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CCVD synthesis of carbon nanotubes with W/Co–MgO catalysts

P. Landois^a, A. Peigney^a, Ch. Laurent^a, L. Frin^a, L. Datas^b, E. Flahaut^{b,*}

^aUniversité Paul Sabatier, CIRIMAT LCMIE – UMR CNRS 5085, 31062 Toulouse cedex 9, France

^bCNRS, Institut Carnot Cirimat, F-31062 Toulouse, France

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ABSTRACT

Carbon nanotubes (CNT) were synthesized from a H₂–CH₄ mixture with W/Co–MgO catalyst by a catalytic chemical vapour deposition (CCVD) method. Different W/Co ratios were investigated. From transmission electron microscopy observations, we observed that both the number of walls and the diameter of CNT increased with the proportion of tungsten. A promoter effect was observed as long as the proportion of tungsten was kept low and CNT with a number of walls ranging from 2 to 5 were obtained. With a higher proportion of tungsten, multi-walled carbon nanotubes (MWNT) up to 10 walls were synthesised, together with additional undesirable carbon nanofibres.

1. Introduction

Catalytic chemical vapour deposition (CCVD) is widely used for the synthesis of carbon nanotubes (CNT). It combines the advantages of a good control of the experimental parameters with low-cost equipments and raw materials, which makes it attractive for the bulk synthesis at the industrial scale. The addition of molybdenum to transition metals such as cobalt is known to increase the yield in CNT but the role it plays in the selectivity towards the number of walls of the CNT is still in debate. In the case of cobalt, many authors have reported that the addition of molybdenum is leading to a clear synergistic effect of the mixture compared to pure cobalt [1–3]. Other metals such as tungsten [4] could play a similar role. Only a few papers have reported the use of tungsten for the synthesis of CNT. Single-wall carbon nanotubes (SWNT) were synthesised by CO decomposition on W/Co catalysts supported on silica [5]. In this case, the selectivity of the W/Co catalysts toward SWNT depends on the stabilisation of Co²⁺ ions which results from an interaction with tungsten, as this was also reported by the same authors for Mo/Co cata-

lysts [2]. Qian et al. [6] have reported the synthesis of so-called few-walled CNT (FWNT) at 1000 °C in H₂–CH₄, from W/Co and Mo/Co catalysts supported on MgO. They observed that molybdenum and tungsten are both promoters of the synthesis of FWNT and that the materials prepared from W/Co catalysts are easier to purify than those prepared from Mo/Co catalysts. Ishikawa et al. [7] have investigated the addition of W or W₂C to Co for the synthesis of multi-walled carbon nanotubes (MWNT) by hot-filament CVD with methanol as the carbon source and also evidenced the promoter effect of tungsten. In this work, we study the influence of the ratio between W and Co in MgO-based catalysts on the diameter and the number of walls of CNT.

2. Experimental

2.1. Catalysts preparation

The catalysts were prepared by combustion synthesis [8] from Mg(NO₃)₂·6H₂O; Co(NO₃)₂·6H₂O and Na₂WO₄·2H₂O in solution with citric acid at a combustion temperature of 550 °C

* Corresponding author: Fax: +33 5 61 55 61 63.

E-mail address: flahaut@chimie.ups-tlse.fr (E. Flahaut).

(15 min). The powders were calcined in air (450 °C, 1 h) to eliminate the carbon residues coming from the partial decomposition of citric acid. The target W/Co ratios (of atomic percent) were fixed to W/Co = 0; 0.33; 0.5; 1; 2; 3; pure tungsten. The catalytic materials obtained were called A–G.

2.2. CCVD synthesis

Three grams of catalyst (A–G) were placed in an alumina boat. CCVD was performed in a tubular silica reactor at 1000 °C in H₂–CH₄ atmosphere (18 mol.% CH₄). The so-obtained CNT–W/Co–MgO composite powders (R–A to R–G) were washed with concentrated HCl aqueous solution in order to dissolve the catalyst [10], thus producing the so-called extracted samples (CNT-A to CNT-G).

2.3. Characterisation techniques

The elemental analysis of the catalysts composition was obtained by atomic absorption spectroscopy. The carbon content in the composite powders and extracted samples was determined by flash combustion with an accuracy of 2 wt.%. Flash combustion is based on the complete and instantaneous oxidation of the sample; carbon is oxidized into CO₂ which is detected by a thermal conductivity detector, giving an output signal proportional to the concentration in the sample. The BET specific surface area of all samples was measured by N₂ adsorption at liquid-N₂ temperature (Micromeritics FlowSorb II 2300), with an accuracy of 3%. X-ray diffraction (XRD) patterns were obtained using Cu–K_α radiation ($\lambda = 0.15418$ nm, Bruker Endeavor D4). Raman spectra (laser excitation 632 nm) were obtained with a Jobin-Yvon LabRAM HR 800. Five Raman spectra were averaged for each sample. FEG-SEM observations were performed at 5kV with a JEOL-JSM-6700F field emission microscope. TEM observations were performed with a JEOL-JEM-1011 at 100 kV for medium magnification and with a JEOL-JEM-2010 operated at 200 kV for HRTEM.

3. Results

3.1. Catalytic materials

Elemental analysis revealed an important loss of tungsten as compared to the target composition and experimental W/Co

ratios were thus: 0; 0.0017, 0.018, 0.076, 0.75, 1.1; pure tungsten (Table 1).

WO₃ is known to sublime at a relatively low temperature (550 °C) in air at atmospheric pressure [9], and we thus propose that tungsten loss occurred mainly during the synthesis of the catalyst by combustion. The specific surface area (SSA) of the catalysts decreased with increasing W/Co ratio from 138 m² g⁻¹ for W/Co = 0 (A) to 23 m² g⁻¹ for W/Co = 1.1 (F). However for catalyst G, the SSA was higher (80 m² g⁻¹). The XRD patterns revealed only peaks corresponding to MgO. SEM images (not shown) showed spherical grains with a diameter ranging from ca. 20 nm to 200 nm.

3.2. Composite powders

Whatever the W/Co ratio, the SSA of the composite powders containing both elements is close to ca. 120 m² g⁻¹. By contrast, R–A and R–G have a significantly lower SSA: (63 and 80 m² g⁻¹, respectively). The smallest addition of tungsten was at the origin of the increase in the carbon quantity (from 4.1% for R–A to 30.8% for R–F) (Table 1). This is in agreement with XRD data showing a continuous increase in the intensity of the (002) carbon peak with increasing W/Co ratio (Fig. 1a). For samples R–B to R–F, the formation of carbon species increased SSA values. This increase was probably not only due to the addition of carbon species because it is known that some sintering of the catalyst generally occurs during CCVD since it is performed up to 1000 °C, i.e. higher than the calcination temperature during catalyst synthesis. In most samples, but not for R–A, this sintering effect was compensated by the formation of carbon species. The SEM images of R–A (Fig. 2a) and R–G revealed only very few filamentous species, in agreement with the low SSA [11]. For all other materials, long and flexible filaments, clearly identified as CNT or CNT bundles (10–40 nm) in previous works, were observed (Fig. 2(b–d)). In all specimens containing both W and Co, the quantity of CNT seemed almost constant, as well as the diameter of the bundles. For the two highest proportions of W (R–E Fig. 2d and R–F), carbon nanofibres (CNF) were evidenced in addition to CNT. The number of CNF was more important in R–F than in R–E.

3.3. Extracted samples

The increasing proportion of tungsten led to a decrease in the SSA of the extracted CNT samples (from 873 m² g⁻¹ for

Table 1 – Description and characteristics of catalysts (A–G), corresponding composite powders (R–A to R–G) and CNT samples (CNT-A to CNT-G).

Catalytic materials			Composite powders			CNT samples		
Ref.	Specific surface area (m ² g ⁻¹)	Experimental W/Co ratio	Ref.	Specific surface area (m ² g ⁻¹)	Carbon content Cn (wt.%)	Ref.	Specific surface area (m ² g ⁻¹)	Carbon analysis Ce (wt.%)
A	138 ± 5	pure Co	R–A	63 ± 2	4.2 ± 0.1	CNT-A	873 ± 27	88 ± 2
B	111 ± 4	0.0017	R–B	121 ± 4	19.5 ± 0.4	CNT-B	664 ± 20	92 ± 2
C	99 ± 3	0.018	R–C	130 ± 4	22.7 ± 0.5	CNT-C	603 ± 19	92 ± 2
D	78 ± 3	0.076	R–D	127 ± 4	24.3 ± 0.5	CNT-D	500 ± 15	92 ± 2
E	41 ± 2	0.75	R–E	120 ± 4	32.1 ± 0.7	CNT-E	366 ± 11	93 ± 2
F	23 ± 1	1.1	R–F	118 ± 4	30.8 ± 0.7	CNT-F	318 ± 10	93 ± 2
G	80 ± 3	pure W	R–G	80 ± 3	16.2 ± 0.4	CNT-G	335 ± 11	82 ± 2

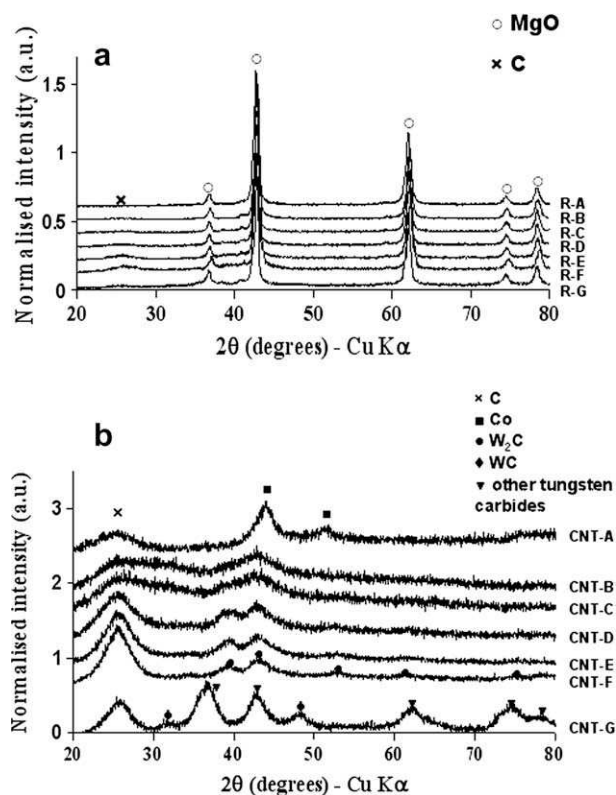


Fig. 1 – XRD patterns of (a) composite powders and (b) extracted samples.

CNT-A to $335 \text{ m}^2 \text{ g}^{-1}$ for CNT-G, Table 1). The decrease in the SSA can be attributed to an increase in the number of walls and/or increase in bundling and/or the quantity of CNF [11].

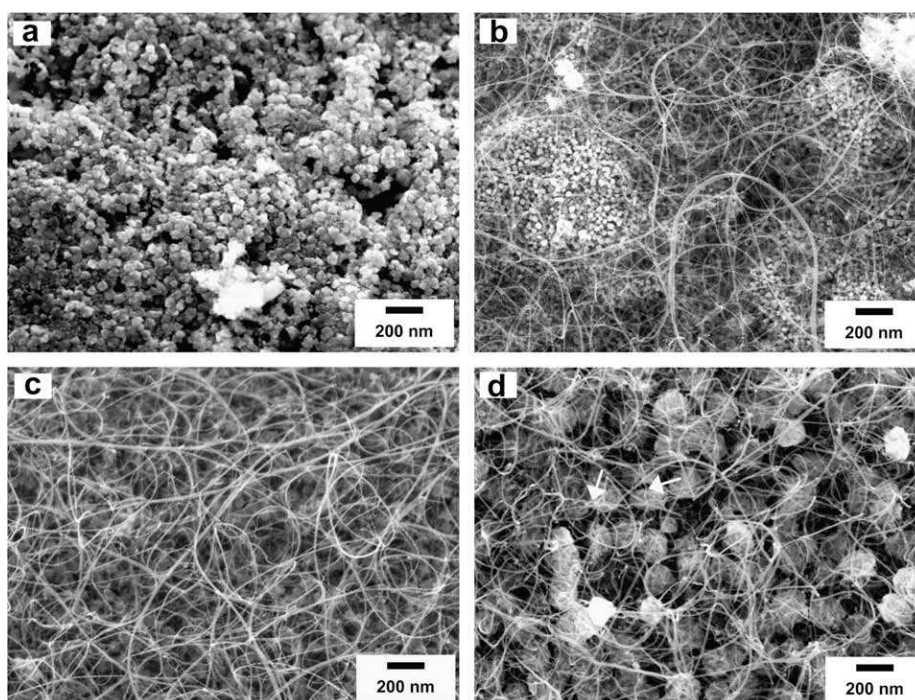


Fig. 2 – SEM images of composite powders (a) R-A (b) R-B (c) R-C and (d) R-E, an example of carbon nanofibres is indicated by a white arrow.

For all W/Co ratios, the carbon content was almost constant (average 92 at.%). For pure W, it was lower but remained high (81 at.%) after extraction. However, SEM images of samples R-A (Fig. 2a) and R-G show only very few carbon filamentous species. In all samples containing both W and Co, W_2C was detected on the XRD patterns (Fig. 1b). The presence of the W_2C peaks was more and more obvious as the proportion of W increased. For CNT-G, peaks corresponding to WC and additional tungsten carbides WC_{1-x} or possibly an oxycarbide $\text{W}(\text{C},\text{O})$ were observed (Fig. 1b). The fact that W_2C is detected only in the samples containing both Co and W indicates that its formation requires their simultaneous presence. The observed broadening of the (002) carbon peak (Fig. 1b) with decreasing W ratio could be correlated with the increase in the number of walls of the CNT [12]. All the extracted samples were observed by TEM (Fig. 3). For sample CNT-G, disorganised carbon was observed. An increase in the proportion of CNF with W/Co ratio (CNT-E and F, Fig. 3e, f) was evidenced. The CNT diameter seemed to increase with the proportion of W. Samples CNT-B to CNT-E were observed by HRTEM (Fig. 4). Measurement of about 80 individual CNT on such images allowed determining the distribution of the number of walls and that of the inner and outer diameters. All these parameters increased with the proportion of W (Table 2, Fig. 4).

For sample CNT-E, some CNT displayed a number of walls which was different on each side of the tube axis (Fig. 4d). This could correspond to a scroll-like structure [13], and would be the signature of a specific growth mechanism. The average inner diameter seems to increase rapidly with W/Co at low W content, but then does not vary anymore. By contrast, the outer diameter keeps increasing. This could be related to a thickening of the CNT by addition of outer walls

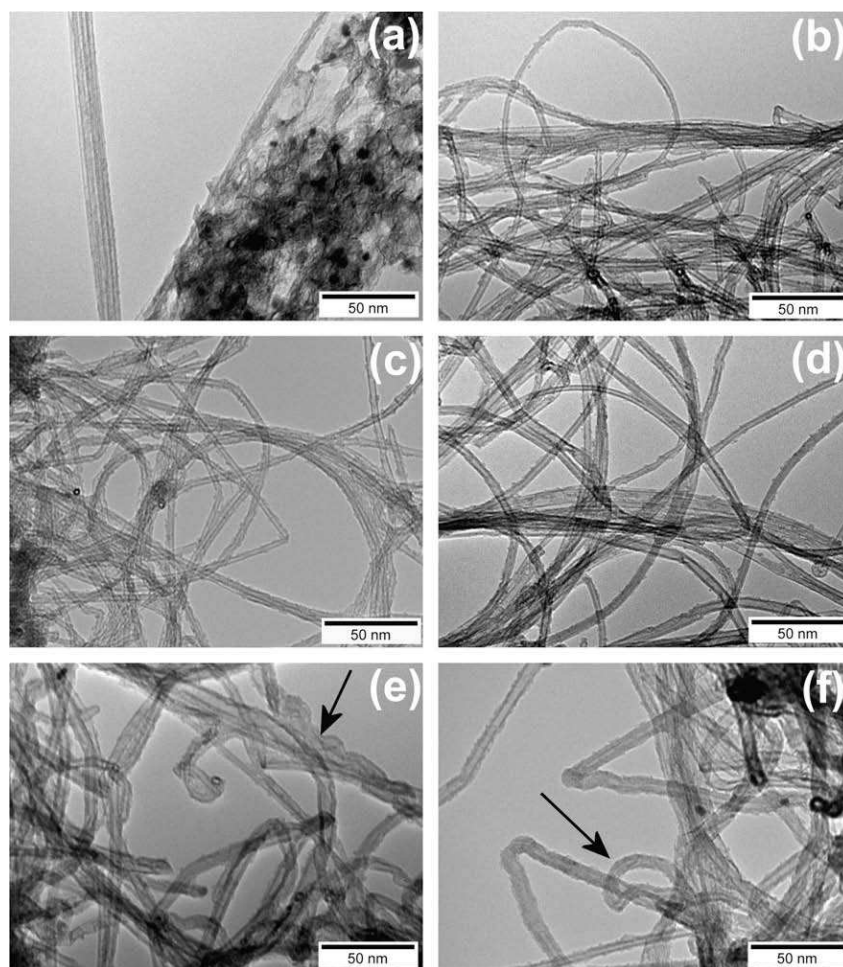


Fig. 3 – TEM images of (a) CNT-A, (b) CNT-B, (c) CNT-C, (d) CNT-D, (e) CNT-E and (f) CNT-F (some carbon nanofibres are indicated by black arrows).

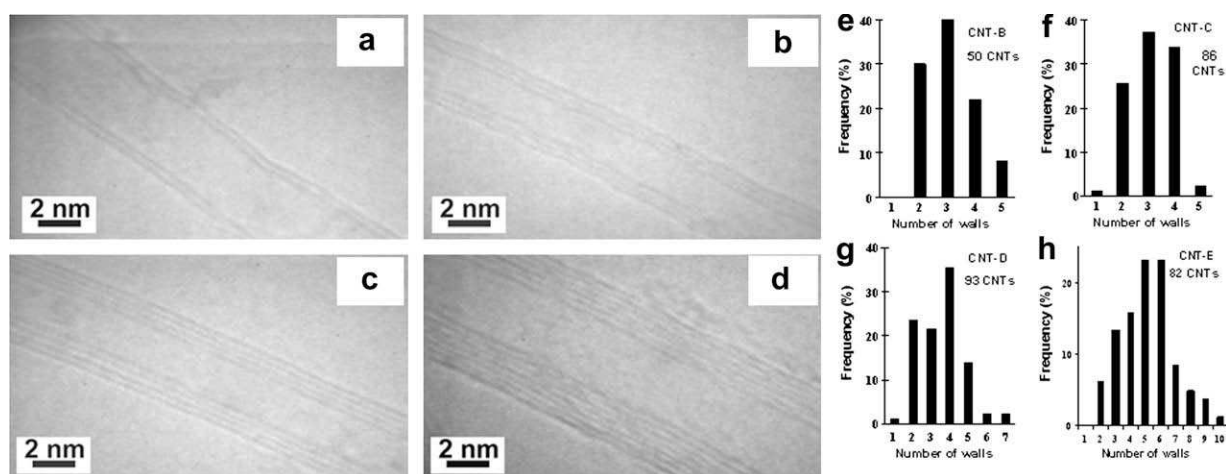


Fig. 4 – TEM images and distribution of the number of walls in samples (a, e) CNT-B, (b, f) CNT-C, (c, g) CNT-D, and (d, h) CNT-E.

as the W/Co ratio increases. This could be a good indication that the *Yarmulke* growth mechanism [14] is probably not involved here, as it is generally used on the contrary to explain the thickening of CNT by progressive addition of inner walls.

The Raman analysis of these samples revealed RBM peaks for all samples except for CNT-G (Fig. 5). The RBM peaks are characteristic of the presence of CNT having a diameter ranging from 0.65 nm to 1.80 nm [15]. The ratio between the inten-

Table 2 – Inner and outer diameter distribution of CNT samples.

	Inner diameter (nm)		Outer diameter (nm)	
	Range	Mean	Range	Mean
CNT-B	0.91–3.65	1.93	2.26–5.07	3.39
CNT-C	0.98–4.94	2.11	1.19–5.64	3.58
CNT-D	0.68–5.07	2.37	1.94–6.22	4.15
CNT-E	0.81–6.57	2.46	2.85–10.07	5.36

sity of the D band and the G band ($I_{D/G}$) allows to roughly estimating the structural quality of the samples. The higher is $I_{D/G}$, the more structural defects are present. $I_{D/G}$ decreased strongly upon the introduction of tungsten ($I_{D/G} = 1.6$ for CNT-A and 0.4 for CNT-B, Fig. 5c). However, when the proportion of W was much higher (CNT-F), $I_{D/G}$ increased up to 1. The highest $I_{D/G}$ value (2.2) was observed for pure W (CNT-G). The increase in $I_{D/G}$ was in good agreement with the HRTEM observations which revealed more and more structural defects when increasing the W/Co ratio. We also noticed the presence of increasing amounts of CNF and amorphous carbon. In the case of CNT prepared from catalysts containing both Co and W, the decrease in SSA with increasing W/Co ratio could be correlated to the progressive formation of more and more CNF. This decrease could also be explained by the thickening of the CNT due to the increasing number of walls [11] (Fig. 4). On the one hand, the carbon content in the composite powders increased with the W/Co ratio, whereas the SSA of the composite powders remained constant, which also indicates that the additional carbon is less and less in the form of CNT. All these observations lead to the conclusion that a very

small addition of W-Co favours the synthesis of CNT. However, as the W/Co ratio increases, the formation of CNF becomes more and more important, to the detriment of CNT.

4. Discussion

Herrera et al. [5] have obtained a better sample quality for Mo/Co catalysts ($I_{D/G} = 0.05$) as compared to W/Co catalysts ($I_{D/G} = 0.14$). Note that their experimental conditions were very different (CO instead of CH_4 , SiO_2 substrate instead of MgO).

Ishikawa et al. [7] have synthesised MWNT with lower selectivity (3–12 walls) and slightly larger diameter (average 6 nm) as compared to this work (from 3.4 nm for CNT-B to 5.4 nm for CNT-E). No information about the yield was given. They prepared their samples from zeolite-supported catalysts (Co, Co + W or Co + W_2C), with methanol as the carbon supply. They reported that a lower sample quality was obtained in the case of Co + W_2C catalysts. This could be correlated with our observation that for the samples prepared from the catalysts containing the highest proportions of W (in association with Co), the quality of the samples decreased with increasing amounts of W (also corresponding to more and more obvious presence of W_2C in the samples from XRD analysis).

Qian et al. [6] have synthesised FWNT with MgO-supported Mo/Co or W/Co catalysts. Their CCVD conditions were close to this study (1000 °C, CH_4 only used during dwell time) and they obtained rather similar results (CNT with 2–5 walls), however with possibly larger diameters. The quality of the samples is difficult to compare with our work because no Raman data was provided.

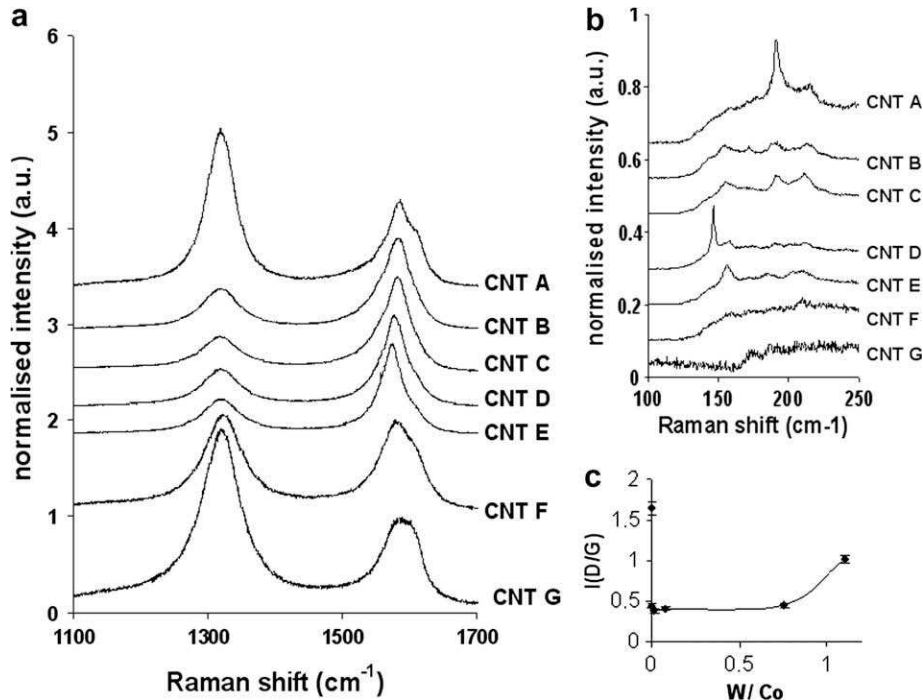


Fig. 5 – (a) Raman spectra of extracted samples (b) RBM spectra and (c) evolution of the intensity ratio between the D and G bands ($I_{D/G}$) with the W/Co ratio.

It seems that in most cases, the actual catalyst composition was not checked after synthesis. We have shown that W is easily lost during the preparation, leading to a final W/Co ratio which can be quite lower from the target. This may also make comparisons even more difficult.

The carbon content is much higher when using W/Co catalysts than Mo/Co catalysts containing a similar proportion of Co [1,10]. The best quality of CNT was obtained with a 1/3 Mo/Co ratio, and lead to ca. 10 wt.% of carbon in the composite powder, and a CNT sample containing ca. 90 wt.% carbon with a SSA of ca. $980 \text{ m}^2 \text{ g}^{-1}$. The corresponding W/Co sample would be obtained with a catalyst composition between samples D and E. The corresponding composite powder would thus have a carbon content close to ca. 28 wt.% and the extracted CNT sample would ca. 92 wt.% carbon with a SSA between 400 and $450 \text{ m}^2 \text{ g}^{-1}$. According to our TEM observations (Fig. 4f, g), this sample would contain CNT with 2–6 walls, with a high proportion of the latter. This must be compared to the high selectivity towards DWNT achieved in the corresponding Mo/Co sample. Thus, the higher activity of W/Co catalysts for the decomposition of CH_4 seems to be correlated to a lesser selectivity. This is also suggested by the important difference between the $I_{D/G}$ ratios for these two samples (ca. 0.09 for Mo/Co to be compared to ca. 0.4 for W/Co).

These results show that addition of very small amounts of W to Co allows the synthesis of CNT with a low number of walls (typically between 2 and 5) with a better yield than in the case of Mo/Co catalysts, but with a lower selectivity.

There is a general agreement that W acts as a promoter for the synthesis of CNT, at least when associated to Co.

5. Conclusion

We succeeded in synthesising CNT from W/Co–MgO catalysts. We have shown that even for very small additions, W acts as a promoter for the synthesis of CNT by decomposition of CH_4 , as molybdenum does. Increasing the W/Co ratio leads to a progressive increase in the number of walls and CNT diameter. Although the selectivity was not as good as for Mo/Co catalysts, CNT with a number of walls ranging between 2 and 5 and with a diameter distribution between 2 and 6 nm were synthesised with a good yield.

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