 MCB, vol.1, no.2, pp.113-121, 2004

Encapsulation of Pt-labelled DNA Molecules inside Carbon Nanotubes

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Abstract: Experiments on encapsulating Pt–labelled DNA molecules inside multiwalled carbon nanotubes (MWCNT) were performed under temperature and pressure conditions of 400K and 3 Bar. The DNA-CNT hybrids were purified via agarose gel electrophoresis and analyzed via high resolution transmission electron microscopy (HR-TEM) and energy dispersive X-ray spectroscopy (EDX). The results showed that the Pt-labelled DNA molecules attached to the outside walls of CNTs could be removed by electrophoresis. The HR-TEM and EDX results demonstrated that 2-3% of the Pt-labelled DNA molecules were successfully encapsulated inside the MWCNTs. The experimental study complements our previous molecular dynamics simulations on encapsulation of single stranded DNA oligonucleotides inside single wall carbon nanotubes under similar conditions in water. The van der Waals interaction between CNT and Pt-labelled DNA is believed to be the main driving force for this phenomenon. The DNA-CNT molecular complex could be further explored for potential applications in bio-nanotechnology.

1 Introduction

Biomolecules are multifunctional nanomaterials which could be used in applications such as self-synthesis or self-assembly of nanosystems and devices, drug delivery and functional imaging (Cui and Gao, 2003). DNA, RNA and proteins have been shown to self-assemble into linear or more sophisticated topological structures; they can also be used as templates for nanofabrication, i.e. their shape and chemical properties can be utilized to fabricate ordered arrangements of inorganic substances such as metal colloids on the nanometer scale (Niemeyer, 2001). Such nanostructures possess unique physical properties that are different from those of the bulk material and could serve as a basis for devices in bio-nanotechnology (Martin and Kohli, 2002).

Carbon nanotubes (CNTs) have become very attractive materials due to their excellent structural, electronic and chemical properties (Saito et al., 1998). Functionalization of CNTs with biomolecules such as nucleic acids and peptides is currently a developing area of nanotechnology, with potential applications in molecular electronics (Reed, 2000), field emission devices (Odom et al., 2000) and biomedical engineering (Bonard et al., 2001). So far, DNA has been widely utilized for applications in nanowire fabrication (Bashir, 2001), nanowire template formation (Keren et al., 2003), and for the synthesis of chain-like arrangements of metal and semiconductor clusters (Warner and Hutchison, 2003). DNA molecules can be used as templates for synthesizing interconnect wires with the smallest possible lateral dimension based on linearly arranged ions (Tanaka et al., 2003). DNA plasmids can align semiconductor particles in a circle, while "double-crossover" DNA molecules with sticky ends can enable the formation of 2D crystals (Winfree et al., 1998); Recombinant techniques (chemical self assembly) can be used to bind several different clusters in well-defined sequences – the coding properties of DNA would then be employed to the full extent. DNA molecules can increase CNT solubility (Shim et al., 2002; O' Connell et al., 2001) and can also be used distinguish metallic CNTs from semi-conducting CNTs (Zheng et al., 2003).

Here we report experiments on encapsulating double stranded DNA molecules inside multiwalled carbon nanotubes (MWCNT). Our previous molecular dynamics simulations (Gao et al., 2003) have shown that a single stranded DNA-oligonucleotide can be spontaneously encapsulated inside a single wall CNT in water, provided that the tube diameter is large enough and the oligonucleotide is appropriately aligned with the CNT. The van der Waals interaction between the CNT and the DNA-oligonucleotide was found to be the main driving force

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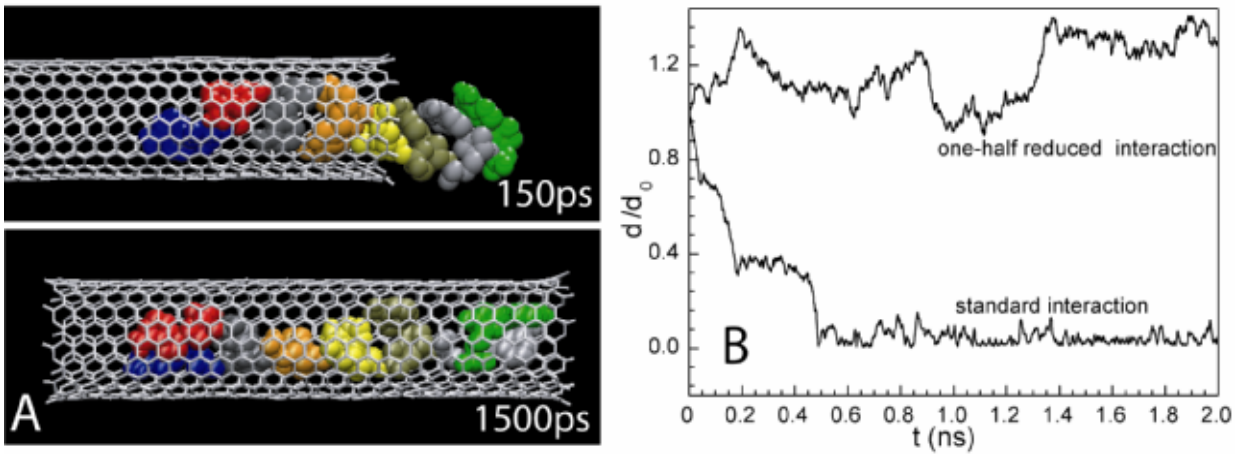


Figure 1 : Molecular dynamics simulations of a DNA oligonucleotide interacting with a carbon nanotube. (A) Simulation snapshots. (B) Normalized oligo-CNT center-of-mass distances (d_0 is the initial centre-of-mass distance). (Gao et al., 2003)

for this phenomenon (Gao et al., 2003). As shown in Figure 1, a small reduction in the van der Waals force dramatically slows down and even stops the encapsulation process. The objective of the present study is to provide an experimental confirmation of this phenomenon. In order to facilitate observations via high-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDX), we used Pt-labelled double stranded DNA molecules and MWCNTs to investigate the DNA-CNT encapsulation process.

2 Experiments

2.1 Materials

Double stranded DNA fragments of 400bp in length were obtained by PCR and diluted in ion-free water to a concentration of 100 μg/ml. MWCNTs 40-70nm in outer diameter, 10-20nm in the diameter of the inner hole and 200-500nm in length were purchased from Nanostructured & Amorphous Materials (Los Alamos, NM). All chemical reagents used in the experiments were purchased from Sigma Chemicals, Inc. The electrophoresis experiment was performed based on the gel electrophoresis device purchased from Bio-Rad Inc. and MinElute gel extraction kit purchased from QIAGEN Company.

2.2 Sample preparation

In order to open the end caps of the MWCNTs, mild oxidation of MWCNTs was carried out by refluxing them in HNO_3 for 24h so that the tip regions of the MWCNTs become oxidized. The MWCNTs were then washed with ion-free water, filtered and dried at room temperature, and finally suspended in ion-free water to a concentration of 10mg/ml. 400bp DNA fragments labelled with Pt nanoparticles (Mertig et al., 2002) were prepared as follows: 1μl 100μg/ml DNA solution was added to 65μl of 1mM solution of K_2PtCl_4, mixed and then incubated at room temperature for 20h. Next, 1μl solution of 10mM DMAB (Borane Dimethylamine Complex) was added to the mixture which was kept at 27 $^\circ$C for 18h. The DNA fragments labeled with Pt nanoparticles were mixed with MWCNTs at a mass ratio of 10:1 and kept at 4 $^\circ$C in an icebox for overnight. 300 μl of 10mg/ml MWCNT suspension was mixed with a 300 μl solution of DNA fragments labelled with Pt nanoparticles under 400K and 3Bar for 20 min. Next, 1% agarose gel electrophoresis was used to remove Pt-labelled DNA fragments attached to the outside walls of MWCNTs by the following procedure: The agarose gel was prepared according to the method described in Molecular Cloning (Sambrook et al., 1998). The Pt-labelled DNA-MWCNT hybrids were added to the agarose gel, and the electrophoresis process was run for 3-4 hours under 60V and 30mA. The gel containing the MWCNTs and the DNA fragments were characterized under UV and white light condition. The gel sample was then excised with a clean sharp scalpel. The gel slices were weighed in colorless tubes and purified based on the process according to the MinElute^{TM}

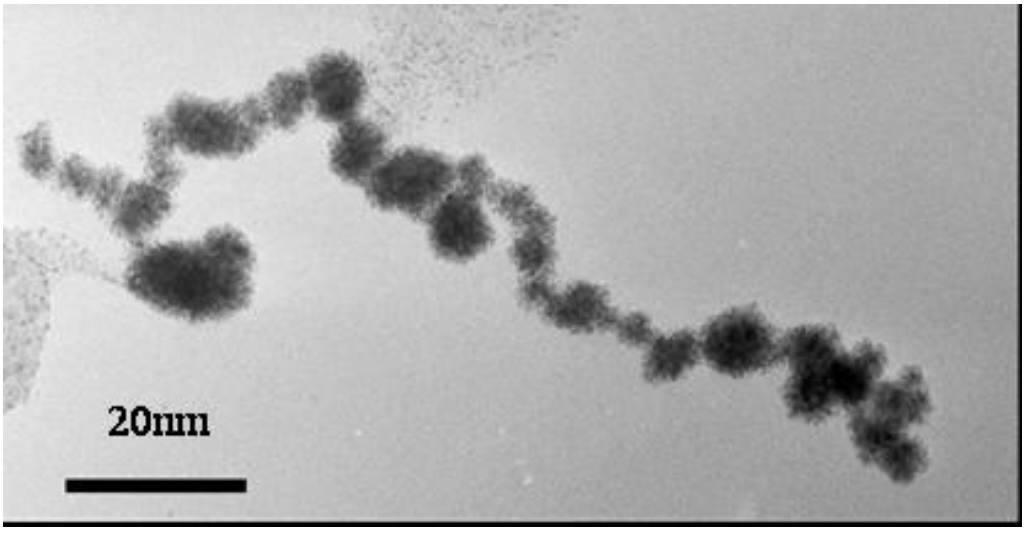


Figure 2 : HR-TEM image of a Pt-labelled DNA fragment in the absence of MWCNTs.

Handbook. Finally, the MWCNTs adhered to the membrane were extracted in an acetone solution.

2.3 Analyses

The DNA-MWCNT hybrids (before and after electrophoresis) were coated over holey carbon sample grids and dried at room temperature for 24 hours. The samples were then characterized using a Philips CM 200 TEM at 200 KeV and a VG 501 STEM equipped with EDX at 100 KeV. EDX analysis of MWCNTs with Pt-labelled DNA fragments was conducted with a 1.2 nm diameter electron probe.

3 Results and Discussion

3.1 Molecular dynamics simulations of a DNA molecule interacting with a CNT

As shown in Figure 1A, a DNA molecule can be encapsulated inside a CNT, and the van der Waals force has been identified to be the dominant driving force for the encapsulation phenomenon (Gao et al., 2003). Figure 1B shows that, when the van der Waals interaction is reduced by 50%, the DNA molecule can no longer be spontaneously encapsulated inside a CNT.

3.2 Preparation of Pt-labelled DNA fragment and MWCNTs

Under the presence of the reductant DMAB (Borane Dimethylamine Complex), Pt nanoparticles around 2nm in diameter can bind with the G (Guanine) and C (Cytosine) bases of DNA molecules via covalent bonding (Mertig et al., 2002), resulting in the formation of Pt-labelled double stranded DNA fragments that are 4-6 nm in diameter. As shown in Figure 2, a linear strand of DNA fragments labeled with Pt nanoparticles has a lateral dimension (diameter) less than 10 nm. In the absence of any DNA fragments, Pt nanoparticles will only form very short range clusters (Richter et al., 2000). Formation of long linear strands is only observed in the presence of DNA fragments. HR-TEM imaging of the oxidized MWCNTs showed that approximately 60% of the MWCNT's had open ends (caps removed).

3.3 Electrophoresis of DNA-MWCNT hybrids

At room temperature, DNA molecules have a negative charge associated with their phosphate backbone; they can form a hydration layer with water molecules, have strong cohesive ability, not only can bind with CNTs via electrostatic or van der Waal's forces and increase the water solubility of CNTs (Shim et al., 2002; Vincenzo and Yao, 2000; Zheng et al., 2003), but also can be used to distinguish metallic CNTs from semiconducting CNTs (Zheng et al., 2003). As shown in

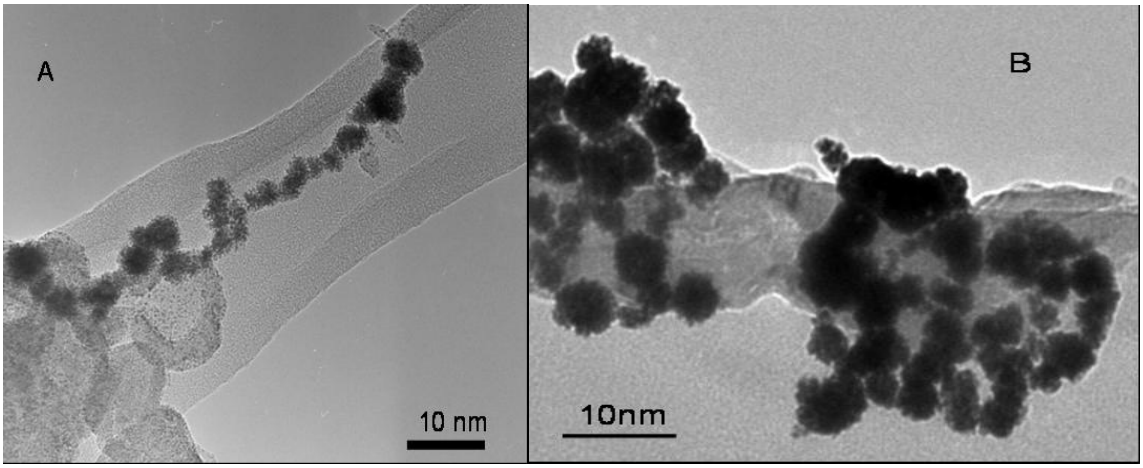


Figure 3 : Pt-labelled DNA molecules attached to the outside walls of CNTs. (A) HR-TEM image of a Pt-labelled DNA molecule attached to the outside wall of a MWCNT. (B) HR-TEM image of two Pt-labelled DNA molecules wrapped around a MWCNT.

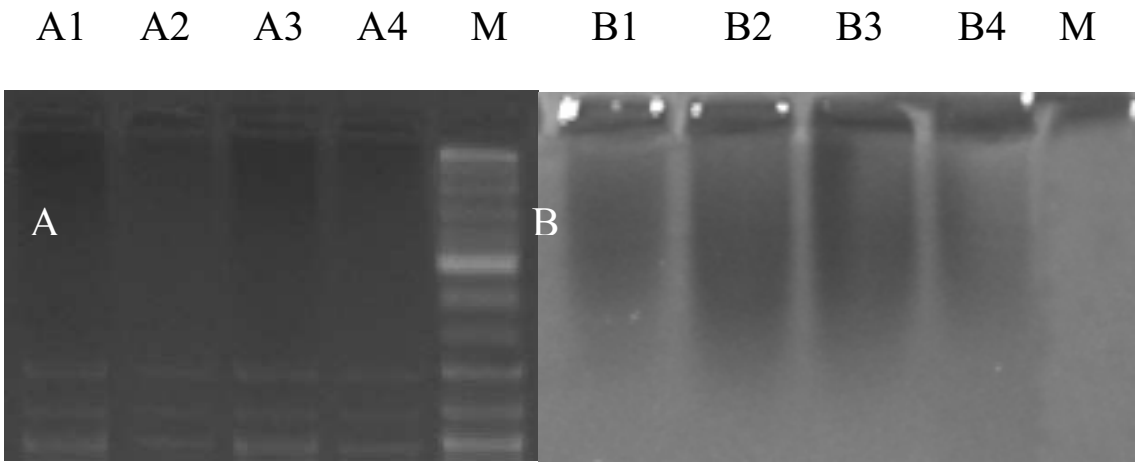


Figure 4 : Electrophoresis of Pt-labelled DNA-CNT hybrids under 60V and 30mA.

Figure 3, Pt-labelled DNA molecules were found to attach to the outside walls of CNTs after being mixed for 20 minutes under 400K and 3 Bar. In order to observe whether the Pt-labelled DNA molecules can be encapsulated inside the MWCNTs, 1% agarose gel electrophoresis was used to remove the Pt-labelled DNA molecules attached to the outside walls of the MWCNTs. Under the application of a constant electric field, molecules with negative charges move towards the positive electrode, and those molecules with positive charges move towards the negative electrode; different charges result in different mobilities during the process (Grossman and Soane, 1991). The Agarose gel acts as a molecular sieve(Kepka et al., 2004) through which smaller molecules move faster than bigger molecules. The result indicates that the DNA molecules attached to the outside walls of the MWCNTs can be removed by electrophoresis. The distinct bands near the lower bottom section on gel lanes shown in Figure 4A are the signature of DNA molecules associated with varying quantities of Pt nanoparticles. Figure 4B shows that MWCNTs exhibited a gradient distribution over the electrophoresis lanes. These observations can be explained as follows. The negatively charged Pt-labelled DNA molecules and the DNA-MWCNT hybrids move towards the positive electrode. Different DNA-MWCNT complexes have dif-

ferent sizes and amounts of charge, and hence significantly different mobility over the electrophoresis lanes. The DNA-MWCNT complexes continue to move until a critical time when the DNA molecules attached to the outside walls of the MWCNTs become separated from the MWCNTs. Afterwards, the DNA molecules move away from the electrically neutral MWCNTs which no longer respond to the applied electric field. In contrast, the DNA molecules encapsulated inside the MWCNTs can not be easily removed via electrophoresis. This provides a basis to purify encapsulated CNT-DNA hybrides.

(A) Electrophoresis results under UV light, showing that DNA molecules can be isolated from the CNTs. The three bands located near the lower bottom of each lane are DNA; A1- A4 are electrophoresis lanes with DNA-CNT hybrids; M is the DNA molecular Marker. (B) Electrophoresis results under white light, showing that the CNT-DNA complexes exhibited a gradient distribution on each lane; B1-B4 are electrophoresis lanes with Pt-labelled DNA-CNT hybrids; M is the DNA molecular Marker.

3.4 HR-TEM and EDX analyses of Pt-DNA inside MWCNTs

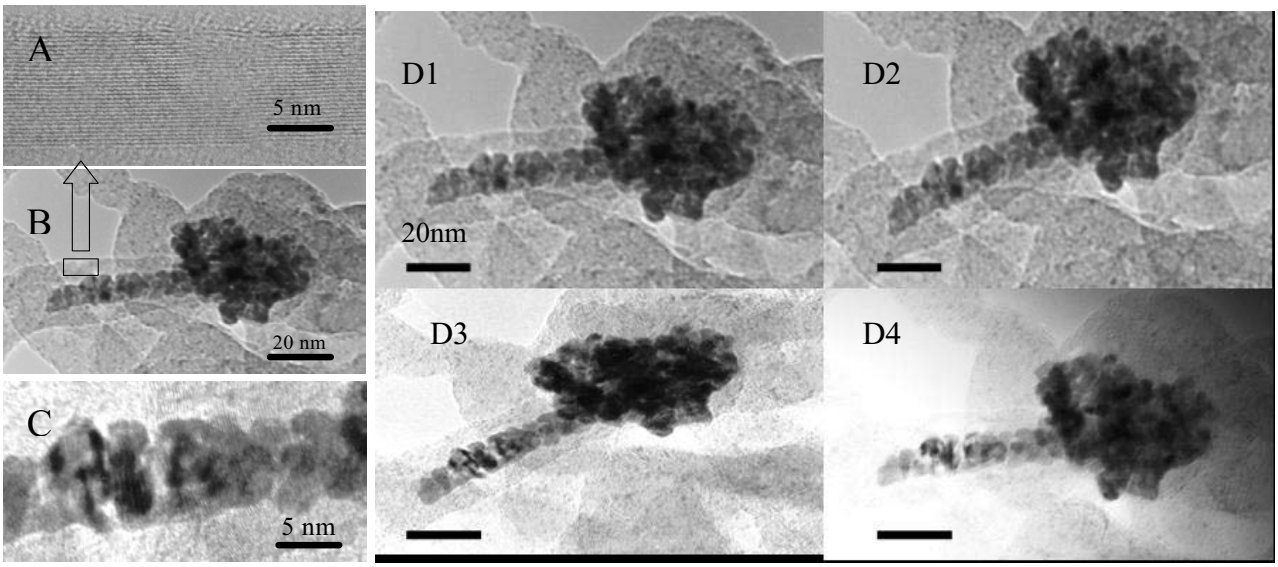
Figure 5A shows layer structure of the MWCNTs used in our experiments. Figure 5B depicts a Pt-labelled DNA fragment partially inserted into a MWCNT. Part of the DNA molecule has been drawn into a straight, linear strand inside the nanotube, while the part outside of the nanotube is folded in a globular conformation. The partial insertion may be due to the blockage of MWCNT near the entrance so that part of the DNA remains outside. As the temperature dropped from 400K to room temperature, the part of DNA outside of MWCNT becomes annealed into a double stranded structure and then folded in a globular conformation. Further details remain to be studied in the future. Figure 5C shows a more magnified view of the encapsulated Pt-labelled DNA strand with clear lattice lines of the MWCNT over the encapsulated DNA.

The presence of Pt-labelled DNA fragments inside the MWCNT was further confirmed via EDX analysis as shown in Figure 5E. The EDX spectrum was obtained with a 1.2 nm probe focused in the vicinity of the Pt-labelled DNA. The spectrum consists of C, N, O, P as well as the Pt peaks, indicating the chemical composition of the DNA phosphate backbone being covalently bonded with the Pt nanoparticles. The C peak has the highest amplitude due to the presence of the CNTs and the holey carbon from the grid sample holder (in addition to the copper line supporting the holey carbon film). The HR-TEM images and the EDX patterns suggested that the Pt-labelled DNA molecule has been encapsulated inside the MWCNT.

In order to distinguish the DNA molecules attached to the outside wall of a CNT from those inside the CNT, we used the following methods. First, we used agarose gel electrophoresis to remove as many DNA molecules outside of CNT as possible and observed the samples at scales of 50-100 nm. After some Pt-labelled DNA molecules were found to locate inside a CNT, the sample was observed by gradually decreasing the scale to 20nm and simultaneously tilting the sample holder to different angles. If the DNA strands are not located inside the CNT, they should exhibit different configurations relative to the nanotube as the sample holder angle changed. If the DNA strands are located inside the CNT, they should be observed to approximately align along the nanotube axis at all angles. Figures 5D1-D3 show that, at different tilting angles, the Pt-labelled DNA strand was always observed to align along the nanotube axis. According to the principles of characterizing and imaging CNT under HR-TEM (Iijima et al., 1992; Ajayan et al., 1993; Bernaerts et al., 1995; Zhang et al., 1999; Edington, 1991), we conclude that the DNA strand is indeed located inside the CNT. Figure 5D4 is a HR-TEM image of a Pt-labelled DNA strand inside CNT under the defocus condition. After examining the encapsulated Pt-labelled DNA strand under different titling angles, the sample was subjected to EDX analysis.

3.5 Mechanism of filling DNA molecules inside CNTs

So far, it has been found that C_{60}, metallofullerences, water, gas, Se, Co, Sb, Ge, Ni, Fe, Au and Cu can be encapsulated inside CNTs (Smith et al., 1998; Hirahara et al., 2000; Hummer et al., 2001; Gogotsi et al., 2001; Tsang et al., 1994; Saito and Yoshikawa, 1993). This paper is the first report of encapsulating DNA molecules inside CNTs. Previously, we have conducted molecular dynamics simulations to show that a single strand DNA oligonucleotide can be spontaneously inserted into a single wall carbon nanotube in water, provided that the tube diameter is large enough and that the oligonucleotide is appropriately aligned with CNT (Gao, et al, 2003). The



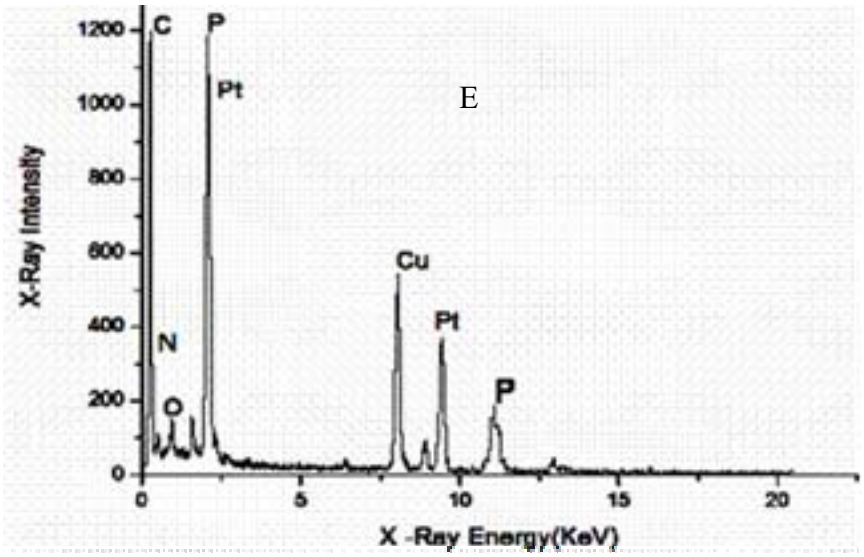


Figure 5 : HRTEM images and EDX spectra of carbon nanotubes with partially encapsulated nucleic acid fragments labelled with platinum nanoparticles. (A) A local HR-TEM image of the MWCNT shell structure. **(**B) An image of a Pt-labelled DNA fragment partially drawn into a linear strand inside a MWCNT. The part of the DNA outside the MWCNT is folded into a globular conformation. The TEM image was obtained at an accelerating voltage of 200 KV. (C) HR-TEM image of a partially inserted Pt-labelled DNA fragment inside a MWCNT, showing that the lattice fringe lines of the MWCNT cross over the encapsulated DNA strand. (D) HR-TEM images of the partially inserted Pt-labelled DNA strand under different titling angles and different focus conditions. D1-3 showed that the Pt-labelled DNA strand is observed to align along the nanotube axis under different titling angles, D4 showed the image of Pt-labelled DNA strand under the de-focus condition. Bar: 20nm. (E) EDX spectrum showing the presence of C, N, O, P and Pt peaks in the vicinity of the Pt-labelled DNA.

van der Waals interaction between CNT and DNA was found to be the main driving force for this phenomenon. A small reduction in the van der Waals force dramatically slows down and even stops the encapsulation process. The encapsulation process strongly depends on the diameter and length of the CNT.

In our experiments, MWCNTs with a 10-20 nm inner hole diameter were selected to ensure that the tube is large enough for encapsulation of a Pt-DNA molecule. Our experiments confirmed that the Pt-labelled double stranded DNA fragments of less than 10nm in diameter can be encapsulated inside the selected MWCNTs under 400K and 3 Bar. It appears that the van der Waals interaction constitutes the main driving force for the encapsulation process.

In contrast to our experiments, it was previously reported that Pt-labelled DNA molecules can not be encapsulated inside CNTs when dissolved in water at room temperature for 2-3 days (Guo et al., 1998). Also, it seems that there has been no report on the encapsulation of Pt inside CNTs. Our study on Pt-DNA interacting with MWCNTs thus also represented a way to encapsulate Pt containing molecular clusters inside CNTs.

At the room temperature and pressure, DNA molecules are hydrophilic, negatively charged, have the capability of forming a hydration layer with water molecules, have strong adhesive ability, can strongly interact with CNTs via electrostatic attraction and van der Waals forces, and can increase the water solubility of CNTs (O'Connell et al., 2001; Zheng et al., 2003; Vincenzo and Yao, 2000; Cui et al., 2003). At the room temperature, the strong adhesion and low mobility of Pt-DNA makes it difficult to encapsulate these molecules inside a CNT as they are more likely to adhere to the outside walls of CNTs (Figure 3).

Under 400K and 3 Bar, the properties of DNA change significantly (Seeman, 1999). For example, hydrogen bonds within a double helix break and double stranded DNA molecules become dissociated into single stranded DNA. The kinetic energy increases, and the Brownian motion of the DNA molecules become more energized. The DNA molecules then exhibit a typical hyperchromic effect (Hua and He, 2003); their adhesive ability and surface tension significantly decreases while buoyancy force increases. These changes result in a loss of the biological activity of DNA; the hydration layer between DNA molecules and water molecules breaks down, the π-bond between DNA molecules and CNTs becomes weaker, and the van der Waals interaction becomes more prominent. All of these factors may have contributed to the observed encapsulation of Pt-labeled DNA molecules inside CNTs.

The temperature, pressure and solvent conditions were important for our experiments. The melting point (Tm) of double stranded DNA molecules is in the range of 60-80 $^\circ$C, the denaturing temperature is around 94-100 $^\circ$C and the time for denaturing a DNA molecule depends on the length of a DNA molecule. In our experiments, a pressure of 3 Bar was applied to keep the solution in the liquid state and to prevent water and DNA molecules from forming floating gaseous colloids. At 400K, gaseous molecules are expected to be driven out of the CNTs, and the Pt-labeled DNA molecules loose their adhesive ability, decrease in surface tension and increase in kinetic energy. The van der Waals forces become more prominent and the DNA molecules become more mobile. Under these circumstances, it becomes more likely that some of the Pt-labeled DNA molecules have sufficient mobile time to enter the interior of a CNT, resulting in encapsulation. Alternative possibility for reducing adhesion between DNA molecules and the outer walls of the CNTs, thereby increasing the tendency for encapsulation, might be to replace water with another solvent. This issue needs further investigation.

Dujardin et al. (Dujardin et al., 1994; Ugarte et al., 1997) pointed out that the wetting ability and capillarity of CNTs are very important for enabling encapsulation of materials inside CNTs. In our experiments, the capillarity forces between Pt-labelled DNA molecules and CNTs should essentially be the van der Waals interactions between them.

In summary, under the experimental conditions of 400K and 3Bar, we observed encapsulation of Pt-labelled double stranded DNA molecules inside MWCNTs. The encapsulation conditions have been chosen to reduce the adhesive capabilities of DNA fragments so as to provide the possibility for encapsulating DNA inside CNTs via van der Waals interactions. Under the same experimental conditions, properties of Pt nanoparticles are expected to change very little from those at the room temperature. Therefore, we believe that the properties of DNA molecules play a dominant role in determining the conditions for the observed DNA-CNT encapsulation. From a different point of view, our results also demonstrate the

possibility that DNA molecules could be used as molecular templates for the encapsulation of metallic clusters to functionalize CNTs. In this way, encapsulation of metallic nanoparticles into CNTs has been achieved using DNA molecules as a delivery vehicle and a template. Our observations under the selected experimental conditions indicated that only 2-3% Pt-labeled DNA molecules are finally encapsulated into MWCNT's. Further work will be directed at investigating the optimal conditions for the encapsulation process. It should also be interesting to characterize the optical, electrical and magnetic properties of CNT-DNA hybrids.

4 Conclusion

Experimental results reported here indicated that Pt-labelled DNA molecules can be encapsulated inside carbon nanotubes in water at 400K and 3 Bar. Further investigations will be conducted to determine the optimum conditions for encapsulation. Further experiments can be devoted to determining whether pure DNA molecules could be encapsulated inside CNTs, although there is no reason to expect otherwise from a theoretical point of view. This line of research may be significant from the point of view of using DNA molecules as novel molecular templates for encapsulating nanoclusters or quantum wires of metallic or semiconducting nanoparticles or quantum dots inside nanotube materials or other nanoporous material systems. Future research will be devoted to characterizing the mechanical, chemical, electronic and biological properties of the CNT-DNA hybrids.

Acknowledgement: We thank S. Kuehnemann, J. Thomas and F. Phillipp of the Max Planck Institute for Metals Research for their assistance with the experiments. F. Phillipp has also provided critical comments on the manuscript.

Supplemental information

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