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ChemComm
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Synthesis of high purity single-walled carbon nanotubes in high yield

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Received (in Cambridge, UK) 14th August 2002, Accepted 18th September 2002
First published as an Advance Article on the web 14th October 2002

A simple method for the synthesis of high purity single wall carbon nanotubes has been developed by using nickel formate as a precursor for the formation of nearly monodispersed nickel seed-nanoparticles as catalysts in the CVD growth process.

The application of carbon nanotubes (CNTs) in many fields arise from their outstanding physical and chemical properties.[1] Single-walled carbon nanotubes (SWCNTs) are particularly useful because of their unique atomic structure.

It would appear that chemical vapour deposition (CVD) provides the best opportunity for the production of high quality SWCNTs on a large scale, as long as a suitable catalyst can be identified.[2] Several useful catalysts have been reported, including Fe/Mo derivatives supported on Al_2O_3 aerogel,[2] M/MgO (where M = Fe, Co, Ni) composites[3] and Fe/Mo/Al_2O_3–SiO_2 combinations.[4] Although these systems have been shown to be efficient in the production of SWCNTs, the required metal nanoparticles can not be directly formed in the CVD growth process, and it is usual to have separate calcination and reduction steps to reduce the catalyst precursors (typically at 700 °C using H_2 gas) prior to the introduction of the carbon source gases. The calcination and reduction steps increase the complexity of the synthetic procedure and thus the cost for a large scale production and increase the risk of sintering the nanoparticles beyond the 1–2 nm size limit suitable for SWNT growth.

In this communication, we report a straightforward method for the synthesis of high-quality SWCNTs in high yields. We have found that nickel formate serves as an ideal precursor for the formation of the Ni nanocatalysts particles. Unlike other inorganic salts or oxides, the desired metal nanoparticles are formed directly from the formate, without the usual calcination and reduction steps. In addition, by optimising the experimental conditions, the Ni nanoparticles remain chemically very active, having a small particle size and a narrow size distribution.

The catalysts were prepared by dispersing nickel formate onto fine powders of a variety of supporting materials, such as SiO_2, Al_2O_3 or $CaSiO_x$. We find that under our experimental conditions, fumed silica powder yields the best results although the other supports listed above are also useful for the production of SWCNTs. At elevated temperatures, and just prior to tube growth, the catalyst was introduced into the growth furnace where thermal decomposition occurred rapidly to yield fresh Ni nanoparticles, signified by a blackening of the substrate. The subsequent CVD growth was performed using an Ar/CH_4 (1 : 1 by volume) atmosphere. Reaction temperatures were set between 600 and 1000 °C, with an optimal temperature of *ca.* 860 °C.

Carbon yields were measured by weighing the samples prior to and after the growth and also by thermal gravimetric analysis (TGA). In the former, yield was calculated on the basis of the following formula: yield (%) = $[(m_1 - m_0)/m_0] \times 100\%$; where m_1 is the mass of the catalyst/support sample after CVD growth, whilst m_0 is the mass of the sample after heating the sample under the same conditions but without methane. In the latter, the nanotube samples were heated under air to 750 °C. The yield was calculated by dividing the weight loss by the remaining sample weight. In both methods, the measured yields represent the carbon gains relative to the loaded supporting materials after CVD growth.

DOI: 10.1039/b207975p

Fig. 1(a) and (b) show electron microscope images (SEM and HRTEM) of SWCNTs grown by this method. The SEM picture indicates that the produced tubes are abundant. The HRTEM image shows that the tubes are pure single-walled, nearly monodispersed in diameter (*ca.* 1.0 nm), and have very little amorphous carbon on the tube surfaces. They are mainly in the form of small ropes or bundles although some individual tubes have also been found in other observations. Double wall nanotubes are rarely observed and thus considered to be in very low concentration in the samples.

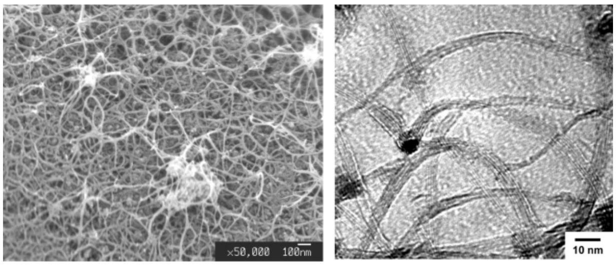


Fig. 1 (a) SEM image, (b) HRTEM image of SWCNTs from the as-prepared sample, grown by using Ar/CH_4 (1 : 1 in volume) at 860 °C. SWCNTs are mainly seen in bundles and have diameters of around 1.0 nm.

Table 1 shows the measured yield data as a function of the Ni wt% loading. Fig. 2 gives an example of the measured TGA profiles. Both analytical techniques result in consistent yield data. TGA shows that the sample begins to burn at about 515 °C, suggesting that relatively little amorphous carbon is present in the sample, in agreement with the HRTEM observations. The lower yields obtained by TGA may reflect the existence of nickel oxide arising from thermal treatment in air.[5] All wt% yields are relative to the weight of the silica support, however they can be converted into the nanotube to Ni yields, which we believe more clearly represents the productivity of the catalyst. In these terms, for example, the 58.3 wt% yield is equivalent to a nanotube to nickel yield of ~ 1940 wt%. In other words, in this case, a gram of nickel metal may assist the growth of 19.4 grams of SWCNTs.

Table 1 The measured yield of carbon nanotubes as a function of the Ni loading on silica support. Both yield and metal loading are relative to the mass of the silica support. The nanotubes are grown by using methane at 860 °C for 2.5 h

Sample no.	Ni loading/ wt%	Tube yield/wt% (weighing method)	Tube yield/wt% (TGA method)	Tube to Ni ratio (weighing method)
1	0.1	34.6	23.2	346
2	0.8	47.9	31.8	59.9
3	3.0	58.3	—	19.4
4	5.4	60.7	57.3	11.2 (containing MWCNTs)
5	6.8	61.2	54.0	9.0 (containing MWCNTs)

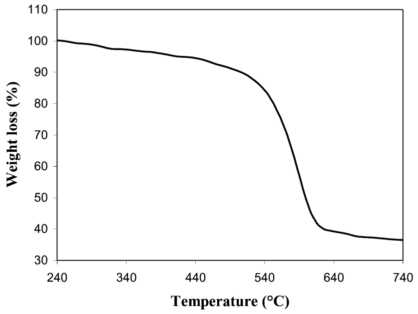


Fig. 2 An example of the measured TGA (thermal gravimetric analysis) profiles showing the weight loss of the as-prepared nanotube/support sample by heating in air. The temperature increasing rate is 10 °C min^{-1}.

Raman spectra have been collected from a range of as-prepared samples. Fig. 3 shows one of these spectra. The relatively broad D peak at 1293 cm^{-1} relates to the presence of defects. The G peak is strong and narrow, showing the three peaks typically associated with single wall nanotubes at 1569, 1582 and 1595 cm^{-1}, relating to the in-plane vibrations of a highly curved graphene sheet. Ratios of the intensities of D to G peak can be used as an indicator of the extent of disorder within the nanotubes.[6] The small ratio shown here, $I_D/I_G \approx 0.15$, indicates that the defect level in the atomic carbon structure is low. The radial breathing modes in the low frequency region show four components at 200, 212, 224 and 231 cm^{-1}, but with the 231 cm^{-1} mode in dominance. The frequency of these modes is known to be inversely proportional to the diameter of the SWCNTs. Based on equation $\nu\ (\mathrm{cm}^{-1}) = 223.75/d$,[7] the tube diameter can be calculated as, $d = 1.12, 1.05, 1.0$ and 0.97 nm, respectively. The average diameter is then $d = 1.04$ nm, with a small diameter distribution (±0.07 nm). This result is consistent with the observation in the HRTEM, indicating a narrow size distribution in the SWCNTs produced.

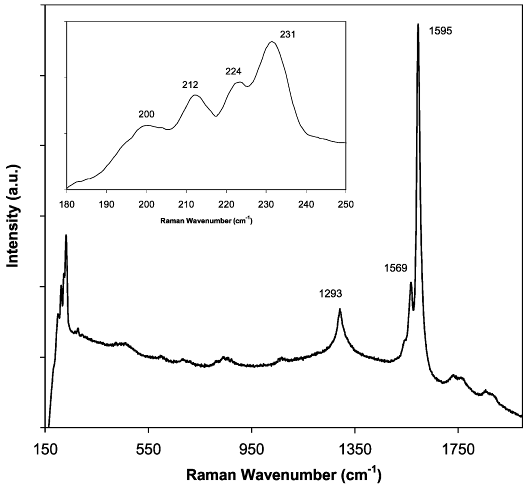
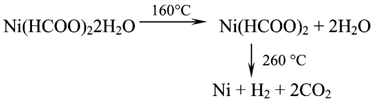


Fig. 3 Raman spectrum (excitation beam wavelength: ~ 785 nm) taken from sample 1 (see Table 1). This spectrum shows peaks in the lower frequency region, characteristic of single-walled carbon nanotubes. It also indicates the low-level atomic defects in the tubes by displaying the small D to G peak intensity ratio.

One question is why nickel formate is such an ideal precursor for the formation of the desired Ni nanoparticles for the growth of SWCNTs. To answer this, we need to consider the decomposition mechanism of this precursor. Measurements by thermal gravimetric analysis (TGA) reveal that this compound dehydrates first at ~ 160 °C followed by a thermal decomposition at ~ 260 °C.[8] Unlike many other nickel salts that normally require H_2 as a reducing agent, nickel formate directly decomposes to metallic nickel and gas species by a self-redox reaction.[8,9]



$$\begin{array}{c}\mathrm{Ni(HCOO)_2 2H_2O} \xrightarrow{160°\mathrm{C}} \mathrm{Ni(HCOO)_2 + 2H_2O} \\ \hphantom{\mathrm{Ni(HCOO)_2 2H_2O} \xrightarrow{160°\mathrm{C}}}\ \big\downarrow\ 260\ °\mathrm{C} \\ \hphantom{\mathrm{Ni(HCOO)_2 2H_2O} \xrightarrow{160°\mathrm{C}}}\ \mathrm{Ni + H_2 + 2CO_2}\end{array}$$

In addition, the nickel particles could be obtained at a residence time as short as 0.1 seconds at 600 °C.[8] Comparing these results with our experimental conditions, particularly the CVD growth temperature (860 °C), we may assume that the formate decomposes instantaneously in our case and a larger number of Ni nuclei are formed simultaneously. This type of decomposition mechanism favours the formation of small metal nanoparticles. Robert *et al.* have studied the thermal decomposition of nickel formate dihydrate by using an *in-situ* QXAFS technique (quick scanning X-ray adsorption fine structure spectroscopy).[10] They concluded that the pyrolysis yields a finely divided nickel metal with mean particle diameter of about 1.2 nm. This finding is consistent with our indirect evidence that we have formed small nickel particles (1.04 ± 0.07 nm). It is difficult to observe directly these very small Ni nanoparticles under the electron microscope after the tube growth presumably because the small metal particles have sintered in the porous silica and constitute only a tiny fraction of the overall yield. However, since the carbon nanotubes have a narrow size distribution with diameters that should match the size of the metal particles,[11] we speculate that the Ni nanoparticles must have a narrow size distribution as well. In addition, we believe that the high purity of the *in-situ* formed nickel nanoparticles plays a vital role in their high catalytic activity.

In summary, we have demonstrated a simple method for the synthesis of high-quality SWCNTs in high yield.[12] We attribute the success mainly to the even distribution of highly active and nearly monodispersed nickel catalysts, formed from their formate precursor, across the support surface. As both the catalyst preparation and the CVD process are rather simple to implement, this method may provide a realistic approach to an industrial-level production of pure SWCNTs for many applications.

We thank helpful discussions given by Dr. David Jefferson (Department of Chemistry, University of Cambridge) and Stephen Cash (Thomas Swan Co. & Ltd.) on this work. J. G. and C. S. are grateful to Thomas Swan Co. & Ltd. UK for financial support. M. S. thanks Trinity College, Cambridge.

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12 The work presented in this paper has been patented with UK patent application No. 0216654.4.