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Gram-scale CCVD synthesis of double-walled carbon nanotubes

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Synthesis of clean double-walled carbon nanotubes by a catalytic chemical vapour deposition (CCVD) method is reported; the catalyst is a $Mg_{1-x}Co_xO$ solid solution containing additions of Mo oxide; this MgO-based catalyst can be easily removed, leading to gram-scale amounts of clean carbon nanotubes, 77% of which are double-walled carbon nanotubes.

Double-walled carbon nanotubes (DWNTs) are at the frontier between single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). Of key interest is the possibility of functionalising the outer wall, which will ensure the connections with the external environment, while retaining the remarkable mechanical and electronic properties of the inner nanotube. This may prove to be very useful for their integration into systems and composites.

The CCVD synthesis of mixtures of SWNTs and DWNTs using $Mg_{0.9}Co_{0.1}O$ solid solutions as starting materials was reported for the first time by our group.[1] The MgO-based support is easily removed by mild acidic treatment that does not damage the carbon nanotubes (CNTs). Subsequent studies reported the synthesis of samples with a very high (800 m^2 g^{-1}) BET specific surface area (SSA)[2] and with an increased yield.[3] The synthesis of DWNTs has emerged as a recent domain of interest, several groups claiming the preparation either by CCVD methods[4–6] or by the electric arc-discharge method.[7] Filling SWNTs with C_{60} followed by a heat treatment can result as well in the formation of DWNTs.[8] However there is generally a lack of precise quantification of the proportion of DWNTs compared to other CNTs, a result that so far can only be obtained using high resolution transmission electron microscopy (HRTEM).[1] This work aims at both increasing the yield and the selectivity towards DWNTs.

The experimental conditions for the already reported[1] auto-catalytic combustion synthesis of the oxide precursor were modified in two ways. Firstly, the required amount of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was added to the solution of magnesium and cobalt nitrates and secondly, the fuel (urea) was replaced by the equivalent amount of citric acid. Note that the total amount of Co and Mo is only one tenth that of the sole Co used in our earlier report.[1]The use of Mo in addition to Co or Fe was reported to increase the CNTs yield in CCVD synthesis and was claimed to increase the selectivity towards the formation of SWNTs. In the case of Co–SiO_2 catalysts, adding Mo favours the formation of $CoMoO_4$, which results in the reduction of cobalt ions to metallic Co at higher temperatures.[9,10] These authors make clear that Co alone is responsible for the formation of CNTs and that the molybdenum ends up as Mo_2C particles, unconnected with the CNTs. In the case of Fe–Mo catalysts, Su *et al.*[11] claim that the catalyst particles are indeed an Fe–Mo alloy, whereas it has also been proposed[12] that the close proximity between Mo and Fe sites could favour the aromatisation of CH_4, thus increasing the yield of CNTs.

The use of citric acid as a fuel results in a milder combustion which allows for the preparation of oxides with a higher SSA.[13] The formula of the desired combustion product could be written as $Mg_{0.99}Co_{0.075}Mo_{0.025}O$. However, X-ray diffraction (XRD) revealed a mixture of the $Mg_{1-x}Co_xO$ solid solution with an undetermined Mo oxide (MoO_y). 6 g of the starting oxide were prepared in one combustion batch and were reduced in a H_2–CH_4 mixture (18 mol% CH_4, heating and cooling rates 5 °C min^{-1}, maximum temperature 1000 °C, no dwell). This resulted in a dense mat of composite powder which was treated with a concentrated aqueous HCl solution to separate the CNTs. The suspension was washed until neutrality and filtered. The sample was dried overnight at 80 °C, yielding 0.8 g of material. XRD analysis revealed some remaining *fcc*-Co and a wide peak centred around 3.4 Å, corresponding to the (002) peak of graphitic-like material. No peak corresponding to any Mo species could be detected. Elemental analysis (flash combustion) gave a carbon content of 89.7 wt%. Thermogravimetry (1 °C min^{-1} in flowing air, not shown) showed only one well-defined weight loss at 420 °C, corresponding to 89.4% of the initial weight, in very good agreement with the elemental analysis. This corresponds to more than 97.7 mol% of carbon, assuming that the sample contains only Co and C. Co is supposed to be present as carbon-encapsulated nanoparticles.[1,14] The BET SSA is equal to 985 m^2 g^{-1}. Raman analysis (λ = 488 nm, not shown) revealed that the ratio between the intensity of the D and G bands is close to 8.9%. Analysis of the radial breathing modes indicated the presence of CNTs with diameters ranging from 0.7 to 2.13 nm and many pairs of peaks appeared (with a difference of about 0.7 nm between the corresponding diameters), which could correspond to the inner and outer diameters of DWNTs.[15] Fig. 1 shows a representative FEG-SEM image of the raw CNTs sample (before removal of the catalyst), revealing a very high density of CNT bundles, showing extensive branching. Their diameter typically ranges between 10 and 20 nm. No carbon nanofiber (a typical by-product of CCVD methods) could be observed. HRTEM observation was performed on the CNTs after elimination of the catalyst (Fig. 2a) and did not reveal any amorphous deposit on the CNTs; they are mainly isolated, or gathered into small bundles, mainly composed of DWNTs, in so far as this is possible to check from HRTEM images (Fig. 2a); electron diffraction data confirm these observations.[16] A few bundles are also made of CNTs with different numbers of walls. Analysis of

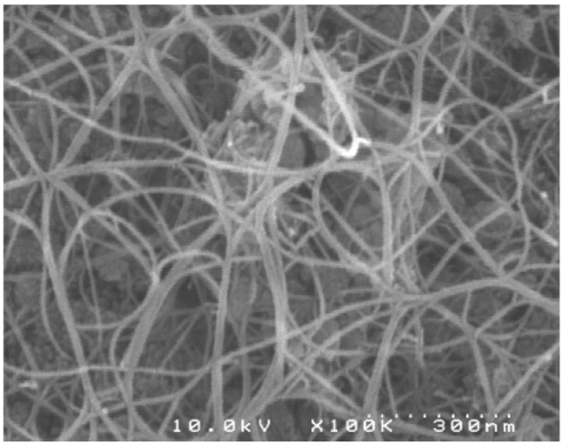

Fig. 1 FEG-SEM image of raw DWNTs. The catalyst can be seen in the background.

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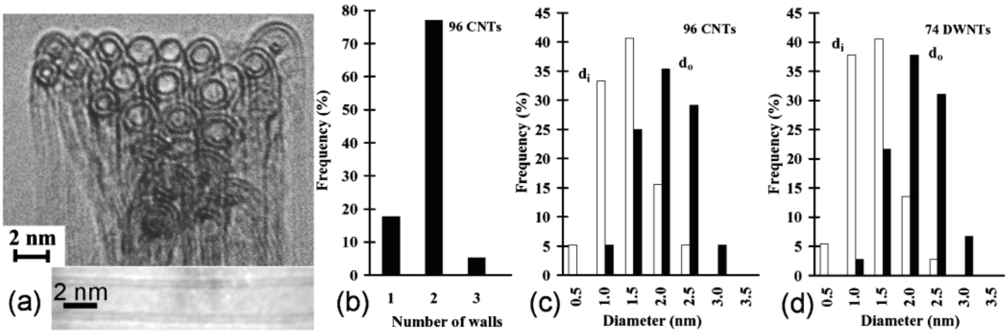

Fig. 2 (a) HRTEM images of DWNTs and (b) distribution of the numbers of walls for the whole population (established from 96 individual CNTs). Distribution of inner (d_i) and outer (d_o) diameter for the whole population of CNTs (c) and for DWNTs only (d).

HRTEM images allowed the determination of the number of walls and inner and outer diameters for 96 isolated CNTs. This kind of analysis can only be done on isolated nanotubes because it is not possible to determine the diameter of all the tubes within a bundle. We could on rare occasions observe the tip of a CNT but have never seen any metal particle there. These results confirm the "one particle–one nanotube" mechanism, generally agreed on for CCVD processes.[17] Bundles of CNTs must have formed after or maybe during the growth of each individual nanotube, but a cooperative growth from a unique larger metal particle[18] seems unlikely here (such particles are never observed by HRTEM). Thus, we believe that the proportion of each category of CNT is similar within the bundles and when the CNTs are isolated. The catalytic nanoparticles being formed *in situ*, it is possible that many of them will have a similar diameter when they become active for CNT growth, and may form almost at the same time. The small diameter of the CNTs, their high aspect ratio and van der Waals interactions all favour the formation of bundles containing thus mainly (but not only) similar CNTs.[16] The distribution of the CNTs *vs.* the number of walls (Fig. 2b) shows that the main species (77%) is DWNTs, far from either SWNTs (18%) or triple-walled CNTs (5%). The distributions *vs.* the diameter for all 96 CNTs and for the DWNTs only are shown on Fig. 2(c) and (d), respectively. The inner and outer diameters range from 0.53 to 2.53 nm and from 1.23 to 3.23 nm, respectively. The median inner diameter is 1.35 nm and the median outer diameter is 2.05 nm. These results obtained from HRTEM observation are in good agreement with the so-called yarmulke mechanism proposed by Dai *et al.*;[19] we think the diameter of the catalytic particle plays a key role because larger particles will need more carbon to reach the saturation point, leading to CNTs with more walls and delayed growth. The diameter of the particle also limits the CNTs' number of walls and thus small particles can only lead to CNTs with a small number of walls, while larger particles can produce a wider range of different CNTs. CNTs with a diameter higher than 3.23 nm are not observed here, which could mean that particles larger than this were not active for CNT growth in our experimental conditions. The reason why DWNTs are the main species is probably that the relation between CH_4 content (carbon feedstock) and the size of the catalytic particles favours their formation compared to the other categories of CNTs.[20] Mo may play a role in the increase of selectivity towards DWNTs because previous results without Mo never showed a selectivity higher than 50%;[1,2] a synergetic effect between Mo and Co is probably increasing the catalyst activity at lower temperatures, allowing the growth of CNTs on smaller particles and thus limiting the formation of CNTs with more walls. Work is in progress to check if there is indeed formation of a Co–Mo alloy and to study the influence of the molar ratio between Co and Mo, as well as the total metal amount in the catalyst. The addition of Mo is generally claimed to favour the growth of SWNTs, but this is obviously not the case here; the most striking fact is the increase of the catalytic activity compared to previous work: the yield of CNTs is more than four times that of a $Mg_{0.99}Co_{0.01}O$ solid solution treated in the same CCVD conditions, and the purity is increased as well. Another batch of 1.3 g of CNTs with similar characteristics to the one detailed here was prepared in one run from 10 g of catalyst, showing the good reproducibility of the results and indicating that scaling up is promising.

In summary, we have prepared gram-scale amounts of clean DWNTs, with a good selectivity and with low residual catalyst content. We have shown that the addition of a very small amount of molybdenum is very efficient at increasing the yield of CNTs and that it also increases the selectivity towards DWNTs. Work is in progress to study the influence of the ratio between cobalt and molybdenum with the aim of achieving a precise control of the number of walls of the CNTs.

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