2004).
- [2] D. N. Futaba, K. Hata, T. Namai, T. Yamada, K. Mizuno, Y. Hayamizu, M. Yumura, and S. Iijima, *J. Phys. Chem. B* **110**, 8035–8038 (2006).
- [3] D. N. Futaba, K. Hata, T. Yamada, K. Mizuno, M. Yumura, and S. Iijima, *Phys. Rev. Lett.* **95**, 056104 (2005).
- [4] T. Yamada, T. Namai, K. Hata, D. N. Futaba, K. Mizuno, J. Fan, M. Yudasaka, M. Yumura, and S. Iijima, *Nature Nanotechnol.* **1**, 131–136 (2006).
- [5] J. P. Salvetat, G. A. D. Briggs, J. M. Bonard, R. R. Bacsa, A. J. Kulik, T. Stoeckli, N. A. Burnham, and L. Forró, *Phys. Rev. Lett.* **82**, 944–947 (1999).
- [6] J. P. Salvetat, A. J. Kulik, J. M. Bonard, G. A. D. Briggs, T. Stoeckli, K. Méténier, S. Bonnamy, F. Béguin, N. A. Burnham, and L. Forró, *Adv. Mater.* **11**, 161–165 (1999).
- [7] K. Lee, B. Lukic, A. Magrez, J. W. Seo, G. A. D. Briggs, A. J. Kulik, and L. Forró, *Nano Lett.* **7**, 1598 (2007).
- [8] J. W. Seo, A. Magrez, M. Milas, K. Lee, V. Lukovac, and L. Forró, *J. Phys. D, Appl. Phys.* **40**, R109 (2007).