Synthesis of single-wall carbon nanotubes by catalytic decomposition of hydrocarbons

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Individual single-wall carbon nanotubes (SWNTs) and bundles can be obtained over different types of supported metal catalysts by decomposition of ethylene, similar to the synthesis of multi-wall carbon nanotubes.

Until now, laser evaporation[1] and electric arc discharge techniques[2] have been used to synthesise SWNTs in high yield, but many previous reports[3–5] have shown that the catalytic decomposition of hydrocarbons could be a possible way to produce SWNTs. In the present work, we describe the synthesis of SWNTs from ethylene decomposition on supported metal catalysts, prepared by impregnation of different supports. The 3d transition metals are known for their efficient production of single- and multi-wall nanotubes.[1,2,6] For this reason, Co, Ni, Fe and mixtures of these metals are used in our catalysts, to produce individual or bundles of SWNTs. Various supported metal catalysts are prepared on different supports (alumina and silica)† and with different metals (Co, Ni, Fe) and metal mixtures (Co-Fe, Ni-Co, Co-Fe, Co-Ni-Fe) by a method already described.[7] The role of the supports involves the dispersion of the metal particles. Catalysts are prepared by impregnating the support with an EtOH solution containing the appropriate concentration (2.5 wt% of each metal) of metal salts or mixture of metals salts. After sonication (1 h) and evaporation of EtOH, the material is dried at 150 °C (12–15 h) and ground into a fine powder. The synthesis of single-wall nanotubes was carried out in a fixed-bed reactor at 1080 °C (60 min). For each synthesis, a quartz boat containing about 200 mg of catalyst was placed in the center of the reactor. The gas flows of the ethylene–nitrogen mixture used were 30 and 80 ml min^{-1}, respectively. The abundance of SWNTs is estimated from TEM observations using JEOL 200CX and Phillips CM 20 instruments for low and high resolution measurements, respectively. The TEM images show unambiguously either the presence of individual SWNTs (with some small bundles) or principally the presence of abundant bundles of SWNTs. These bundles seem to be similar to those produced by arc discharge or laser evaporation techniques with the one difference, however, that they are longer (up to several μm). All the catalysts prepared are active in the formation of SWNTs, with varying efficiency. In fact, in all cases, SWNTs have been observed, but their abundance seems to be dependent on the nature of the metal and the type of support. The synthesis of SWNTs is more efficient for the metal catalysts supported on alumina than on fumed silica. Moreover, in the case of fumed silica using the same reaction parameters, the SWNTs are coated with a thick layer of amorphous carbon. Concerning the influence of the nature of the metal, it is very difficult to discrimate among the catalysts containing a single metal. For all the metals, individual SWNTs are observed, but Co and Fe seem to be more active than Ni. In addition, some SWNT bundles are also found in these samples. For the catalysts prepared from a mixture of metals, the best activity is found for Fe-Co and Fe-Co-Ni mixtures supported on alumina. On these two catalysts, a significant amount of SWNT bundles is observed (Fig. 1). The catalysts prepared from a mixture of metals are more efficient for SWNT production than those prepared with a single metal. The bundles of SWNTs are larger and longer than those synthesised by arc discharge and the laser evaporation. Details of these SWNT bundles are shown on Fig. 2, where a large bundle of about 20–35 nm of diameter can be observed [Fig. 2(*a*)]. Moreover, the SWNT diameter can be estimated by transmission electron microscopy: Fig. 2(*a*) shows that the SWNTs in the bundles have a uniform diameter and they form crystallite-like entities organized in a two-dimensional triangular lattice, with a lattice constant *a*, about 1.0 nm, corresponding to nanotubes of 0.7 nm in diameter separated by the van der Waals intertube distances of 3.4 Å. The diameter estimated for the SWNTs is around 0.7 nm. For comparison, a lattice constant of 1.7 nm has been given for the SWNT bundles produced by laser evaporation[1] and the smallest SWNTs organised in ropes found in the synthesis by arc discharge have 1.2–0.9 nm diameter when argon is used instead of helium.[8] The estimated diameter of SWNTs in the bundle is confirmed by Fig. 2(*b*) showing the cross section of the bundles which gives the same small diameter. In fact, on the top of this picture, some graphitic layers also appear and the distance between them is equal to 3.4 Å. These data confirm the accuracy of the value of the tube diameter. The tube diameters found for the SWNT bundles are the smallest produced until now. In the case of individual SWNTs, a distribution of diameter is also observed and individual SWNT diameters range from 1.6 to 5 nm. The tubes which have the largest diameter are often double-wall nanotubes. Most of the individual SWNTs have diameters

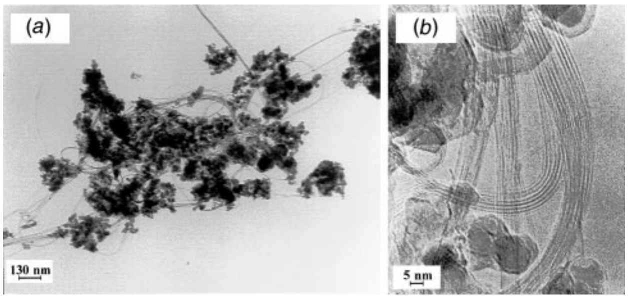

Fig. 1 (*a*) Low and (*b*) high resolution TEM images of SWNT bundles produced on Co-Ni-Fe/alumina catalyst by decomposition of ethylene at 1080 °C.

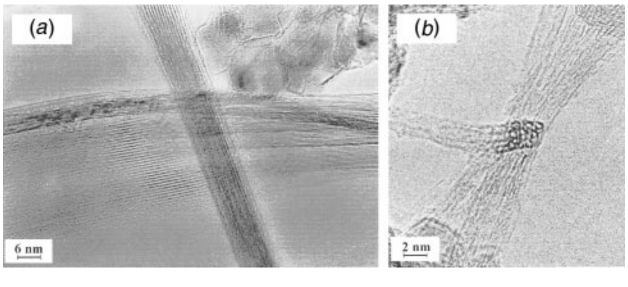

Fig. 2 TEM images of (*a*) large SWNT bundle and (*b*) higher magnification of SWNT bundle cross section.

around 1.8–2 nm. In comparison, isolated SWNTs have larger diameters than those produced by the other two techniques (around 1.4 nm). Recently, very small diameters (0.6–0.8 nm) were found for isolated SWNTs synthesised by the electric arc discharge method in the presence of argon.[8]

In the case of multi-wall carbon nanotubes (MWNT) synthesis, the influence of support on the growth mechanism is rather well-documented.[6] The mechanism depends on the interactions between the metal particles and the support. In the case of SWNTs produced by the catalytic process, Dai *et al.*[3] have proposed a growth mechanism close to that of MWNTs, because metal particles have been found trapped in the tip of SWNTs, and the diameter of the SWNTs is related to the size of the catalytic metal particle attached to their end. This fact could explain the large diameter distribution of isolated SWNTs (average diameter about 2 nm) synthesised by the catalytic decomposition of hydrocarbons compared to the ones obtained by the other techniques. In our different samples, no catalytic particles were found trapped at the end of the individual SWNTs, but the closed ends of the SWNTs are not incompatible with this proposed mechanism, where the individual SWNT could grow from a supported particle at one end and be closed at the other. This growth mechanism is strengthened by the fact that the synthesis of SWNTs can also be carried out at low temperature (750–850 °C)[5] similarly to the synthesis of multi-wall nanotubes.

In the formation of the SWNT bundles, the support does not seem to play an important role on the growth mechanism, contrary to what has previously been proposed.[4] Bundles of SWNTs were observed in all cases (on both alumina and silica) where the catalysts are composed of mixtures of metals. Possibly, the support plays a role in the dispersion of the metal on the surface, and influences the pyrolytic cracking of the hydrocarbon in certain cases, but the presence or the absence of SWNT bundles is not governed by the support. The formation of SWNT bundles increases when mixtures of metals are present. Possibly, the preparation of catalysts with mixtures of metals induces a better dispersion of the metals on the catalyst surface. Moreover, the formation of each SWNT in the bundle may not depend on a small metal particle, and the growth mechanism of SWNT bundles could be different for individual SWNTs. One of the hypotheses involves SWNT bundles grown from single bigger metal particles so that bundle formation would be linked to the nature of the metal surface. This hypothesis could also explain the presence of SWNT bundles in the samples synthesised on single metal supported catalysts. Reinforcing this hypothesis is the very small size of the SWNT diameters in the bundles compared to the diameter of isolated SWNTs (linked to the size of catalytic metal particle).

In conclusion, isolated SWNTs and SWNT bundles can be produced by catalytic decomposition of hydrocarbons. Supported catalysts containing either a single metal or a mixture of metals seem to induce the growth of isolated SWNTs or SWNT bundles, respectively. Bundles of SWNTs have been synthesised with very small and uniform diameter (around 0.7 nm), and isolated SWNTs with larger diameter (around 2 nm). In the near future, the synthesis conditions could be optimised to obtain SWNTs in large quantities, as is already the case for MWNTs obtained *via* catalytic decomposition of hydrocarbons.

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Notes and references

† Supports used are Alumina Al_2O_3 δ crystalline form from Degussa with surface area 100 $m^2 g^{-1}$ and Silica SiO_2 type fumed with surface area 380 $m^2 g^{-1}$.

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