NANO
LETTERS

2002
Vol. 2, No. 6
665−667

Monodisperse Multiwall Carbon Nanotubes Obtained with Ferritin as Catalyst

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Received March 26, 2002; Revised Manuscript Received April 28, 2002

ABSTRACT

The iron-containing cores of ferritin were used as catalyst for the growth of patterned films of multiwall carbon nanotubes by chemical vapor deposition of C_2H_2 at 720 °C. The catalyst was delivered onto SiO_2/Si substrates by microcontact printing and onto SiO/Cu transmission electron microscopy grids by dipping. The adjunction of $Al(NO_3)_3 \cdot 9H_2O$ to ferritin has proven to be essential to prevent diffusion and coalescence of the catalyst particles and allows to produce monodisperse carbon nanotubes with an outer diameter of 5.2 ± 0.6 nm, which represents a significant improvement compared to existing solutions.

As the number of academic and industrial scientists involved in carbon nanotube research[1] steadily increases, and therewith the demonstrations for their application in various fields, it is becoming increasingly apparent that one of the keys to a successful use of these nanostructures is growth control. Ideally, one should be able to place one or an assembly of nanotubes with well-defined properties (length, diameter, and chirality) on precise locations on a support, for example to realize a field effect transistor[2,3] or the cathode for a flat panel display.[4,5] Several approaches have been developed up-to-now, with varying degrees of success.

For example, the diameter of single-wall nanotubes can be adjusted with the catalyst used in laser ablation,[6] but at present there is no possibility available to tune the length. The arc discharge, while producing high quality multiwall nanotubes, does not offer any possibility to influence the properties of the structures. Furthermore, the materials produced by laser ablation and arc discharge have to be purified and chemically modified to be subsequently delivered at specific locations on a substrate.[7] Nanotubes can also be produced by chemical vapor deposition (CVD), where a gaseous carbon source is decomposed over a transition metal catalyst. As the growth is activated by the catalyst, the placement of the nanotubes can be controlled by defining patterns of catalyst on a support, either by photo- or electron-beam lithography,[8] shadow masking,[4] or by soft lithographic techniques such as microcontact printing (μCP).[9] The challenge now is to control not only the placement but also the diameter and the length of the nanotubes.

As noted already by researchers studying carbon filaments in the 1970s, the diameter of CVD-grown structures is controlled to a large extent by the catalyst particle.[10] To obtain monodisperse nanotubes, one therefore needs to assemble or deliver well-defined catalyst particles onto a surface. This has proven to be surprisingly difficult, and the techniques that are currently used are not entirely satisfactory. The first possibility is to evaporate a thin metallic film that is fractioned by high-temperature annealing to form the catalyst particles.[11,12] The diameter of the nanotubes can be effectively controlled by varying the thickness of the metal film. It appears, however, that a film of Ni of only 1 nm thickness produces particles that are already 30 nm in diameter, resulting after annealing in nanotubes of over 40 nm diameter.[12] The lower limit reachable with this technique, which depends on the catalyst and on the deposition parameters, is around 20 nm. Instead of fractioning a continuous film, one can also start from metallic ions that are dissolved in solution, e.g., a 20 mM ethanolic solution of $Fe(NO_3)_3 \cdot 9H_2O$.[13] In this case, the particles form by an aging process in solution and/or by assembly during annealing at the growth temperature, and mean diameters under 20 nm can be obtained.[13,14] This approach allows to obtain single-wall nanotubes by CVD with the admixture of structure-directing agents.[15,16]

The mean size of the multiwall nanotubes is difficult to control with the above-mentioned methods and the size distribution is often broad. This is due primarily to the fact that the catalyst particles are formed from a thin film or from ions in solution during annealing to the growth temperature, which makes the obtention of small (under 10 nm) and monodisperse particles problematic. We demonstrate in this paper a third approach which allows to obtain multiwall carbon nanotubes of well-defined diameter by using the iron-containing cores of ferritin as catalyst.

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10.1021/nl0255606 CCC: $22.00

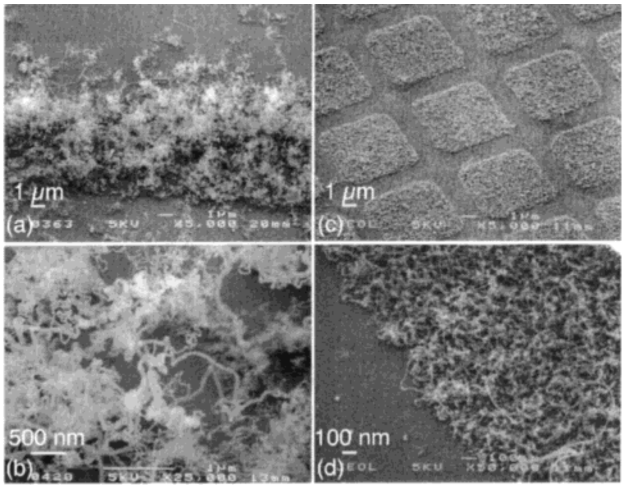

Figure 1. SEM micrographs of patterned nanotube films on SiO_2/Si obtained with (a,b) 50 μg/mL ferritin and 50 μg/mL albumine in phosphate buffered saline (PBS) and (c,d) 500 μg/mL ferritin and 50 mM $Al(NO_3)_3{\cdot}9H_2O$ in H_2O delivered by μCP.

Ferritin is a protein used by a variety of living organisms (among them humans) to assimilate nonheamoglobinian iron.[17] Mammalian ferritins are composed of 24 polypeptide chains that form a hollow shell and encapsulate a crystalline core of ferrihydrite, FeOOH. The ferritin used in this study[18] shows cores of 5 nm diameter (see below) that contain typically 3000 Fe(III) atoms. Our idea was to utilize the sharp size distribution of natural ferritin to produce thin and monodisperse nanotubes, and to use μCP to deliver selectively the catalyst onto a Si substrate. Note that a similar approach was used very recently by Zhang and co-workers with modified apo-ferritin to obtain single-wall nanotubes.[16]

We used SiO_2/Si substrates for patterned growth on which the catalyst solution was delivered by μCP with patterned and hydrophilized poly(dimethylsiloxane) stamps.[13] For transmission electron microscopy (TEM), Cu grids covered with a continuous SiO film (Plano) were dipped in the solution. The multiwall carbon nanotubes were grown in a horizontal flow CVD reactor (quartz tube of 34 mm diameter in a horizontal oven) at a reaction temperature of 720 °C under 20 mbar of acetylene for 5 min.

Figure 1(a,b) shows scanning electron microscopy (SEM) micrographs of nanotubes obtained with a standard solution for the μCP of ferritin (and other proteins), which incorporates albumine as a ligand and PBS as the solvent.[19] The printing was unsatisfactory and the results were disappointing: the nanotubes are highly defective with a broad diameter distribution that extends beyond 100 nm. The thinnest tubes we found had diameters of at least 10 nm, which is far larger than anticipated given the small size of the catalyst particles. TEM observations revealed that diffusion and coalescence of the particles occurred and that the growth took place only on the largest particles. Albumine is clearly unsuited as a ligand and could not prevent the agglomeration of the cores even when low ferritin concentrations (10 μg/mL) were used.

One possibility to avoid particle coalescence is to hinder their diffusion by immobilizing or embedding them in a matrix that is both stable at the growth temperature and inert for the CVD growth. We therefore replaced the albumine ligand by $Al(NO_3)_3{\cdot}9H_2O$, which has proven to be a very effective additive to our usual $Fe(NO_3)_3{\cdot}9H_2O$ catalyst for the production of patterned films of thin and sparse nanotubes (see also below),[20] and we used H_2O instead of PBS as solvent. As shown in Figure 1(c,d), the outcome is far more satisfactory as the replication of the stamp pattern is very good and the diameter appears to be in the expected range.

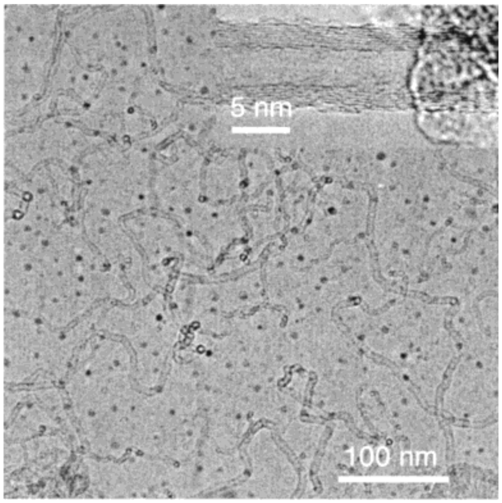

Figure 2. TEM micrographs of a nanotube film on a SiO/Cu grid obtained with 10 μg/mL ferritin and 50 mM $Al(NO_3)_3{\cdot}9H_2O$ in H_2O.

We confirm the superiority of the ferritin−$Al(NO_3)_3{\cdot}9H_2O$ catalyst in the TEM images of Figure 2: the diameter is very homogeneous and comparable to the particle diameter. We also note that about 25% of the iron cores give rise to a nanotube. The high-resolution image of Figure 2 further indicates that the grown structures are well-graphitized multiwall nanotubes with diameters under 10 nm.

We examine next the size distributions of the catalyst particles and of the resulting nanotubes in Figure 3(a) for ferritin and for two ethanolic solutions used for patterned growth by μCP, namely $Fe(NO_3)_3{\cdot}9H_2O$−$Al(NO_3)_3{\cdot}9H_2O$ in Figure 3(b)[20] and $Fe(NO_3)_3{\cdot}9H_2O$ in Figure 3(c).[9] The ferritin cores show a mean diameter of 4.9 nm with a spread of 1.1 nm. The particles produced from the two inks based on $Fe(NO_3)_3{\cdot}9H_2O$ show larger diameters and, more importantly, a significant proportion of large particles. In fact, the distribution is more log-normal than Gaussian as is the case for ferritin. Note, however, that both catalysts yield particles that are smaller than 10 nm in diameter, to be compared with a minimal size of 20 nm for catalysts realized from metallic thin films.

The progression in particle diameter is reflected in the final nanotube diameter. The largest particles yield the largest nanotubes with a mean diameter that remains below 20 nm and also the highest spread in diameter. The use of $Al(NO_3)_3{\cdot}9H_2O$ in conjunction with $Fe(NO_3)_3{\cdot}9H_2O$ produces smaller particles, but the resulting nanotubes are twice as large as the ones produced with ferritin. Maybe the most remarkable property of the ferritin catalyst is that the outer nanotube diameter matches closely the particle diameter. The ratio

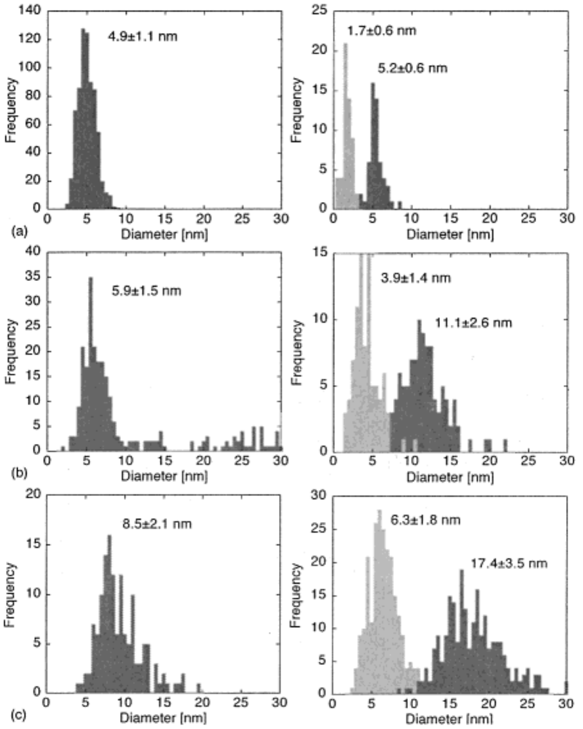

Figure 3. Diameter distribution as determined from TEM micrographs of catalyst particles (left-hand graph) and inner/outer nanotube diameter (right-hand graph) obtained with (a) 10 μg/mL ferritin and 50 mM $Al(NO_3)_3{\cdot}9H_2O$ in H_2O; (b) 15 mM $Fe(NO_3)_3{\cdot}9H_2O$ and 50 mM $Al(NO_3)_3{\cdot}9H_2O$ in ethanol; and (c) 15 mM $Fe(NO_3)_3{\cdot}9H_2O$ in ethanol.

between outer nanotube diameter and particle size is close to 1, while it amounts to 2 for the $Fe(NO_3)_3{\cdot}9H_2O$ catalysts. We surmise that the iron core, which consists of ferrihydride that is transformed to bcc-Fe upon annealing, shrinks slightly during the growth. Note also that the spread in the diameters is far narrower for ferritin: even taking into account the fact that the mean nanotube diameter is smaller for ferritin as compared to the other catalysts, we observe that the diameter dispersion is lower by a factor of 2.

It appears from our results that the addition of $Al(NO_3)_3{\cdot}9H_2O$ is essential for the obtention of small-diameter nanotubes with ferritin as well as with $Fe(NO_3)_3{\cdot}9H_2O$. TEM reveals that the catalyst particles are surrounded by a highly porous Al-containing material, which acts as a matrix that prevents both the diffusion and the coalescence of the particles. This matrix is formed at high temperature from the $Al(NO_3)_3{\cdot}9H_2O$ and embeds the particles, which explains also the small proportion of nanotubes with respect to catalyst particles in Figure 2 as only the particles at or close to the matrix surface will be exposed to the hydrocarbon gas.

In conclusion, we have demonstrated an attractive possibility for the CVD growth of multiwall nanotubes, namely the use as catalyst of well-defined particles dispersed in solution. We were able to realize patterned films of thin monodisperse nanotubes on Si substrates by delivering the iron-containing cores of ferritin, with the adjunction of $Al(NO_3)_3{\cdot}9H_2O$, by μCP. TEM confirmed that the mean diameter of the produced structures was close to the particle diameter (5.2 as compared to 4.9 nm), with a spread in the diameter well below 1 nm. We believe that this simple, yet powerful, method is not restricted to ferritin but can be applied to other types of colloidal particles in solution, such as those obtained through inversed micelle synthesis, opening thereby a whole range of possibilities for the development of advanced catalysts for the growth of carbon nanotubes.

Acknowledgment. The idea of using ferritin as a catalyst for nanotube growth was suggested by Jean-Philippe Renault (Laboratoire de Radiolyse, CEA/Saclay), and we thank him heartily for helpful discussions. We acknowledge also important inputs from Hannes Kind (Department of Chemistry, Berkeley, CA) and Bernard F. Coll (Motorola Physical Science Research Laboratory, Tempe, AZ). We are greatly indebted to the Centre Interdépartemental de Microscopie Electronique of EPFL (CIME-EPFL) for access to SEM and TEM facilities. This work was supported in part by the Swiss National Science Foundation as well as by the European Community and the Federal Office for Education and Science of Switzerland in the frame of the project CANADIS (IST-1999-20590).

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NL0255606