Phys. Status Solidi C **7**, No. 3–4, 1236–1240 (2010) / **DOI** 10.1002/pssc.200982972

physica status solidi c
www.pss-c.com
current topics in solid state physics

Production of high quality carbon nanotubes for less than $1 per gram

R. Smajda[1], M. Mionic[1], M. Duchamp[1], J. C. Andresen[1], L. Forró[1], and A. Magrez[*1,2]

[1] Laboratoire de Nanostructures et Nouveaux Matériaux Electroniques, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland
[2] Center for Research on Electronically Advanced Materials, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

Received 13 September 2009, revised 12 October 2009, accepted 12 October 2009

PACS 81.05.Tp, 81.20.Ka, 89.20.Db

---

[*] Corresponding author: e-mail arnaud.magrez@epfl.ch, Phone: +41 21 693 7656, Fax: +41 21 693 4470

In this article, we report on the mass production of carbon nanotubes using a continuous production system based on a rotary tube furnace. At first, we have optimized the composition of the metallic nanoparticles. Bimetallic Fe_2Ni and Fe_2Co alloys exhibit higher catalytic activity than pure Fe, Co or Ni. Then, catalyst production process has been modified for the preparation of large quantity of catalyst with low aggregation suitable for large scale synthesis of CNTs. A production rate of about 1.2 kg per day has been achieved. This is yielding to a cost production of less than $1 per gram. Finally, we show that the CNTs growth can also be obtained on naturally occurring calcite support for further cost reduction of the synthesis. Quality of the CNTs produced has been established by measuring their mechanical properties using AFM. Young's modulus of the CNTs can be as high as the ideal value of 1 TPa.

1 Introduction Since their discovery [1], carbon nanotubes (CNTs) have been at the forefront of nanotechnology because of their remarkable electrical, optical, thermal and mechanical properties in combination with their extraordinary chemical stability. Developing applications for carbon nanotubes requires the production of pure materials in commercial quantities at affordable prices. Chemical Vapour Deposition (CVD) is considered by the industrialist to be the most suitable process to produce CNTs at low cost. Presently, the market price of pure carbon nanotubes is higher than $10 per gram for a production capacity of few hundreds metric tonnes per year. They remain expensive compared to carbon black, with a price being of the order of $1 per metric tonne. It is expected that the price of CNTs will fall as the demand increases and as the process improves in terms of production yield. However, it is important that the supply of carbon nanotubes remains of high quality.

In this paper, we demonstrate that with our continuous production system based on a rotary tube furnace a production rate of more than 1 kg/day can be achieved with a cost of less than $1 per gram. 75% of the nanotubes produced have a diameter smaller than 10 nm and a young modulus close to the ideal 1 TPa.

2 Experimental

2.1 Optimisation of the metal catalyst MWCNTs were synthesized by CVD of acetylene and carbon dioxide over supported Fe, Co, Ni catalysts alloys. In a typical catalyst preparation, a stoichiometric amount of metal salts (cobalt (II) nitrate hexahydrate-Sigma Aldrich 60832 ≥99%; and/or iron (III) nitrate nonahydrate-Sigma Aldrich 254223 ≥99.99% and/or nikel(II) nitrate hexahydrate-Sigma Aldrich 72252 ≥98.5%) are dissolved in distilled water. Support ($CaCO_3$- Fluka C4830 ≥99%) is subsequently dispersed into the solution. The resulting mixture (with $Fe_2M/CaCO_3 = 5\%$; M= Ni or Co) was dried on a hot plate under continuous stirring. Large batches of as-prepared catalyst were produced as well and kept in boxes without special care. The syntheses of CNTs were carried out in a horizontally mounted quartz tube furnace (stationary conditions) in the temperature range of 350 and 850 °C.

For the CNTs synthesis, the as-prepared catalyst was placed on a quartz boat and was rapidly introduced into the reaction chamber. The furnace was flushed with Ar for 10 min and finally exposed to a mixture of C_2H_2 and CO_2 with a flux of 1 L/h. After 15 min growth time, the furnace was flushed again with Ar for 10 min.

2.2 Large scale synthesis of CNTs using the rotary tube furnace We elaborated a continuous production method based on a rotary tube furnace (Fig. 1) to overcome the limited capacity and scalability of the fixed bed reactor [2, 3]. The oven has an 80 mm diameter rotating quartz tube. The catalyst was continuously introduced into the reaction tube with an endless screw place at the end of the catalyst container. Acetylene and argon were fluxed at 10 L/h and 80 L/h respectively. After collecting, the material is purified. The catalyst and support are dissolved in a 1.5 M hydrochloric acid during the purification process. MWCNTs are subsequently filtered, washed with distilled water and dried at 120 °C overnight.

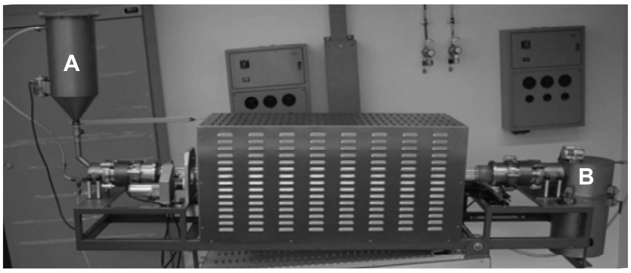

Figure 1 View of the rotary tube furnace used for large-scale synthesis of CVD. *A*: Catalyst stock continuously driven inside the 3 inch quartz tube. Raw materials (CNTs + Catalyst) are collected in *B*

2.2 CNTs preparation for mechanical properties characterisation Atomic Force Microscopy (AFM) samples are prepared by dispersing the CVD grown CNTs in ethanol and suspended by 10 minutes sonication using an ultrasonic finger. One droplet of CNT suspension is deposited on the micro-fabricated Si_3N_4 membrane. After one minute, the solution was dried off with a nitrogen flux. Individual CNTs were found to bridge holes of the Si_3N_4 membrane, with their entire length in contact with the membrane surface. AFM images are taken with contact mode and varying loads on each image. Bending modulus of the CNTs is extracted by measuring the vertical deflection at the middle of the suspended part of the nanotube.

3 Results and discussion

3.1 Optimisation of the catalyst composition The Chemical Vapor Deposition developped is based on the equimolar reaction between acetylene and CO_2 at the surface of a supported metal catalyst [4]. We have already shown that best supports for the growth of CNTs are alkaline earth carbonate [5]. Here we have focused our study on the composition of the metallic nanoparticles of the catalyst. Beside pure Fe, Ni and Co metals, bimetallic alloys with Fe_2M (M= Ni and Co) composition have been tested. We have shown that when catalyst is introduced inside the CVD reactor, an intermediate oxide (spinel with Fe_2NiO_4, Fe_2CoO_4 composition) of metal transition is formed prior to the reduction into metal nanoparticles, proceeding when acetylene and CO_2 gases are introduced. This oxide is single phase when Fe_2M stoichiometry is applied (as well as for pure Fe, Ni and Co metals). Any deviation from this composition (Fe/M=2) induce the presence of a second phase with lower catalytic activity [5]. We clearly see in Table 1 that the mass of CNTs bimetallic alloys exhibits higher catalytic activity compared to pure Fe, Co, and Ni transition metals. The reaction yield, calculated as the ratio between the mass of nanotubes produced and the mass of carbon introduced (as acetylene) is dramatically enhanced by a factor of more than 4 for Fe_2Ni and Fe_2Co compared to Ni and Co respectively.

Catalyst composition	mg of CNTs produced per g of catalyst	Reaction yield (%)
Co	250	9
Fe	350	13
Ni	370	14
Fe_2Co	1310	49
Fe_2Ni	1670	62

Table 1 Maximum mass of CNTs produced for different supported metallic nanoparticles. Growth was performed at 650-700 °C.

Element	Content (wt%)
Co	0.15 ± 0.02
Fe	0.47 ± 0.03
Ca	0.21 ± 0.02
Total	0.83 ± 0.03

Table 2 Impurities content within the purified CNTs as a result of the ICP MS analysis.

3.2 Large scale production of CNTs For the mass production of CNTs, larger quantities of catalyst should be produced. Compared to previous report [5, 6], we developed a new process based on the co-precipitation of the transition metals on the surface of $CaCO_3$ by the addition of a weak base. In a typical catalyst preparation, $CaCO_3$ is dispersed in water by a strong stirring. Transition metal nitrates are added to the slurry. Triethylamine, ammoniac, or urea is added while the pH raises 10. This induces the deposition of Fe, Co or Ni mixed hydroxides. The slurry (solid/liquid ratio is about 1/3) of $CaCO_3$ coated with metallic nanoparticles is consequently frozen by dropping in liquid nitrogen and dried afterwards by sublimation. With our equipment, about 3 kg of ice can be collected in 24 hours. It has been found that freeze drying process (also known as lyophilisation) produces less aggregated powder. Therefore, almost all catalytic particles are exposed [7]. This is suitable for mass production and for increasing the production yield compared to those reported in the Table 1. It has to be noticed that despite being widely used in food industry, lyophilisation remains relatively expensive. Other drying processes like spay drying or roller drying processes, widely used in powder industry, can be used as well and are probably more suitable for large scale production of catalyst at low cost.

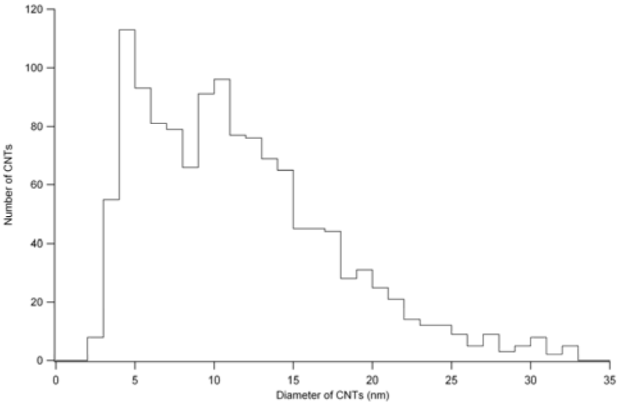

Figure 2 Diameter distribution of CNTs produced in the rotary tube furnace. Diameters of 1000 CNTs have been measured from TEM micrographs.

To evaluate the yield of the synthesis, we have introduced 2.1 g of catalyst in the quartz tube of our rotary tube furnace. The growth was performed in conditions described in the experimental part of the paper but in stationary conditions (quartz tube not rotating). The mass of CNTs produced is 13.1 g. This corresponds to about 4300mg of CNTs per gram of catalyst and a reaction yield of about 85%. In contrast to the values reported in Table 1, no noticeable difference has been observed between Fe_2Co and Fe_2Ni transition metal alloys. However, the reaction yield is enhanced and the mass of CNTs produced per gram of catalyst dramatically increased.

Large quantities of catalyst have been produced and the furnace was run for couple of hours. Catalyst is introduced in the rotating quartz tube at a rate of about 10 g per hour.

A production rate of about 1200 g of CNTs per day has been achieved.

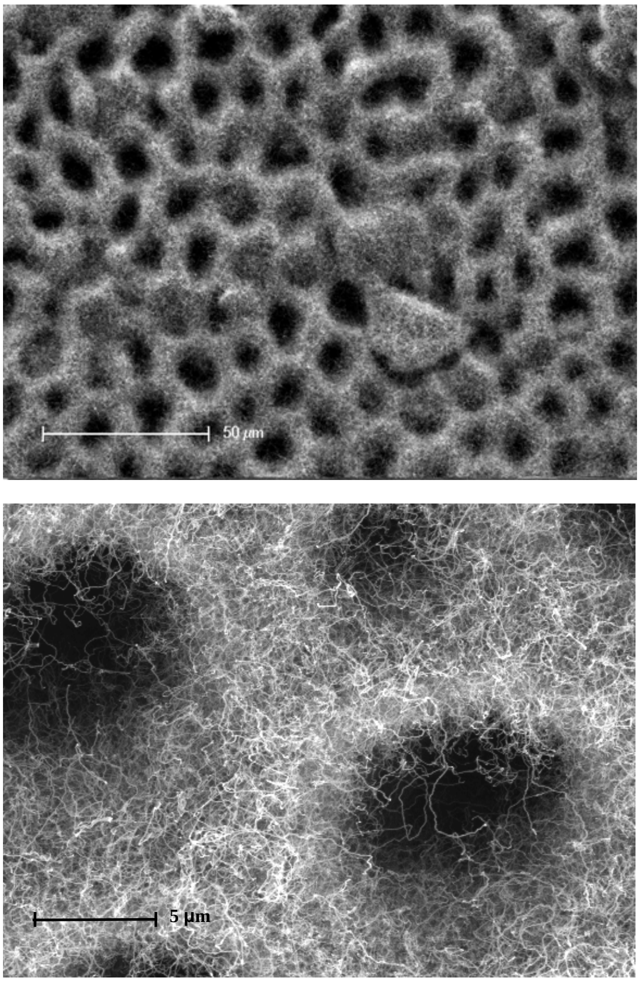

Figure 3 SEM micrographs of carbon nanotubes grown on a sea urchin shell. The growth was performed at 500°C to preserve the porous structure of the shell. Mass production experiments with the rotary tube furnace are performed at 640 °C.

The diameter distribution, Fig. 2, shows that CNTs have a mean diameter of about 11 nm. 75% of CNTs have a diameter below 15 nm (Fig. 2). After purification with HCl, most of the supported catalyst has been removed such as the C content is higher than 99 % (Table 2).

We calculated the cost of the CNTs production using our rotary tube furnace over one year. The cost of the chemicals (for catalyst preparation (support, precursor salts…) and CNTs purification (distilled water, acids…)) is estimated from the price of the products provided by Sigma Aldrich. Acetylene and argon are purchased from Air liquid. The price of the furnace as well as the salary for one technician for one year is included in the calculations. The electricity required to run the rotary tube furnace is accounted as well. This leads to a production cost of $0.5 per gram of purified CNTs. This represents a drastic cost reduction since only 1.2 kg per day can be produced in our reactor, as compared to a price of $10 per gram achieved for few hundreds metric tons production capacity of industrial reactors.

Beside the possibility of increasing the size of the reactor of our rotary tube furnace to process more catalyst simultaneously, production cost could be further reduced by using less expensive chemicals as compared to high grade materials used for the mass production of CNTs, previously reported in this paper. Hence, $CaCO_3$ is a sedimentary rock being the third most common constituent of the earth's crust. We have performed the growth of CNTs using the shell, made in calcite, of a sea urchin as support (Fig. 3). The sea urchin shell was collected in Bodrum (Mediterranean Sea, Turkey) and did not experience any surface treatment before or after the Fe film deposition. After exposing the Fe coated shell to acetylene at 600°C, the shell surface is entirely covered with CNTs while the production yield is preserved as compared to CNTs growth process performed over catalyst produced from high grade material. It shows that CNTs can be grown on naturally occurring minerals. This paves the way towards further cost reduction for CNTs production. On the other hand, purification of CNTs produced from natural calcite will be achieved with oxidizing acids (HNO_3, H_2SO_4…) and/or basic solutions (NH_3, NaOH…) to ensure a complete dissolution of impurities present in natural calcite support. However, further study of the influence of the impurities on the CNTs quality will have to be carried out.

3.3 Mechanical properties of CNTs The mechanical properties of CNTs have been measured by the “swiss cheese” method [8, 9]. CNTs can be easily 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 modelled the suspended nanotube as a doubly clamped beam (see Fig. 4). 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

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

where L is the suspended length and I is the second moment of area of the beam, which for a filled cylinder is $\delta D^4/64$. 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.

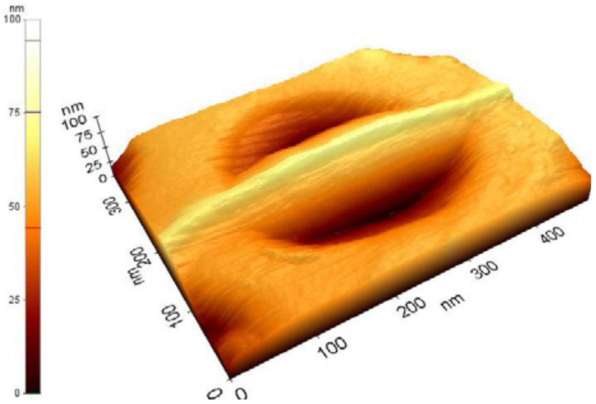

Figure 4 Typical AFM image of CNT bridging the hole of a Si_3N_4 membrane.

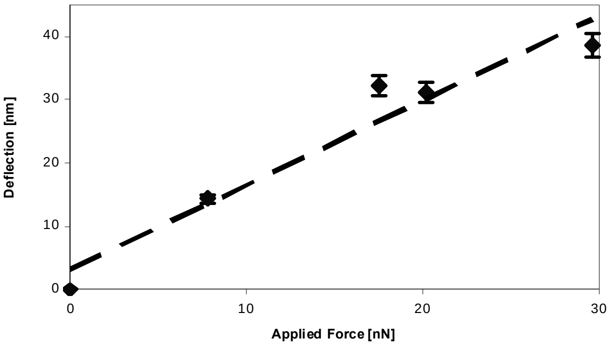

Figure 5 F-δ curve obtained for a CNTs of a diameter of 10(± 1) nm and of a suspended length of 500(± 10) nm. The calculated Young's modulus of the CNT is 1013 (± 354) GPa.

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. 5). CNTs are known to exhibit exceptional mechanical properties. Very high Young's moduli of about 1TPa have been obtained for CNTs produced by high temperature process like arc discharge or laser ablation [8, 9]. 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 20nm exhibit clear diameter dependence [10, 11]. CNTs with smaller diameter have better structure quality and consequently mechanical properties similar to high temperature grown CNTs.

In this study, we measured the mechanical properties of CNTs produced in the rotary tube furnace at 640 °C. They exhibit exceptional mechanical properties. When CNTs diameter is lower than 10 nm, the Young's modulus can be as high as 1 TPa (Fig. 5). In the materials produced in mass, 53% of CNTs have a diameter lower than 10 nm and 75%

of CNTs have a diameter lower than 15 nm (Fig. 2) for which the Young's modulus is higher than 100 GPa [11].

4 Conclusion In this work, we have reported the mass production of high quality CNTs at low cost by Chemical Vapour Deposition Process. As a result of catalyst composition optimisation, we have shown that bimetallic alloys with Fe_2M (M=Ni or Co) exhibits higher catalytic activity than pure Fe, Co or Ni. Using our rotary tube furnace, we have produce CNTs at a rate of 1.2 kg per day. 85% of acetylene is transformed into CNTs. They exhibit a mean diameter of XX nm and have good mechanical properties with Young's modulus close to 1 TPa. The cost for the production of such CNTs is about $0.5 per gram. This can be further reduced by using natural calcite.

Acknowledgements We thank the Centre Interdisciplinaire de Microscopie Electronique (CIME) for access to electron microscopes and the technical support of A.J. Kulik for the AFM measurements is acknowledged. This work was partially funded by the European Framework. "VIACARBON" as well as the Swiss National Foundation and its NCCR "Nanoscale Science".

References

[1] M. Monthioux and V.L. Kuznetsov, Carbon **44**, 1621-1623 (2006).
[2] E. Couteau, K. Hernadi, J.W.Seo, L.Thien-Nga, Cs. Mikó, R. Gaál, and L. Forró, Chem. Phys. Lett. **378**, 9-17 (2003).
[3] J.W. Seo, E. Couteau, P. Umek, K. Hernádi, P. Marcoux, B. Lukić, Cs. Mikó, M. Milas, R. Gaál, and L. Forró, New J. Phys. **5**, 120.1-120.22 (2003).
[4] A. Magrez, J.W. Seo, V.L. Kuznetsov, and L. Forró, Angew. Chem. Int. Ed. **46**, 441-444 (2007).
[5] A. Magrez, J.W. Seo, Cs. Mikó, K. Hernádi, and L. Forró, J. Phys. Chem. B **109**, 10087-10091 (2005).
[6] J.W. Seo, A. Magrez, M. Milas, K. Lee, V. Lukovac, and L. Forró, J. Phys. D:Appl. Phys. **40**, R109-R120 (2007).
[7] M. Mionić, D.T.L. Alexander, L. Forró, and A. Magrez, Phys. Status Solidi B **245**, 1915-1918 (2008).
[8] 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).
[9] 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).
[10] B. Lukić, J.W.Seo, R.R. Bacsa, S. Delpeux, F. Béguin, G. Bister, A. Fonseca, J.B. Nagy, A. Kis, S. Jeney, J.A. Kulik, and L. Forró, Nano Lett. **5**, 2074-2077 (2005).
[11] K. Lee, B. Lukic, A. Magrez, J.W. Seo, G.A.D. Briggs, A.J. Kulik, and L. Forró, Nano Lett. **7**, 1598-1602 (2007).