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Structure in nascent carbon nanotubes revealed by spatially resolved Raman spectroscopy

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ABSTRACT

The understanding of carbon nanotube (CNT) growth is crucial for the control of their production. In particular, the identification of structural changes of carbon possibly occurring near the catalyst particle in the very early stages of their formation is of high interest. In this study, samples of nascent CNT obtained during nucleation step and samples of vertically aligned CNT obtained during growth step are analysed by combined spatially resolved Raman spectroscopy and X-ray diffraction measurements. Spatially resolved Raman spectroscopy reveals that iron-based phases and carbon phases are co-localized at the same position, and indicates that sp^2 carbon nucleates preferentially on iron-based particles during this nucleation step. Depth scan Raman spectroscopy analysis, performed on nascent CNT, highlights that carbon structural organisation is significantly changing from defective graphene layers surrounding the iron-based particles at their base up to multi-walled nanotube structures in the upper part of iron-based particles.

1. Introduction

Aligned multi-walled carbon nanotubes (A-MWNTs) are promising nanostructured networks for a large range of applications in various fields such as separation or filtration [1], supercapacitors [2], and composite materials [3,4]. They are mainly prepared by CVD (chemical vapour deposition) processes involving, either a deposition of a metal film before the reaction with a carbonaceous source [5–7], or the formation of catalyst particles from a metal precursor which is injected together with the carbon precursor [8–11]. Concerning this latter method, liquid precursors are generally injected in the reactor either with syringes or as liquid aerosols and A-MWNTs are subsequently grown with, generally, a high growth rate and almost no by-products (amorphous carbon) among nanotubes [8–12]. Such processes offer the advantage to be continuous and to be easily scalable. Their development, in order to extend their potentialities, is strongly related to the precise control of carbon nanotube (CNT) growth which is a direct result of the understanding of their growth mechanisms. This is one of the motivations for the study of nanotube formation which has been widely investigated by researchers all over the world [13]. Ex-situ physico-chemical analyses of samples synthesized under precise conditions are focused on the size and shape of catalyst particles as well as on their physical state and their chemical composition and structure [11, 14–16]. The analysis of carbon in such samples has been also investigated by different techniques such as electron microscopy (SEM or TEM), Raman spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy [11,15,17–19]. Nevertheless, complementary information regarding global quantitative carbon structure changes occurring on nanotubes near the catalyst particles, from the CNT nucleation step up to the CNT growth step, still needs to be completed.

Our previous works regarding A-MWNT carpet synthesized by aerosol-assisted CCVD (Combustion chemical vapour deposition) process studied through ex-situ analysis demonstrated that (i) different iron-based phases are occurring in the same sample [15,19], (ii) iron oxide is formed during the cooling step [15], and (iii) nanotubes are obtained through a base-growth mechanism [11,20]. X-ray diffraction allows one to quantify the alignment degree of nanotubes in macroscopic carpets [19,21]. Raman spectroscopy demonstrates that such nanotubes exhibit a high structural quality as compared to nanotubes generally grown by CVD [12], and XPS experiments (X-rays photoelectron spectroscopy), performed on samples resulting from the early stages of nanotube growth, show the occurrence of sp^2 carbon in the

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early stages of CNT growth [11]. More recently, in-situ X-ray diffraction experiments on A-MWNT carpet synthesized by aerosol-assisted CCVD process allowed us to show that particles giving rise to CNT growth are cementite nanoparticles [22].

The present study couples global and local analyses, based on ex-situ X-ray diffraction and Raman spectroscopy. The recent developments in spatially resolved Raman spectroscopy allowed us to analyse samples obtained during CNT nucleation step (very early stages of CNT synthesis), formed of nascent CNT on the catalyst particles. Thus, it was possible to get Raman mapping of both catalyst nanoparticles and CNT. Our work gives evidence of carbon structural changes between nucleation and growth stages. By analysing the D and G bands obtained on CNT samples produced during the nucleation step, we report that carbon structural organisation is significantly changing from defective graphene layers surrounding the particles at their base up to multi-walled nanotube structures in the upper part of particles. Alignment of CNT, as determined by X-ray diffraction, differs between the CNT nucleation and growth step.

2. Experimental section

Aligned carbon nanotube samples are synthesized by aerosol-assisted catalytic chemical vapour deposition (AA-CCVD) from toluene and ferrocene precursors [12,20]. The synthesis set-up and standard procedure have been described previously [9,17]. Briefly, the precursor mixture is made of ferrocene (2.5 wt.%) dissolved in toluene, and the resulting solution is injected through an aerosol and carried by a helium flow (purity 99.999; oxygen impurities 3 ppm-mol H_2O and 2 ppm-mol O_2) in the reactor heated at 850 °C and placed at atmospheric pressure. The cooling step is also performed under helium (same quality). This flexible technique allowed us to control the CNT length thanks to the duration of the continuous injection of precursors and thus to obtain different samples at different growth steps of the CNT. It is important to note that even if the metal catalyst source is injected continuously, the resulting A-MWNT carpets exhibit a high purity with almost no catalyst particles deposited in between the MWNT.

For this study two types of samples are obtained corresponding to two key steps of the growth chronology with different AA-CCVD durations. The first one (sample 1) is obtained after 15 s of synthesis and the second one after 15 min corresponding respectively to MWNT nucleation and growth steps. These two samples are then cooled down [15].

The general morphology and arrangement of the resulting CNT samples were examined in a field emission scanning electron microscope (FEG-SEM; Carl Zeiss Ultra 55). Raman spectroscopy and X-ray diffraction are also carried out ex-situ at room temperature on the resulting samples. Sample corresponding to nucleation step (catalyst nanoparticles and few nucleating CNT) was analysed by Raman spectroscopy first on its top surface and second in the depth of nanoparticles initiating CNT growth (one spectrum every 230 nm) in order to evaluate the carbon changes along nanoparticle agglomerates (few μm). Sample corresponding to the growth step (CNT carpet) was analysed by Raman spectroscopy along the carpet height (one spectrum every 40–50 μm) in order to evaluate the carbon structure changes along the carpet (400 μm thick). Therefore, Raman analysis scale along nanoparticles (nucleation step) is more local as compared to the one performed in the case of carpet (growth step).

Raman spectroscopy was performed with a commercial Witec Alpha 500 spectrometer in a back-scattering configuration. We used excitation wavelengths at 532 nm from a solid state laser diode. The power of the laser beam was kept below 600 μW to prevent any damage on the A-MWNT carpet. All Raman spectra were recorded with a Nikon ×50 objective (NA = 0.75) focusing the light with a 350 nm diameter spot. A dual axis XY piezo stage coupled to a confocal microscope allows mapping Raman intensity with subwavelength accuracy (ca. 120 nm) and in the Z direction with accuracy of about 350 nm. Raman spectra are recorded on each pixel and the integrated intensity of a chosen mode is displayed on a false colour scale.

Furthermore, spectral resolutions of our spectrometer (UHTS300) are (i) <3 cm^{-1} (i.e. 0.009 nm) with a 600 grooves/mm grating and (ii) <0.9 cm^{-1} (i.e. 0.025 nm) with a 1800 grooves/mm grating. In this paper, maps are performed with a 600 grooves/mm grating and spectra with a 1800 grooves/mm grating.

X-ray diffraction experiments were performed on two different setups:

(i) microdiffraction measurements are performed with a monochromatic Cu-Kα ($\lambda = 1.542$ Å) X-ray microbeam of 20 μm diameter size obtained with a multilayer optics coupled with a laboratory rotating-anode generator [23]. The 2D direct-illumination CCD detector allows to measure weak scattering signals such as the (002) CNT peak from the carpet. Measurement along the height of the carpet with a 10 μm step is performed thanks to a motorized translation stage.

(ii) standard laboratory diffraction experiments with a millimetre-size and monochromatic Mo-Kα ($\lambda = 0.711$ Å) beam are performed in order to measure iron phases [15]. The intense X-ray beam allows detecting the weak scattered signals from the small amounts of iron. The short Mo-Kα wavelength gives access to a large Q wavevector domain (1.5–4.5 $Å^{-1}$). It also avoids the X-ray fluorescence background that hinders the weak signals to be observed with Cu-Kα radiation.

3. Results and discussion

Fig. 1 shows SEM images of two different samples formed respectively during CNT nucleation step and CNT growth step on silicon substrates. The first one (sample 1) is obtained during the early growth stages of CNT formation (15 s) corresponding to the CNT nucleation step (Fig. 1(a)). The second one (sample 2) is obtained after a longer CCVD synthesis duration (15 min) corresponding to the CNT growth step (Fig. 1(b)).

In Fig. 1(a) (sample 1), we observe a layer of iron-based catalyst nanoparticles covering the whole silicon wafer surface, and constituting the main part of the sample. We also observe a significant amount of catalyst particle agglomerates with various dimensions from 500 nm to 2 μm [11]. These two areas (A: agglomerated particles and B: film of catalyst nanoparticles) are designated in Fig. 1(a) by two white crosses and are shown with higher magnification in Fig. 1(c) and (d) respectively. Some nanotubes are already occurring even for this early stage and are localized mainly on catalyst particles which are agglomerated. In Fig. 1(b), large scale SEM image of sample 2 shows a typical well-aligned MWNT carpet exhibiting a thickness of 400 μm. These MWNTs are partially filled with iron based phases as described by Pinault et al. [11,24].

In this work, we emphasize first on the study of the CNT obtained during the nucleation step by performing both Raman spectroscopy and X-ray diffraction analysis (XRD) on sample 1. These two techniques are complementary: Raman spectroscopy gives spatially localized information (laser spot ~350 nm) whereas XRD allows one to perform statistical average (XRD beam ~1 mm for this experiment). For this sample grown during the early stages and thus exhibiting a low amount of carbon, Raman spectroscopy is sensitive to both iron-based and carbon phases whereas XRD is mainly sensitive to iron-based phases.

Fig. 2 shows Raman spectroscopy performed on the top surface and XRD measurements on sample 1. White crosses designed in Fig. 1(a) correspond to the two areas (A and B) studied by Raman spectroscopy. The first spectrum is achieved on the top surface of agglomerated catalyst particles (Fig. 2(a, c)) and the second one on the film of catalyst nanoparticles (Fig. 2(b, d)). On particle agglomerates (Fig. 2), we can observe several peaks between 100 and 600 cm^{-1} (Fig. 2(a)) and one at 1316 cm^{-1} (Fig. 2(c)). We can assign most of them to iron