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# Spark plasma sintering of double-walled carbon nanotubes

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## A B S T R A C T

Bulk samples of double-walled carbon nanotubes are prepared for the first time. The best spark plasma sintering conditions are (1100 °C, 100 MPa). Raman spectroscopy and scanning electron microscopy show that the nanotubes are undamaged. The density is equal to 1.29 g cm<sup>-3</sup> and the pores are all below 6 nm in diameter. The electrical conductivity is equal to 1650 S cm<sup>-1</sup>. The transverse fracture strength is equal to 47 MPa.

The preparation of bulk carbon nanotubes (CNTs) materials is currently attracting a growing interest because such materials may have exceptional technical and functional properties. Interestingly, all the reported works [1–5] are performed on multi-walled CNTs (MWCNTs) 10–40 nm in diameter, except two where single-wall carbon nanotubes (SWCNTs) are used [6,7]. An early study used hot-pressing [1] and recent works [2–6] use spark plasma sintering (SPS). SPS [8] typically differs from hot-pressing by the application of a current to the pressing die and sample, as opposed to radiative heating. Thus, higher heating rate and lower temperatures could allow to avoid damaging the CNTs. In the present paper, the preparation of bulk double-walled carbon nanotubes (DWCNTs) by SPS is reported for the first time. DWCNTs are widely considered as an intermediate class bridging the gap between SWCNTs and MWCNTs. The first aim was to establish experimental conditions that result in no damage to the DWCNTs. Density and porosity have been characterized. The electrical conductivity (1650 S cm<sup>-1</sup>) and the transverse fracture strength (47 MPa) have been measured.

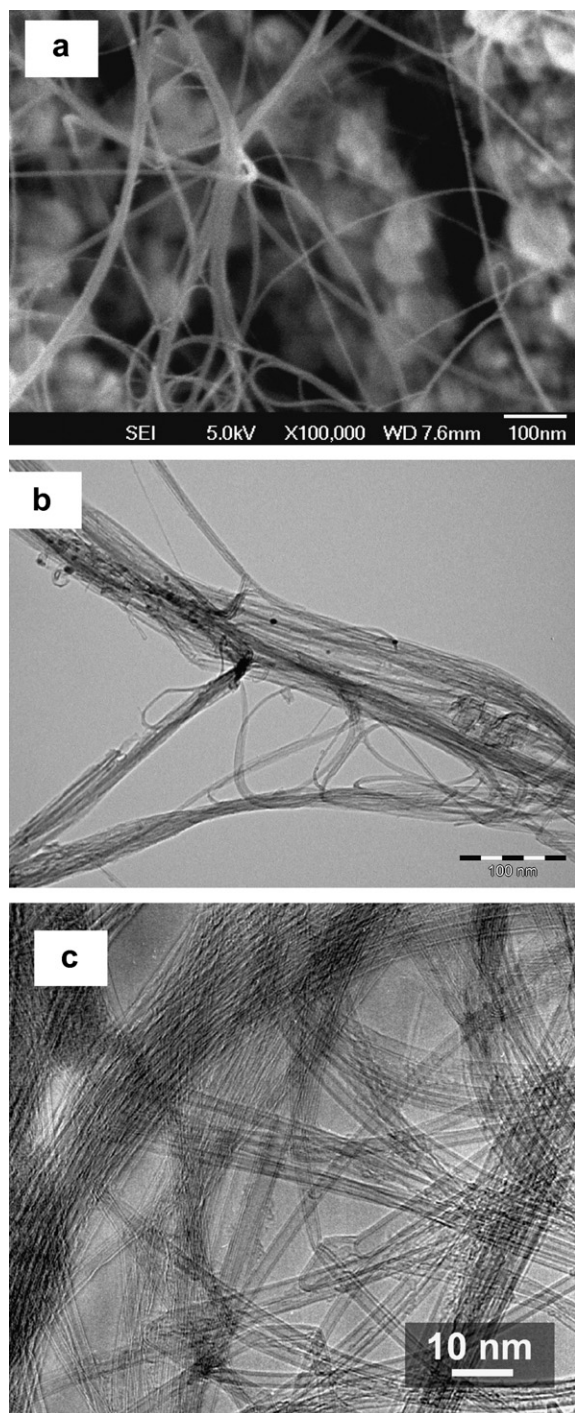
The DWCNTs synthesis was described elsewhere [9]. Briefly, a Mg<sub>0.99</sub>(Co<sub>0.75</sub>Mo<sub>0.25</sub>)<sub>0.01</sub>O powder was submitted to a catalytic chemical vapor deposition treatment (H<sub>2</sub>-CH<sub>4</sub> with 18 mol% CH<sub>4</sub>, maximum temperature 1000 °C) producing a CNT-Co/Mo-MgO nanocomposite powder. It was shown [9] that the CNT are mostly DWCNTs (80%), SWCNTs (15%) and CNTs with three walls (5%), with the outer diameter in the range 1–3 nm and the inner diameter in the range 0.5–2.5 nm. This powder was soaked in a 37% HCl aqueous solution in order to dissolve MgO and most of the metal catalyst, without damage the DWCNTs [10]. The DWCNTs suspension was washed with deionized water until neutrality and subsequently filtered and washed with ethanol. Finally, the sample was dried overnight at 80 °C in air. The carbon content (88.4 ± 0.2 wt% corresponding to ca. 97 mol%) was determined

by flash combustion. Typical field-emission-gun scanning electron microscopy (FEG-SEM, JEOL JSM 6700F) before the HCl treatment (Fig. 1a), transmission electron microscopy (TEM, JEOL JEM 1011) (Fig. 1b) and high-resolution TEM (HRTEM, JEOL JEM 2100F) (Fig. 1c), both after the HCl treatment, indeed reveal low diameter CNTs either isolated or in bundles. The high-frequency range of the Raman spectrum (Fig. 2) (averaged on four spectra, Jobin-Yvon LabRAM HR 800, laser excitation at 632.82 nm) shows the D band (ca. 1320 cm<sup>-1</sup>) and the G band (ca. 1580 cm<sup>-1</sup>). The ratio between the intensity of the D band and the G band, I<sub>D/G</sub>, is equal to 0.17. An increasing I<sub>D/G</sub> value corresponds to a higher proportion of sp<sup>3</sup>-like carbon, which is generally attributed to the presence of more structural defects. The radial breathing modes (RBM) are observed in the low-frequency range of the spectrum (inset in Fig. 2). The peak frequencies are inversely proportional to the CNT diameters. The detected diameters are in the range 0.9–2.2 nm. Note firstly that since the Raman process is influenced by optical resonance, it is impossible to detect all present CNTs using only one wavelength, and secondly that the peak intensities do not reflect the real amount of individual CNTs because of the resonance effect which amplifies the Raman signal from some CNTs. The specific surface area (1000 ± 100 m<sup>2</sup>/g) was measured by the BET method using N<sub>2</sub> adsorption at liquid-N<sub>2</sub> temperature (Micromeritics ASAP 2000). It is in good agreement with the expected value for the sample [11]. The pore size distribution calculated from the N<sub>2</sub> desorption curve will be presented later in the paper.

The DWCNTs powder was divided into several batches (about 120 mg each), which were consolidated by SPS (Dr. Sinter 2080, SPS Syntex Inc.). They were loaded into a graphite die 8 mm in diameter. A sheet of graphitic paper was placed between the punch and the powder as well as between the die and the powder for easy removal. The DWCNTs were sintered

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**Fig. 1 – FEG-SEM image (a) of the CNT-Co/Mo-MgO nanocomposite powder, TEM image (b) and HRTEM image (c) of the carbon nanotubes after HCl dissolution of the catalyst.**

in vacuum (residual cell pressure <5 Pa). A pulse configuration of 12, 3.3 ms-pulses followed by two periods (6.6 ms) of zero current was used. Heating rates of 300 °C/min and 100 °C/min were used from room temperature to 600 °C and from 600 °C to the maximum temperature (1000–1850 °C), respectively. A uniaxial pressure (2 or 100 MPa) was gradually applied during the ramp to 600 °C and maintained up to the maximum tem-

perature where a dwell time (3 or 5 min) was applied. Natural cooling and uniaxial pressure release were applied. Eight materials (noted A–H in the following) were prepared using different (T and P) couples : (A = 1000 °C, 100 MPa), (B = 1100 °C, 100 MPa), (C = 1200 °C, 100 MPa), (D = 1600 °C, 100 MPa), (E = 1800 °C, 100 MPa), (F = 1600 °C, 2 MPa), (G = 1800 °C, 2 MPa) and (H = 1850 °C, 2 MPa). Only three pellets (B, C and H) did not break during removal from the die, although C broke after the FEG-SEM observations. The density calculated from the mass and dimensions is equal to  $1.23 \text{ g cm}^{-3}$ ,  $1.13 \text{ g cm}^{-3}$  and  $0.87 \text{ g cm}^{-3}$  for pellets B, C and H, respectively. The lower value for H could reflect the lower applied pressure (2 MPa). FEG-SEM images (Fig. 3) of the polished surface of specimens B and C reveal an orientation of the DWCNTs, probably due to shear stresses developed during polishing. However, the DWCNTs do not appear to be damaged. By contrast, FEG-SEM images (not shown) of specimen H do not show many DWCNTs, which could reveal important damage. The Raman spectra (averaged on six spectra) for B and H (Fig. 4) confirm these results. Indeed,  $I_{D/G}$  for specimen B (16%) is similar to the value found for the powder (17%) whereas it is much higher (51%) for specimen H. Moreover, RBM peaks are still clearly detected for B but not for H. These results are in sharp contrast with the report for SWCNTs [7] that the normalized  $I_G/I_D$  ratio strongly decreases, i.e. that  $I_D/I_G$  strongly increases, upon the increase of the SPS temperature, the more so if a higher uniaxial pressure is applied. The difference between the damaged SWCNTs [7] and the present undamaged DWCNTs could arise from their origin (arc-discharge SWCNTs and CCVD DWCNTs) and the purification method. Indeed, a mild acidic soaking that does not damage the DWCNTs is used here, whereas the purification procedure described by Yamamoto et al. [6] involves thermal treatments in air at a temperature as high as 500 °C prior to the acidic treatment, which is much more prone to damage the SWCNTs. The specific surface area was found equal to  $482 \text{ m}^2/\text{g}$  for specimen B, which is about half the value found for the powder. The pore size distribution for the powder (Fig. 5a) and specimen B (Fig. 5b) was calculated from the  $\text{N}_2$  desorption curve, the detailed analysis of which is beyond the scope of this paper. The results clearly show that all the pores for specimen B have a diameter lower than 6 nm. Zhang et al. [2] reported TEM observation of nanometric pores for a sample of MWCNTs (SPS, 2000 °C, 50 MPa). The pores with a higher diameter detected for the powder have been eliminated by the SPS treatment, reflecting probably the influence of the applied pressure and the strong increase in the compacity of the material.

For the last part of the study, specimens B and H were prepared by SPS in the form of pellets 20 mm in diameter. The sheet of graphitic paper was removed by very gentle polishing using SiC paper (grade 800). The density for pellets B and H is equal to  $1.29 \text{ g cm}^{-3}$  and  $0.89 \text{ g cm}^{-3}$ , respectively. The slightly higher values compared to the 8 mm pellets could reflect the more favourable thickness/diameter ratio. The transverse fracture strength ( $\sigma_f$ ) was determined by the three-point-bending test on five ( $1.6 \times 1.6 \times 18 \text{ mm}^3$ ) specimens machined with a diamond blade. Cross-head speed was fixed at 0.1 mm/min.  $\sigma_f$  is equal to  $47 \pm 20 \text{ MPa}$  for specimen B and  $14 \pm 3 \text{ MPa}$  for specimen H. The value for B is similar to that reported by Li et al. [4] for MWCNTs (SPS, 600 °C,

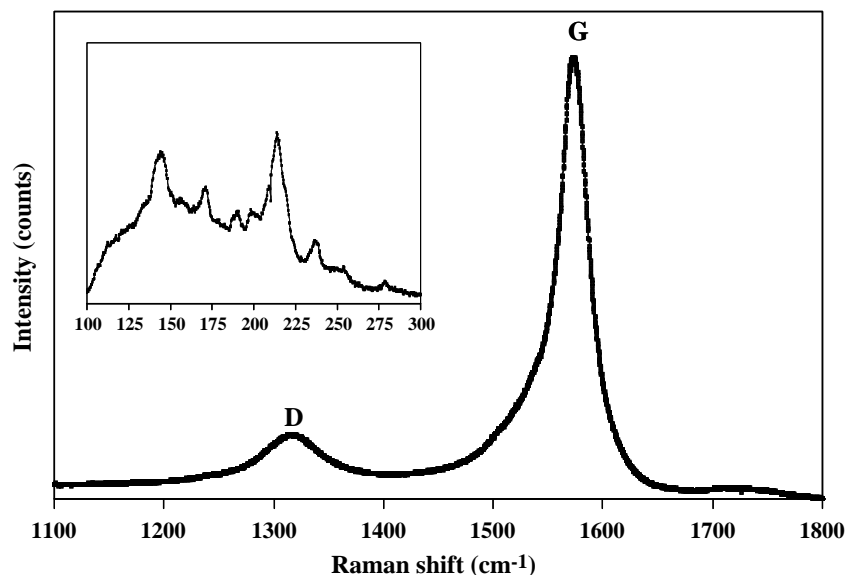


Fig. 2 – High-frequency range of the Raman spectrum (632.82 nm) of the DWCNTs powder and (inset) the low-frequency range showing the RBM.

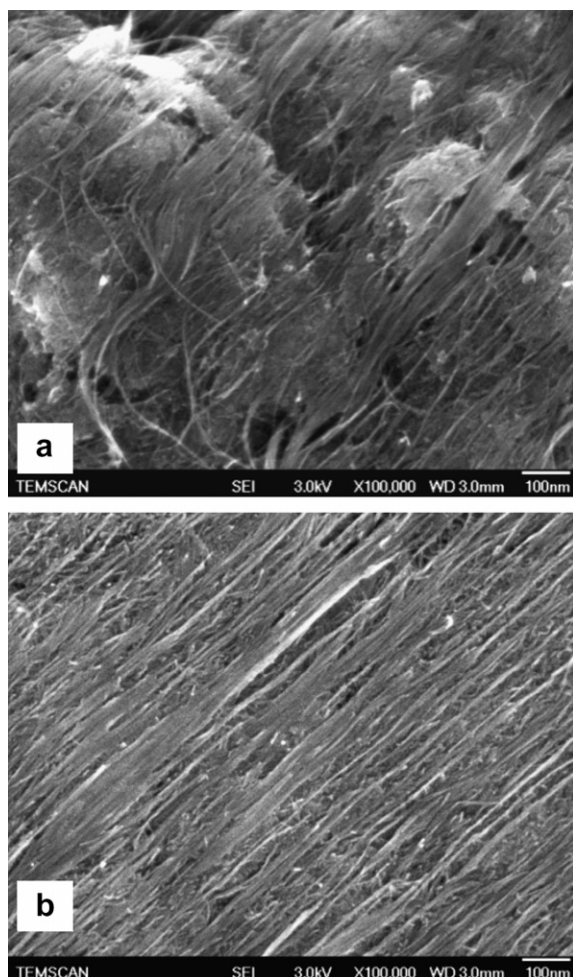


Fig. 3 – FEG-SEM images of the surface of (a) specimen B and (b) specimen C, showing alignment after polishing.

60 MPa) and is thought to reflect a weak interfacial force between neighbouring DWCNTs. Note also that the fracture is accompanied by delamination, which could reflect a certain degree of alignment of the DWCNTs in the pressing plane. The electrical conductivity was measured at room temperature with dc currents on parallelepipedic specimens ( $1.6 \times 1.6 \times 8 \text{ mm}^3$ ), parallel to their length, i.e. perpendicular to the pressing axis. The current densities used were lower than  $160 \text{ mA/cm}^2$  (Keithley 2400). The electrical conductivity is equal to  $1650 \text{ S cm}^{-1}$  for specimen B and much lower ( $200 \text{ S cm}^{-1}$ ) for specimen H due to damaged DWCNTs. These values are lower than those ( $3300\text{--}5000 \text{ S cm}^{-1}$ ) claimed [1] for MWCNTs 30–40 nm diameter (hot-pressing,  $2000 \text{ }^\circ\text{C}$ , 25 MPa). However, they are much higher than the conductivity ( $80 \text{ S cm}^{-1}$ ) reported [3] for MWCNTs (SPS,  $1700 \text{ }^\circ\text{C}$ , 60 MPa).

In conclusion, bulk samples of DWCNTs have been prepared for the first time. The best SPS experimental conditions are ( $1100 \text{ }^\circ\text{C}$ , 100 MPa). The density is equal to  $1.29 \text{ g cm}^{-3}$  and the pores are all below 6 nm in diameter. The electrical conductivity is equal to  $1650 \text{ S cm}^{-1}$ . The transverse fracture strength is equal to 47 MPa. Work is in progress to increase the interfacial force between neighbouring DWCNTs.

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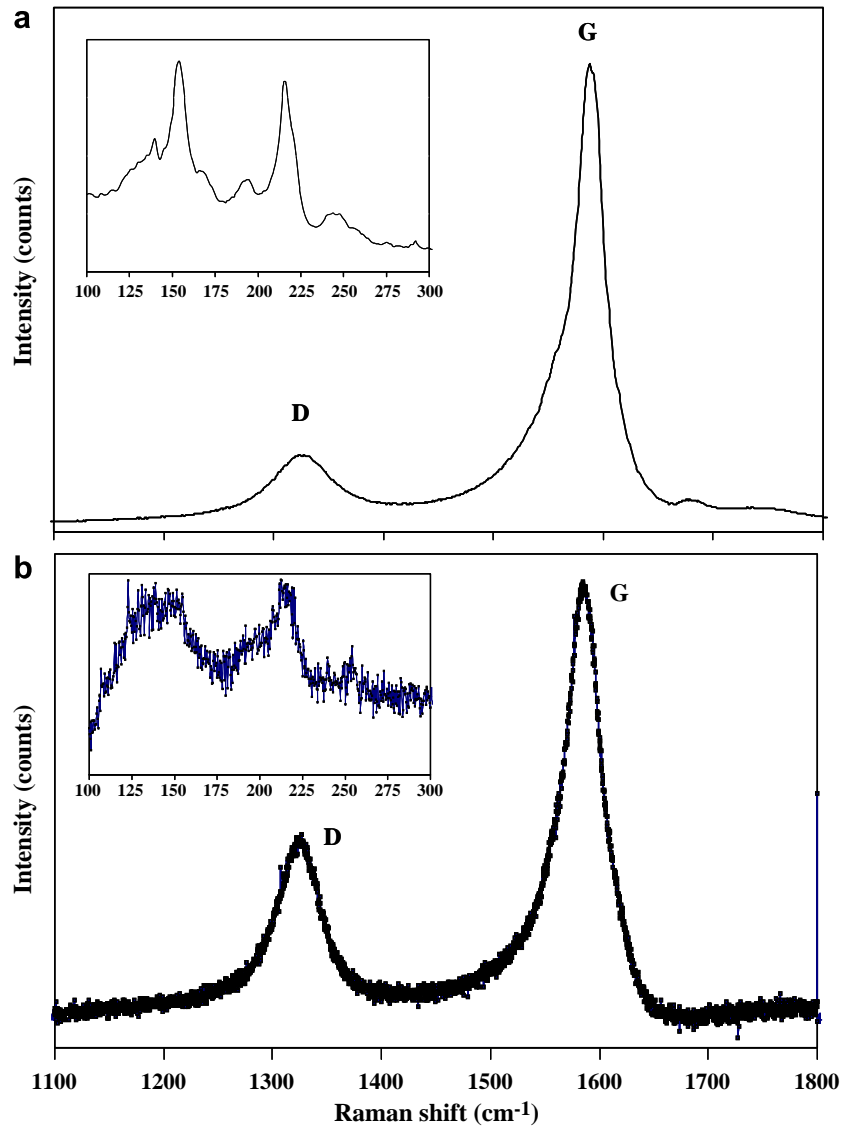


Fig. 4 – High-frequency range of the Raman spectrum (632.82 nm) and (inset) the low-frequency range showing the RBM for (a) specimen B and (b) specimen H.

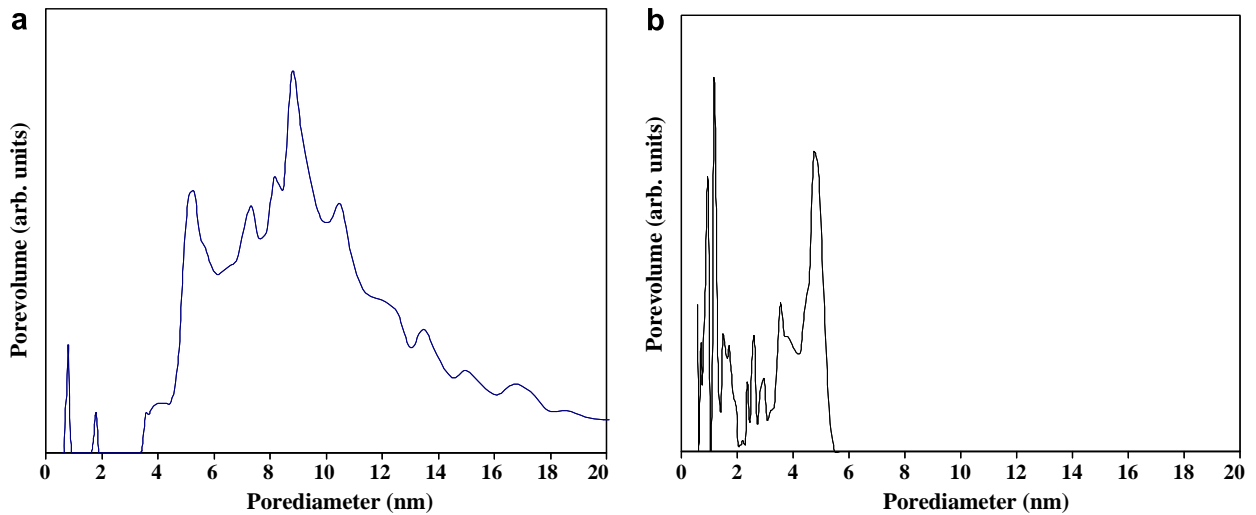


Fig. 5 – Pore size distribution as deduced from N<sub>2</sub> desorption curves for (a) the DWCNTs powder and (b) specimen B.

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