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1 One-step synthesis of highly pure and well-crystallized vertically aligned  
2 carbon nanotubes

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6 **Abstract (197 words)**

7 The one-step aerosol-assisted catalytic chemical vapor deposition (CCVD) process, when  
8 operated in a H<sub>2</sub>-based carrier gas, is shown to be effective at an extremely low ferrocene  
9 content (0.1wt.% in toluene), which enables to efficiently prepare forests of vertically aligned  
10 multiwalled carbon nanotubes (VACNTs) with high purity and good crystalline level. The  
11 resulting iron content in VACNT sample is only 0.5wt.% corresponding to a high catalytic yield  
12 of 200 while the steady growth rate (20 μm/min) is maintained at a significant value. The iron  
13 content in the sample is found proportional to the ferrocene concentration in the precursor, and  
14 when it decreases, a noticeable reduction in the iron encapsulation frequency in the nanotube  
15 channel is plainly observed. Lowering the ferrocene concentration generates a reduction in the  
16 VACNT number density while the growth rate increases and CNT diameters and crystalline  
17 structure remain similar. Such significant purity and crystalline levels involves a high oxidation  
18 resistance of the VACNT forest. These results, together with the *in-situ* continuous growth  
19 feature of the one-step aerosol assisted CCVD process, open up towards a new VACNT range  
20 made of pure and well-crystallized multi-walled carbon nanotubes, which is of interest for  
21 industrial production and commercial applications.

22

23 **Keywords:** vertically aligned carbon nanotubes; one-step catalytic chemical vapour deposition;  
24 iron content; purity; crystallinity; oxidation resistance.

25

## 26 **1 Introduction**

27 Vertically Aligned Carbon NanoTubes (VACNT) arrays have demonstrated outstanding  
28 potentialities as a novel material to prepare nanostructured composite or multifunctional  
29 materials. The carbon nanotube (CNT) alignment allows to take advantage of their anisotropic  
30 properties. This is useful for many applications of high societal interest such as heat transfer [1],  
31 energy storage [2,3], or high performance structural composites [4,5]. Efforts are currently  
32 underway to develop efficient synthesis processes for the manufacture of VACNTs in order to  
33 achieve mass production while reducing costs [6,7]. In particular, the process must be as simple  
34 as possible and must be operated at atmospheric pressure. The most effective method for  
35 synthesizing VACNT is catalytic chemical vapor deposition (CCVD) [8] which can be operated  
36 at atmospheric pressure. However, it often involved several preliminary steps at low pressure  
37 to prepare the layer of catalytic nanoparticles from which the nanotubes will then grow. It is  
38 why the aerosol-assisted version of the CCVD process has been developed [9–14], where  
39 catalyst nanoparticles are produced in situ and continuously refreshed due to the simultaneous  
40 injection of both metal and carbon precursors[15]. This process involves a base-growth  
41 mechanism [16] enabling the continuous growth of VACNTs at steady growth rate over very  
42 long synthesis duration, which allows VACNTs greater than 1mm to be achieved. Therefore,  
43 aerosol-assisted CCVD is a versatile, cost-effective and scalable one-step process operated at  
44 atmospheric pressure potentially applicable for a roll to roll production of multi-walled  
45 VACNTs. The continuous supply of ferrocene, which is essential to sustain the growth through  
46 the refreshment of the catalyst nanoparticles [16], induces the encapsulation of short nanowires  
47 in the inner channel of the nanotubes [17,18]. As a consequence, the iron content of the pristine  
48 VACNTs (Table 1) is typically around a few wt.% [15,19–21]. Such metallic by-products can  
49 alter the intrinsic nanotube properties and be detrimental for several applications [22]. In  
50 addition, it is also recognized that they can catalyze the oxidation of nanotubes and thus affect  
51 their stability in air at moderate temperatures [23–25]. Therefore, these CNTs need to be  
52 purified and several methods have been developed to remove metal by-products [22], either by  
53 acid treatment [26], but their complete removal is difficult to achieve without altering the  
54 nanotube structure [27,28], or by high temperature annealing which is the most effective  
55 method for their removal while improving the nanotube crystallinity [22,29,30]. However, such  
56 treatments complicate the CNT production process and are not always compatible with the  
57 targeted application.

58 Therefore, efforts must be done directly on the aerosol-assisted CCVD production process in  
59 order to reduce drastically the iron content in the pristine VACNTs. Recently and in the  
60 meantime of our study, this issue was addressed by T. Kinoshita *et al.* [31] who reported a  
61 modified floating catalyst CCVD method (similar to the aerosol-assisted one) enabling the  
62 growth of CNT forests containing very low concentration of impurity (0.8 wt%). However, the  
63 changes made to the process have turned it into a two-step process involving in the first step  
64 the in-situ formation of the catalyst particles, then in the second step the CNT growth with  
65 carbon precursors only. Such experimental conditions do not allow the refreshment of the  
66 catalyst particles so that the lifetime of their process is limited. Moreover the second step was  
67 performed at low pressure which limits the industrial interest of the method.

68 In this context, the aim of our work is to reduce the Fe content of pristine VACNTs while  
69 preserving their crystallinity, alignment and growth rate by increasing the catalytic yield of the  
70 one-step aerosol-assisted CCVD process operated at atmospheric pressure. In the literature  
71 (Table 1), few studies [15,19–21] report the measurement of iron content of VACNTs formed  
72 by the one-step aerosol-assisted CCVD, but it is generally found that iron content increases  
73 with ferrocene concentration in the precursor solution [19,21]. Cho *et al.* [20] studied the [0.2-  
74 9] wt.% ferrocene range at 760°C and obtained 1.9wt.% as the lowest iron content in CNT  
75 samples for 1.5wt.% of ferrocene in toluene. However, they did not observe any growth of  
76 VACNT forests at 0.2wt.% of ferrocene, in agreement with the result of Singh *et al.* [13].  
77 Similarly, Castro *et al.* [15] observed no growth of VACNT at 0.1 and 0.5wt.% when studying  
78 the [0.1-5] wt.% range of ferrocene at 850°C and the lowest iron content obtained is 3wt.% at  
79 2.5wt% ferrocene with a higher growth rate due to a higher synthesis temperature. To our  
80 knowledge, for one-step aerosol-assisted CCVD process, the lowest concentration of ferrocene  
81 responsible for the growth of VACNTs is 0.1wt.% [32] but the growth rate at 750°C is  
82 particularly low (0.4  $\mu\text{m}/\text{min}$ ) and the iron content in the resulting sample is not reported. The  
83 highest growth rate obtained with a low ferrocene concentration (0.58wt.%) is 13.6  $\mu\text{m}/\text{min}$  at  
84 780°C [33] but the iron content is not indicated. The latter result was obtained with 15% H<sub>2</sub>  
85 added to Ar as carrier gas.

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**Table 1 : Lowest ferrocene concentrations giving rise to VACNT growth reported in the literature for the one-step aerosol-assisted CCVD synthesis. The most relevant experimental parameters are reported, as well as, the growth rate and iron content of the final product when available. Ferrocene concentrations in the precursor solution were converted to wt.%. Note that 1wt.% of ferrocene in toluene corresponds to a Fe/C ratio of 0.07at.%.**

	Ferrocene concentration (wt.%)	Carbon source	Carrier gas	T (°C)	Substrate	Growth rate (μm/min)	Iron content (wt.%)	Raman ID/IG λ (nm)
Bai 2005 [33]	0.58	xylene	Ar/H <sub>2</sub> 87/13	780	quartz	13.6	-	-
	1.14					20.4		-
Ionescu 2011 [32]	0.1	xylene	Ar	750	Sputtered Al Si wafer	0.4	-	0.49 785 nm
	1					4.7		0.68 785 nm
Cho 2012 [20]	1.5	toluene	Ar	760	quartz	2.5	1.9	0.33* 633 nm
McKee 2009 [19]	0.54	benzene	Ar	750	various	-	0.7 - 3	0.3 measured at 1.75 wt% Fe 514 nm
Meysami 2013 [21]	1	toluene	Ar	800	quartz	16	2.5	0.29 532 nm
Castro 2010 [15]	1.25	toluene	Ar	850	quartz	11	3.5	0.52* 532 nm
	2.5					20		3
Castro 2013 [34]	2.5	toluene	Ar/H <sub>2</sub> 80/20	850 800	quartz	29	5.3	-
						23		6.2

98 \* Area ratio

99 Despite the wide disparity in the experimental conditions, the results of the literature highlight  
100 the important role played by the synthesis temperature and the hydrogen presence in the carrier  
101 gas to maintain a realistic growth rate while decreasing the ferrocene concentration in the  
102 aerosol. In a previous paper [34], we studied the effect of adding hydrogen to Ar carrier gas and  
103 showed that it has a major impact on the aerosol-assisted CCVD process. Increasing the  
104 hydrogen content strongly shifts the CNT growth to the reactor inlet and reduces the CNT  
105 diameters, while the CNT number density increases. Indeed, hydrogen demonstrably affects the

106 gas phase phenomena by lowering the decomposition temperature of ferrocene, promoting the  
107 formation of a larger number of smaller iron nanoparticles in the gas phase and increasing the  
108 nucleation site density of the catalytic nanoparticles. In addition, the optimal synthesis  
109 temperature in terms of yield and homogeneity of growth is reduced to 800°C under hydrogen  
110 (Table 1) [34]. In these previous experiments, the concentration of ferrocene in toluene was set  
111 at 2.5wt.%, the optimal concentration determined at 850°C without H<sub>2</sub> [15]. It should be  
112 reminded that without H<sub>2</sub>, no growth of VACNTs is obtained below 1.25wt.% of ferrocene,  
113 neither at 850°C nor at 800°C. However, the situation may change in the presence of H<sub>2</sub> due to  
114 the significant improvement in the ferrocene decomposition it induces. Therefore, our objective  
115 is to determine, in the presence of H<sub>2</sub>, the lowest concentration of ferrocene in toluene allowing  
116 the growth of a VACNT forest with low impurity level while maintaining a high growth rate  
117 and a good structural quality.

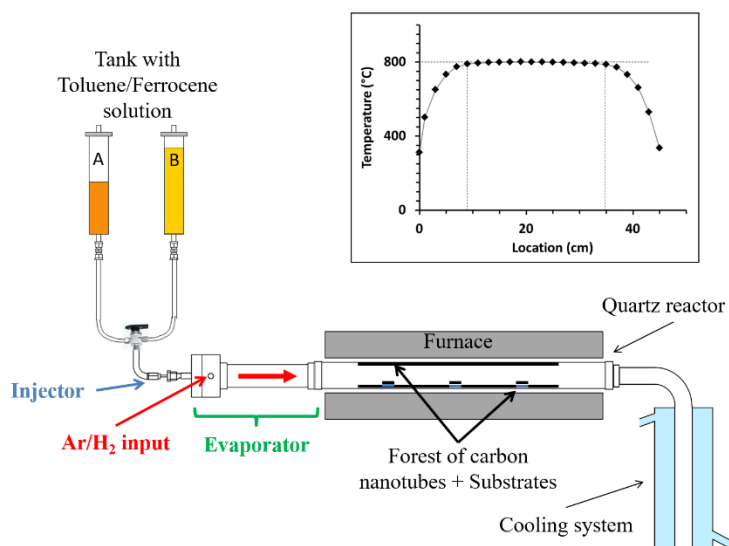
118 In this paper, we investigate the role of ferrocene concentration in the precursor solution  
119 (toluene/ferrocene) on the VACNT growth and characteristics (iron content, length, diameter,  
120 density, structure, oxidation resistance as well as on growth efficiency (yields and growth rate).  
121 As hydrogen was reported to be a determining chemical player in the decomposition rate of  
122 ferrocene [34], all the synthesis of this study are performed by the one-step aerosol assisted  
123 CCVD process with hydrogen diluted in argon as carrier gas. The approach combines global  
124 analysis by Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA) and  
125 Raman Spectrometry, with local analysis by Transmission Electron Microscopy (TEM). Since  
126 in this one-step aerosol assisted CCVD process a continuous supply of ferrocene is essential to  
127 sustain growth [35], our first objective is to determine the ferrocene concentration threshold  
128 above which VACNT growth is maintained once the catalytic particles are formed. To this end,  
129 we first carry out double injection experiments, by designing a specific set-up allowing to use  
130 a solution containing 2.5wt.% ferrocene in a first short injection sequence to form the catalyst  
131 particles, and then to use a second solution with a lower ferrocene concentration in a second  
132 long injection sequence. These experiments demonstrate that a very low ferrocene  
133 concentration (0.01wt.%) used in the second sequence can sustain the growth of VACNT forest,  
134 which is considerably lower than the ones reported in the literature for this one-step aerosol  
135 assisted CCVD process. Subsequently, by operating this process in a single injection mode with  
136 a ferrocene concentration decreasing from 2.5 to 0.01wt.%, we show that it is possible to  
137 determine conditions to synthesize a pristine VACNT carpet with unprecedented reported low  
138 iron content (0.5 wt%) and high oxidation resistance.

## 139 2 Experimental

### 140 2.1 Synthesis

141 The set-up (Fig. 1) and standard procedure used to synthesize VACNTs by the one-step aerosol-  
142 assisted CCVD process at atmospheric pressure are similar to those described by Castro *et*  
143 *al.* [34]. Note that syntheses in the presence of H<sub>2</sub> cannot be done under the same conditions as  
144 in its absence because the addition of H<sub>2</sub> considerably shifts the VACNT growth towards the  
145 reactor inlet. The synthesis temperature must then be lowered to restore growth in the reactor  
146 center. This is why all syntheses here are made in the presence of H<sub>2</sub> and at the optimal  
147 temperature of 800°C [34]. The furnace exhibits an isothermal area larger than the previous  
148 one. It is a 45 cm long tubular furnace equipped with a quartz reactor (16 mm inner diameter).  
149 At 800°C, the isothermal area ( $\pm 10^\circ\text{C}$ ), is extended from 10 to 35 cm from the furnace inlet  
150 (Fig. 1). A flat quartz substrate of 1.5x0.75 cm<sup>2</sup> is placed in the isothermal area at 14 cm from  
151 the reactor inlet. The VACNTs grown on this substrate are analyzed together with the VACNTs  
152 grown on the reactor walls. The VACNTs grown on the reactor walls are collected with a  
153 stainless scraper, a procedure which keeps intact their morphology and structure. They are  
154 weighed according to the location in the reactor, divided into 5 cm long sections with a surface  
155 area of 25 cm<sup>2</sup> each, in order to assess the distribution of the VACNT deposit. All the  
156 characterizations will be carried out on the VACNTs coming from the substrate of zone 2 and  
157 the VACNT powder coming from zone 3. These zones were chosen because the yield is better  
158 there. To perform double injection experiments, the present set-up is equipped with two liquid  
159 precursor tanks. Solutions of ferrocene dissolved in toluene at different concentrations are  
160 poured into these tanks connected to an injection system and an evaporator where they are  
161 nebulized and carried to the reactor by a gas flow of 1 L/min at a rate about 0.8 g/min. The gas  
162 flow is a mixture of Ar and 30 vol.% of H<sub>2</sub>. A solution with 2.5wt.% of ferrocene is poured into  
163 tank A (Fig. 1) while in tank B, the solution has variable concentrations. The solution in tank  
164 A is injected for 1 min 40 s and then the solution in tank B for 13 min 20 s. The switch from  
165 tank A to tank B is instantaneous, so that the process remains a one-step continuous process. In  
166 single injection experiments, only the solution in tank B is injected for 15 min, with ferrocene  
167 concentrations ranging from 0.01 to 2.5wt.%.





168

169 **Fig. 1: Experimental set-up used for the one-step aerosol-assisted CCVD process operated**  
 170 **at atmospheric pressure. Insert: temperature profile at 800°C measured with a**  
 171 **thermocouple moved along the quartz reactor.**

## 172 2.2 Characterizations

173 Morphology and thickness of VACNT carpets grown on the substrate and on the walls in the  
 174 center of the reactor are investigated by SEM (Carl Zeiss Ultra 55). CNT structure and statistical  
 175 analysis of external and internal diameters are obtained from TEM (Philips CM12, 120 kV)  
 176 after ultrasonic dispersion of CNTs in ethanol and deposition on standard TEM holder (copper  
 177 grids). For high resolution TEM, we use a JEOL 2011 operating at 200 kV, equipped with a  
 178 CCD camera (GATAN system ORIUS SC100, 4008×2672 pixels, pixel size: 0.014 nm).

179 TGA under air of products collected in the area in the center of the reactor is performed with a  
 180 92–16.18 SETARAM apparatus, at a temperature rate of 10°C/min in the 20–1000°C range,  
 181 which leads to the complete gasification of carbon. The rusty residue is used to determine the  
 182 iron content of the sample (weight percentage of iron in the collected products), as well as the  
 183 catalytic yield (ratio between the carbon and iron masses). This iron content is calculated  
 184 knowing that the residue consists of Fe<sub>2</sub>O<sub>3</sub> as shown by X-ray diffraction [36]. In the unlikely  
 185 event that FeO contributes to the residue, the error would be small since the mass of iron in  
 186 Fe<sub>2</sub>O<sub>3</sub> is 70%, while it is 78% in FeO. We will see in the following that this error would be  
 187 negligible given the magnitude of the variation in iron content in our experiments.

188 Raman spectra are acquired from the substrate samples in ambient conditions using a Renishaw  
 189 INVIA microspectrometer equipped with an Ar laser (514.5 nm wavelength), focused through  
 190 a Leica microscope. A very low incident power (2 mW) is used to avoid heating effects. Spectra

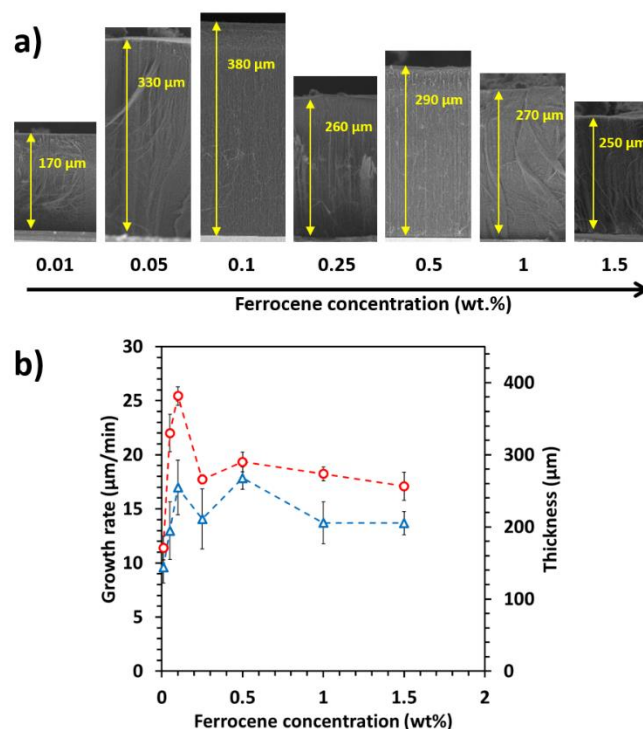
191 are recorded in the middle of the carpet cross-section in the 1000-3500  $\text{cm}^{-1}$  range. Pertinent  
192 quantitative Raman parameters are obtained by conventional fitting procedures [37] for the  
193 classical G, D, D' and 2D bands [38] and the corresponding position, full-width at half  
194 maximum (FWHM) and intensity (band height) relative to the G band are reported in [Table S1](#)  
195 (Supplementary data).

## 196 **3 Results**

### 197 **3.1 Thickness and growth rate of the VACNT forests**

#### 198 **Double injection experiments**

199 Double injection syntheses are performed with a first injection sequence with 2.5wt.% ferrocene  
200 in toluene during 1 min 40 s immediately followed by a long injection sequence of 13 min 20 s  
201 with a ferrocene concentration varying between 0.01 and 1.5wt.%. In preliminary experiments,  
202 we checked that the 1 min 40 s duration is long enough to initiate a VACNT carpet  
203 representative of a VACNT growth with a ferrocene concentration of 2.5wt.% (See Fig. S1 in  
204 supplementary data). SEM images of the products grown on quartz substrates placed in the  
205 oven center ([Fig. 2a](#)) reveal VACNT forests of the same good quality as usually reported [34].  
206 The shortest carpet (170  $\mu\text{m}$ ) is obtained for 0.01wt.% of ferrocene in the second injection  
207 sequence, but then, the thickness increases sharply to 330  $\mu\text{m}$  for 0.05wt.% and up to 380  $\mu\text{m}$   
208 for 0.1wt.%, after which it remains around 270  $\mu\text{m}$  for higher concentrations. The  
209 corresponding growth rate ([Fig. 2b](#)) exceeds 25  $\mu\text{m}/\text{min}$  at 0.1wt.% of ferrocene and stabilizes  
210 between 15 and 20  $\mu\text{m}/\text{min}$  at higher concentrations.



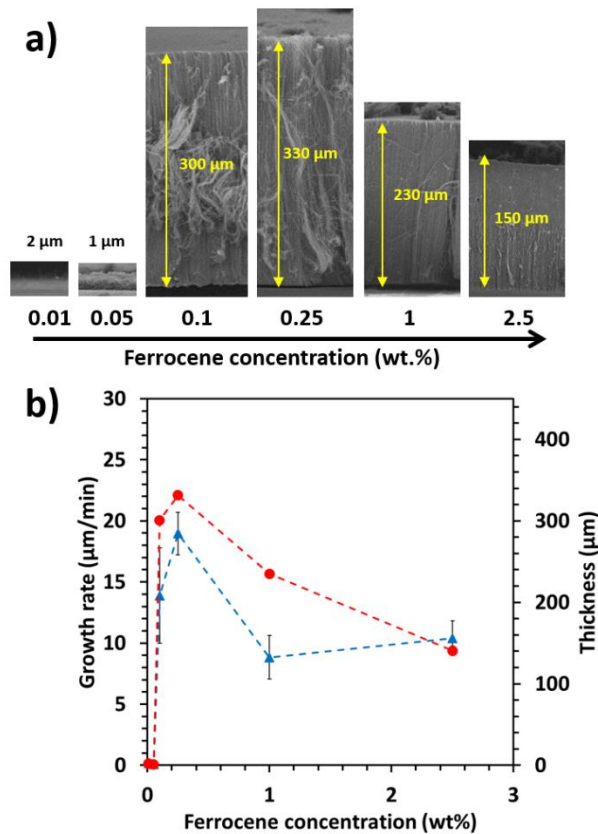
211  
 212 **Fig. 2: Double injection. (a): SEM images of the VACNT carpets grown on the central**  
 213 **substrate (side-view) for increasing ferrocene concentration in the second long injection**  
 214 **sequence. (b): mean carpet thickness and growth rate on the substrate (red dot) and on**  
 215 **the reactor walls (blue triangle) as a function of ferrocene concentration. Dashed lines are**  
 216 **added as eyes guide only. The thickness distribution was measured by SEM on the same**  
 217 **samples with 20 measurement points for the CNTs on the walls of the reactor and 3**  
 218 **measurement points for the CNTs on the substrate.**

219 The values on the substrate are slightly higher than those obtained on samples collected on the  
 220 reactor walls. (Fig. 2b). It is because the substrate is placed upstream along the reactor of the  
 221 zone where the samples used for the SEM analysis are collected and that, in aerosol-assisted  
 222 CCVD, the growth yield decreases along the reactor due to the dynamics of the catalytic  
 223 nanoparticles deposition as observed previously by us [15,34] and others [36]. This effect is  
 224 confirmed by the measurement of the mass distribution along the reactor displayed in Fig.S2.  
 225 As detailed in Supplementary Data, Fig.S2 shows that, whatever the ferrocene concentration,  
 226 the yield is optimal in zone 2 where the substrate is placed while the collected zone considered  
 227 in Fig.2 is zone 3 where the yield is slightly lower.

228 The most striking result of these double injection experiments is that, in the presence of H<sub>2</sub>, a  
 229 ferrocene concentration as low as 0.01wt.% in the second injection sequence is sufficient to  
 230 sustain the growth, and a rate higher than 15 μm/min is obtained for a concentration from  
 231 0.05wt.%.

232 **Single injection experiments**

233 Considering the very low ferrocene concentration (0.01 wt%) able to sustain the growth in  
234 double injection synthesis, single injection synthesis with ferrocene concentration from 0.01 to  
235 2.5wt.% are performed (Fig. 3a). For 0.01 and 0.05wt.% ferrocene, only a thin layer of  
236 entangled nanotubes is observed. However, as soon as the ferrocene concentration reaches  
237 0.1wt.%, the growth of a well-defined VACNT forest becomes effective with a growth rate as  
238 high as 20  $\mu\text{m}/\text{min}$ , close to its maximum of 22  $\mu\text{m}/\text{min}$  obtained with 0.25wt.% (Fig. 3b). For  
239 higher concentrations, the growth rate decreases to values in the 10-15  $\mu\text{m}/\text{min}$  range. The  
240 trends are the same on the substrate located at the center of the furnace and on the reactor walls,  
241 with still mean values slightly lower for samples collected on the walls, due to variation along  
242 the reactor (Fig. S2). The VACNT carpet thickness increases linearly with the synthesis  
243 duration in the tested duration range up to 420 min, with a growth rate of 11.4  $\mu\text{m}/\text{min}$  at  
244 1.25wt.% and 2.5wt.% ferrocene (Fig. S3 in supplementary data).



245

246 **Fig. 3: Single injection. (a): SEM images of the VACNT carpets grown on the central**  
247 **substrate for increasing ferrocene concentration. (b): mean carpet thickness and growth**  
248 **rate on the central substrate (red dot) and on the reactor walls (blue triangle) as a function**  
249 **of ferrocene concentration. Dashed lines are added as eyes guide only. The thickness**  
250 **distribution was measured by SEM on the same samples with 20 measurement points for**

251 **the CNTs on the walls of the reactor and 3 measurement points for the CNTs on the**  
252 **substrate.**

253 Therefore for this one-step aerosol assisted CCVD process operated at 800°C with hydrogen in  
254 the gas phase, the ferrocene concentration threshold allowing an efficient growth of VACNTs  
255 is as low as 0.1wt.%, while no growth at all was observed without hydrogen at 850°C for  
256 ferrocene concentration equal to 0.1 or 0.5wt% [15]. More generally, the present results  
257 represent a great improvement as compared to the state of the art related to the one-step CCVD  
258 process (Table 1) in terms of growth rate at very low ferrocene concentration.

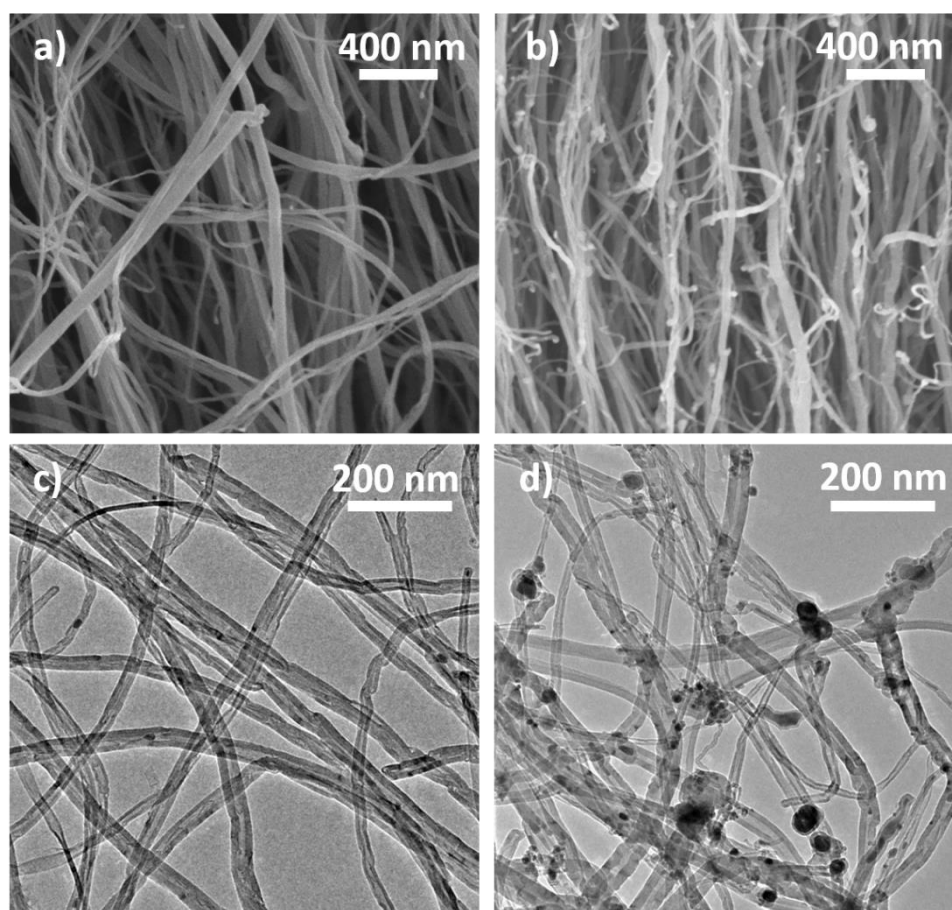
### 259 **3.2 Purity, diameter and structure of carbon nanotubes**

260 The main characteristics of the VACNTs are similar regardless of the injection mode and  
261 depend only on the ferrocene concentration. Results obtained for the single injection mode will  
262 be discussed here and the ones regarding the double injection reported in Supplementary data.

263 Let's focus on single injection samples and compare SEM and TEM images of the formed  
264 nanotubes with 0.1wt.% and 2.5wt.% of ferrocene respectively (Fig. 4). The striking difference  
265 between both samples is in terms of cleanliness. At 0.1wt.%, the forest is very clean and no  
266 parasitic particles can be observed outside the nanotubes at the resolutions used for the  
267 observations. There are very few iron-based nanowires inside the nanotubes (Fig. 4a and 4c).  
268 The number of embedded Fe nanoparticles has been drastically reduced as compared to our  
269 previous results. Indeed, TEM micrographs on figure 4c) clearly indicate a high purity of CNT  
270 at low ferrocene concentration. On the contrary, at 2.5wt.% numerous iron-based particles  
271 exhibiting a nanowire shape are located inside the nanotubes (see also Fig. S4). In addition, a  
272 considerable amount of nanoparticles are located on CNT surface (Fig. 4b and 4d), as observed  
273 by others when the ferrocene concentration is high [19,21,33]. They are of varying sizes, some  
274 of them being encapsulated into carbon shells and some others giving rise to the growth of  
275 nanotubes of very small diameter which represent a low fraction of the sample mass and are not  
276 considered in the diameter distributions reported below. Such iron nanoparticles located on the  
277 CNT surface and the thin nanotubes observed on samples prepared with 2.5wt.% of ferrocene  
278 (Fig. 4d) cannot be detected in the sample obtained with 0.1wt.% of ferrocene (Fig. 4c).  
279 Therefore, lowering the ferrocene concentration induces a drastically reduction of the iron  
280 impurities inside the VACNT samples.

281 A detailed HRTEM analysis of a few individual nanotubes over their length (see Fig. S4) is  
282 used to characterize the iron-based nanowires found in the inner channel of the tubes. Their

283 average length and number density decrease significantly as the ferrocene concentration  
284 decreases. This detailed TEM analysis at higher magnification (Fig S4) shows also a highly  
285 reduced frequency of incorporation of nanowires into the tubes as well as a much lower mean  
286 size of these nanoparticles when the ferrocene concentration is reduced. Therefore, the amount  
287 of embedded nanoparticles is really low, and it is a great improvement for a one-step CCVD  
288 process. For 0.1wt.% ferrocene, only 2% of the length of the nanotube inner channel is occupied  
289 by iron nanowires, while it is 24% for 2.5wt.%. On average, it can be estimated that there is 1  
290 nanowire every 2  $\mu\text{m}$  at 0.1wt.% ferrocene while there is one nanowire every 0.4  $\mu\text{m}$  at 2.5wt.%  
291 (See Table S2). An analysis of structural defects (corking) in the inner channel also shows a  
292 decrease in their occurrence for 0.1wt.% as compared to 2.5wt.%, but not in the same proportion  
293 as nanowires (Table S2).

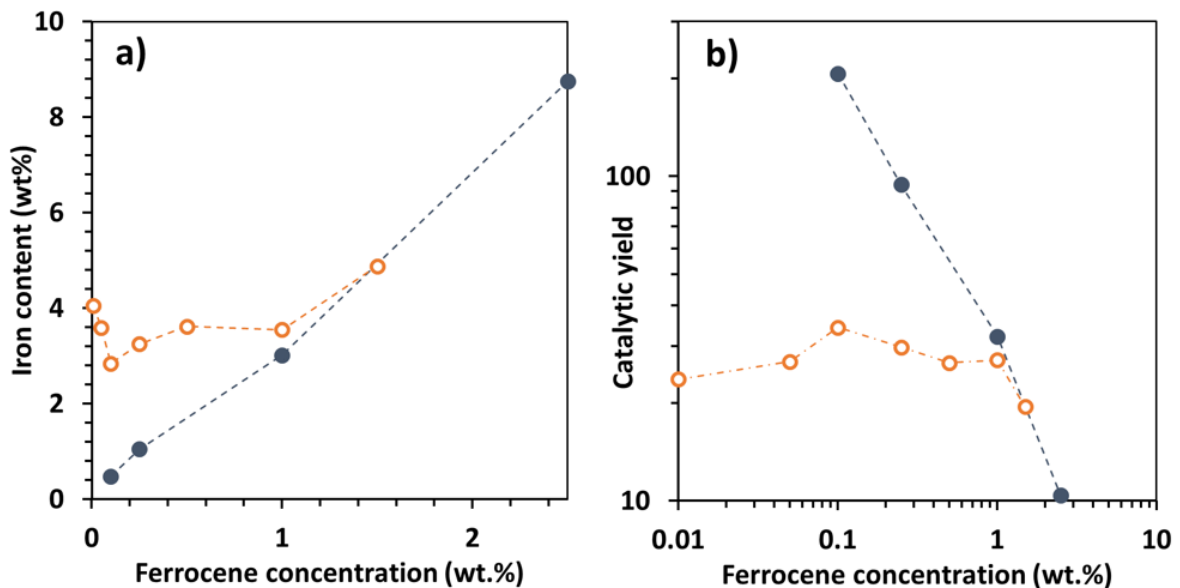


294  
295 **Fig. 4: Comparison in single injection between samples obtained with ferrocene**  
296 **concentration of 0.1 and 2.5wt.%. a) SEM image of 0.1%; b) SEM image of 2.5%; c) TEM**  
297 **image of 0.1%; and d) TEM image of 2.5%.**

298 The iron content of VACNT forests is determined by TGA analysis under air (Fig. 5a) on  
299 samples taken in the same central area of the reactor as the ones used for the SEM and TEM

300 analysis above. In single injection, the iron content varies greatly and linearly with the ferrocene  
301 concentration, from 0.5wt.% at 0.1wt.% ferrocene up to 9wt.% at 2.5wt.% ferrocene. This value  
302 of 0.5 wt% of iron in VACNT sample is a remarkably low value as compared to the literature  
303 (see Table 1 and references herein) and is even lower than that of 0.56 recently published in a  
304 paper related to a two-step floating CCVD process[31]. It confirmed the great increase in the  
305 VACNT purity at low ferrocene concentration as observed by TEM above. In double injection,  
306 iron content variations are less pronounced as compared to single injection (Fig. 5a) due to the  
307 first injection sequence at 2.5wt.%. To verify that the variation in iron content with the ferrocene  
308 concentration is not due to a similar variation in iron chemical yield, we estimate the proportion  
309 of injected iron found in the final product. In single injection, the incorporated iron represents  
310 40% of the injected iron at 0.1wt.% ferrocene and 50% at 2.5wt.%. Therefore, the incorporation  
311 rate of iron remains similar regardless of the ferrocene concentration and cannot be responsible  
312 for the high difference in iron content.

313 The catalytic yield (Fig. 5b) scales as the inverse of the ferrocene concentration for single  
314 injection. A very high and maximum catalytic yield about 200 (200g of carbon produced by  
315 iron gram) is obtained for the lowest concentration of ferrocene (0.1wt.% ) and then decreases  
316 rapidly down to 10 when the ferrocene concentration increases. For double injection, the  
317 catalytic yield is varying in a slighter range, between 16 and 35, for the whole ferrocene  
318 concentration range.

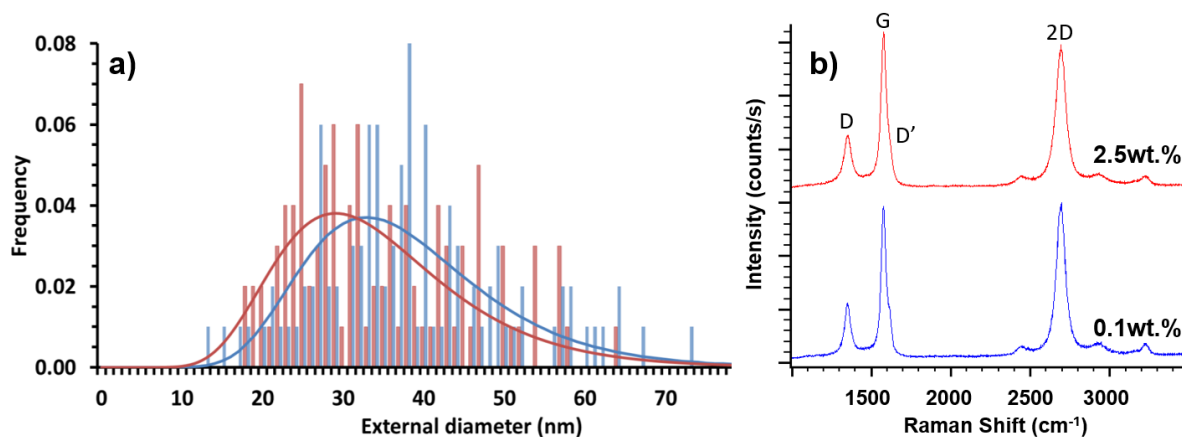


319

320 **Fig. 5: Ferrocene concentration effect on a) iron content and b) catalytic yield, for single**  
321 **(full dot) and double (open dot) injection (in this last case, it is the ferrocene concentration**  
322 **of the second long injection sequence). Dashed lines are added as eyes guide only.**

323 Regarding the CNT diameter, the distribution does not change with the ferrocene concentration  
324 (Fig. 6a), with external and internal average diameters around 35 nm and 9 nm respectively.  
325 Similar results are found in the case of double injection (Fig.S5). In terms of structural quality,  
326 the Raman spectra of the samples obtained with 0.1 and 2.5 wt% ferrocene are compared in  
327 Fig. 6b (see Fig. S6 for double injection): G, D and D' bands at 1580 cm<sup>-1</sup>, 1350 cm<sup>-1</sup> and  
328 1615 cm<sup>-1</sup> respectively, as well as the 2D band at 2700 cm<sup>-1</sup> are occurring. In multi-walled  
329 carbon nanotubes, the D band is associated with defects and disorder and is influenced by the  
330 curvature of the walls, while the G band is inherent to in plane tangential stretching of carbon-  
331 carbon bonds. The ratio between the D and G band intensities ( $I_D/I_G$ ) is commonly used as a  
332 qualitative measure of the defect density in defective tubes: the higher this ratio, the lower the  
333 crystalline level [38,39]. This ratio is dependent on the excitation wavelength. The analysis of  
334 the Raman spectra recorded at 514 nm on the samples obtained in the current study gives rise  
335 to a  $I_D/I_G$  ratio remaining similar whatever the injection mode and the ferrocene concentration.  
336 This ratio is around 0.3 and the lowest value of 0.28 is obtained at 0.25wt.% ferrocene  
337 concentration in single injection (Table S1). Such values are low for multi-walled carbon  
338 nanotubes produced by CVD and are related to a low defect density as discussed by Meysami  
339 et al. [21]. These values compare well with those reported in Table 1 obtained with similar  
340 Raman wavelengths (514 or 532 nm) for samples formed in similar conditions in terms of  
341 carbon precursors and synthesis temperatures (750-850°C) [15,19,21]. By contrast, they are  
342 much lower than those reported in the range [0.56-0.79] by Kinoshita et al. [31] from synthesis  
343 at 700°C with acetylene as carbon source. However, it has been shown that the G band in CNT  
344 can be affected by defects [39], therefore as the 2D band does not represent a disorder-induced  
345 mode, the relative intensity of the D and 2D bands ( $I_D/I_{2D}$ ) is also used as a qualitative measure  
346 of the defect density. Kinoshita et al. [31] found a  $I_D/I_{2D}$  ratio between 0.8 and 2. In the present  
347 work, this ratio is around 0.3 for almost all the ferrocene concentrations, apart for 2.5wt.% of  
348 ferrocene which gives rise to a ratio of 0.36. Such low  $I_D/I_{2D}$  ratio indicates a really good  
349 structural quality of the CNT forest that is well preserved and even slightly improved at low  
350 ferrocene concentration. This result corroborates the same trend observed by Cho *et al.* [20]  
351 and McKee *et al.* [19] with a similar one-step aerosol-assisted process.





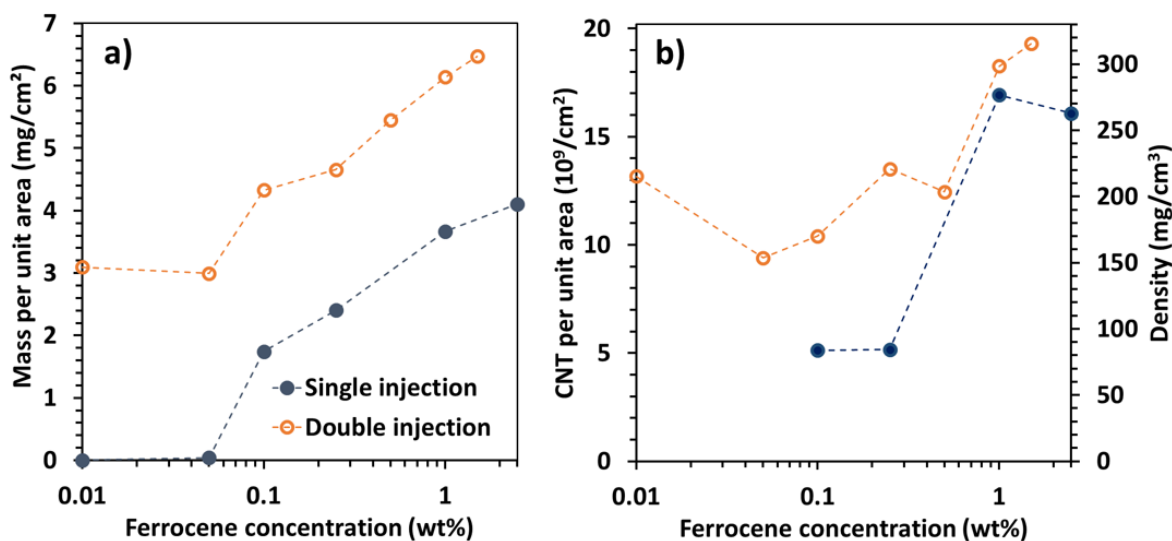
352  
 353 **Fig. 6: Comparison in single injection between samples obtained with ferrocene**  
 354 **concentration of 2.5 (red) and 0.1wt.% (blue), respectively. a) Nanotube external diameter**  
 355 **distributions from the TEM analysis of more than 100 CNTs; b) Raman spectra acquired**  
 356 **at 514 nm at the center of forest cross-sections.**

### 357 3.3 VACNT forest density

358 The mass per unit area of VACNTs collected on the reactor walls in the oven center (Fig. 7a)  
 359 increases with ferrocene concentration for both single and double injection experiments,  
 360 meaning that the chemical yield improves in both cases. In single injection, the areal mass is  
 361 close to 2mg/cm<sup>2</sup> at 0.1wt.% and then increases gradually up to 4 mg/cm<sup>2</sup>. In double injection,  
 362 the areal mass is already equal to 3 mg/cm<sup>2</sup> at 0.01wt.% ferrocene in the second injection and  
 363 then rises up to more than 6 mg/cm<sup>2</sup>, with values systematically higher than in single injection.  
 364 The gap between the two curves remains approximately constant around 2.5 mg/cm<sup>2</sup> in excess  
 365 in double injection as compared to single injection. This difference can be attributed to the  
 366 effect of the first injection sequence with 2.5wt.% in the double injection mode. Reproducibility  
 367 has been tested for experiments performed with ferrocene concentration of 0.1, 0.25 and 2.5  
 368 wt.% in single injection and 0.1, 0.25 and 0.5 wt.% in double injection. The observed deviations  
 369 do not affect the general trends, particularly for single injection experiments (Fig. S6 in  
 370 supplementary information).

371 From measurements of areal masses (Fig. 7a) and forest thicknesses (Fig. 2b and Fig. 3b), the  
 372 forest density can be determined and increases with the ferrocene concentration, especially in  
 373 single injection (Fig. 7b). Since nanotube diameters are similar whatever the ferrocene  
 374 concentration, this density increase must be related to an increase in N, the number density of  
 375 nanotubes (CNTs/cm<sup>2</sup>). N can be estimated knowing the mean external diameter of the  
 376 nanotubes and taking 1.8 g/cm<sup>3</sup> for the intrinsic carbon nanotube density as estimated by helium

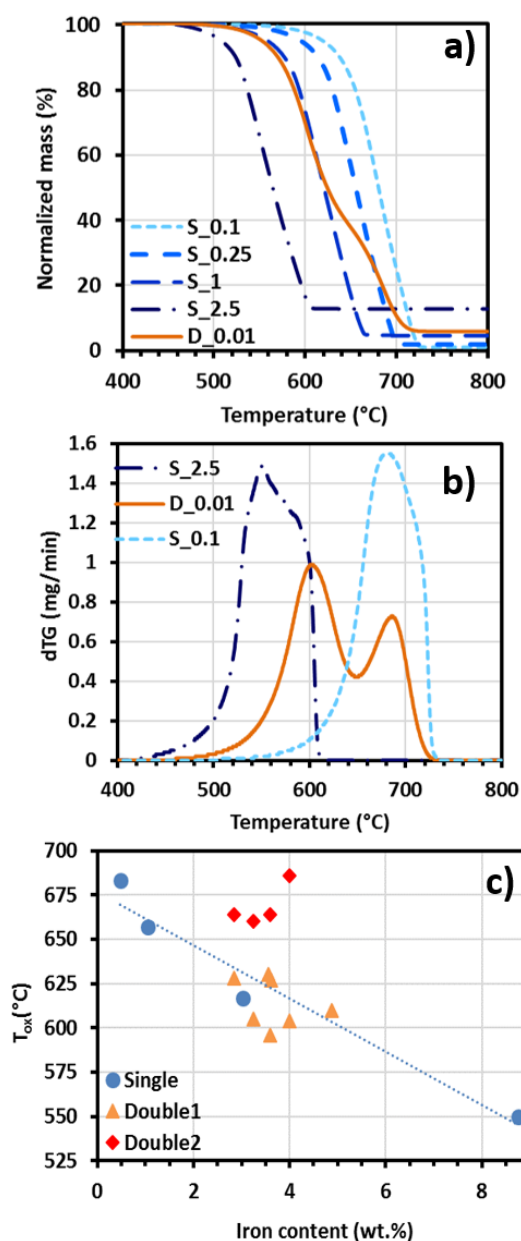
377 picnometry. N is found about  $\sim 5 \cdot 10^9$  CNT/cm<sup>2</sup> at low ferrocene concentration, but reaches  
 378  $\sim 1.7 \cdot 10^{10}$  CNT/cm<sup>2</sup> at 1wt.%. This result suggests that the number density of catalytic  
 379 nanoparticles increases as well.



380  
 381 **Fig. 7 – Ferrocene concentration effect on a) mass per unit area of carbon collected on the**  
 382 **reactor walls in the center zone, and b) measured mass density, for single (full dot) and**  
 383 **double (open dot) injection (in this last case, it is the ferrocene concentration of the second**  
 384 **long injection sequence). Dashed lines are added as eyes guide only.**

### 385 3.4 Oxidation resistance

386 The TGA mass-loss profiles are very dependent on the ferrocene concentration (Fig. 8a; see  
 387 also Fig. S8). In single injection, the profile is strongly shifted towards the high temperatures  
 388 when the ferrocene concentration decreases. The oxidation temperature ( $T_{ox}$ ), taken as the  
 389 temperature of the peak in the TGA graph derivatives (Fig. 8b and Fig. S8), decreases quasi-  
 390 linearly from 685°C down to 550°C when ferrocene increases from 0.1 to 2.5wt.%. Since in  
 391 single injection the iron content of the sample was previously found to be a linear function of  
 392 the ferrocene concentration (Fig 5a),  $T_{ox}$  appears to be a linear function of the iron content as  
 393 well (Fig. 8c and Fig. S9). In the case of double injection, the TGA profile exhibits a remarkable  
 394 shoulder on the high temperature side when the ferrocene concentration in the second injection  
 395 sequence is lower than 0.5wt.%, so that two  $T_{ox}$  (labelled Double1 and Double2) can be  
 396 identified at low ferrocene concentrations (Fig. 8c and S9). The difference between both values  
 397 is really significant (nearly 100°C) which points to the existence of two distinct components in  
 398 the samples as discussed below.



399

400 **Fig. 8:** a) TGA graphs obtained at a temperature rate of 10°C/min and b) their derivatives  
 401 for single injection samples (blue dashed lines labelled from S\_0.1 to S\_2.5 according to  
 402 the ferrocene concentration) compared to the double injection with 0.01wt.% ferrocene  
 403 in the second injection sequence (orange solid line labelled D\_0.01). c) Oxidation  
 404 temperature as a function of iron content. In double injection the label “Double2”  
 405 corresponds to the second peak at high temperature when observed in the dTG graph.  
 406 See also Fig. S8.

#### 407 4 Discussion

408 The present results show that the one-step aerosol-assisted CCVD process can be operated at  
 409 very low ferrocene concentration (0.1 wt.%) using an Ar/H<sub>2</sub> gas mixture as carrier gas. Using  
 410 these conditions and a synthesis temperature of 800°C, we demonstrate that this one-step

411 process enables the formation with a high catalytic yield (200) of VACNT forests exhibiting  
412 low impurity level (0.5 wt.% of Fe). Such low ferrocene concentration does not involve any  
413 reduction of CNT growth rate since it remains higher than 20  $\mu\text{m}/\text{min}$ . Compared to the  
414 literature (Table 1), it is, to our knowledge, the lowest concentration of ferrocene reported so  
415 far for aerosol-assisted CCVD process leading to such growth rates and impressive catalytic  
416 efficiency, thus involving the formation of high purity VACNT forests. The growth of a  
417 VACNT forest becomes impossible only when the ferrocene concentration falls below 0.1wt.%.  
418 When it increases up to 1wt.%, the growth rate decreases by a factor of 2, while the number  
419 density  $N$  is multiplied by more than 3 going from  $5 \cdot 10^9$  to  $1.7 \cdot 10^{10} \text{ cm}^{-2}$ .

420 Regarding the mechanisms at play, hydrogen plays a significant role in the process of ferrocene  
421 decomposition. Indeed, our previous results obtained at  $850^\circ\text{C}$  with 2.5wt.% ferrocene [34]  
422 have shown that including 30% of  $\text{H}_2$  in the Ar gas flow induces an increase of  $N$  from  $5 \cdot 10^9$  to  
423  $2 \cdot 10^{10} \text{ CNT}\cdot\text{cm}^{-2}$  as well as a decrease of the mean CNT external diameter. These results were  
424 attributed to the hydrogen induced enhancement of the dissociation rate of ferrocene. As a  
425 consequence, there is a fast rise of the iron partial pressure in the reactor and a high level of  
426 supersaturation which affects the homogeneous nucleation process of the iron nanoparticles. A  
427 much higher number of smaller nuclei forms, which leads to a higher number density of  
428 catalytic nanoparticles deposited on the substrate and therefore to a higher density of growing  
429 CNTs. Such very efficient effect of hydrogen on the catalytic particles density is responsible  
430 for the remarkable decrease in the ferrocene concentration allowing to reach the threshold in  
431 density of CNTs needed to form a self-supporting forest structure [40]. Interestingly, in the  
432 present work at 0.1wt.% ferrocene in single injection mode,  $N$  is equal to  $5 \cdot 10^9 \text{ CNT}\cdot\text{cm}^{-2}$ , a  
433 value similar to the one obtained without hydrogen at 2.5wt.% ferrocene with the same one-  
434 step aerosol assisted CCVD process [18]. This number allowing the vertical self-organization  
435 of the interacting CNTs is comparable to the value of about  $2 \cdot 10^9 \text{ CNTs}/\text{cm}^2$  reported by  
436 Bedewy *et al.* [40]. This threshold is obviously not reached below 0.1wt.%, explaining the  
437 absence of VACNT growth at such low concentration. This threshold was also not reached  
438 without hydrogen for ferrocene concentration below 1.25wt.%, explaining why no VACNTs  
439 were observed at 0.1 and 0.5wt.% by Castro *et al.* [15].

440 In double injection synthesis, the first injection sequence with 2.5wt.% ferrocene determines  
441 the density of catalytic nanoparticles. So  $N$  is higher from the beginning of the precursor  
442 injection and its evolution is less pronounced with the ferrocene concentration increase in the

443 second injection sequence, where a ferrocene concentration as low as 0.05wt.% is sufficient to  
444 sustain the growth.

445 The existence of a clear threshold in the ferrocene concentration allowing the self-organization  
446 of VACNTs is responsible for the sharp increase in the growth rate with ferrocene concentration  
447 observed for single injection experiments (Fig. 3b). The slow decrease observed after the  
448 maximum (Fig. 3b), as also observed by others [32,33], is generally attributed to an increase in  
449 VACNT density. Call *et al.* [41] show that ferrocene concentration dictates forest density but  
450 that forest thickness is limited by density presumably due to diffusion-limited precursor supply.  
451 However, in our case, the forest thickness is found proportional to the synthesis duration at least  
452 up to 90 min even at 1.25 wt.% ferrocene where the forest density is above  $10^{10}$  CNT/cm<sup>2</sup> (Fig.  
453 S3). Indeed, the flow rate is too high and the average inter-tube distance too large (between 60  
454 and 150 nm) to encounter feedstock resistance [42]. Same conclusion was reported by Cho *et al.*  
455 [20] leading them to invoke, as Bai *et al.* [33], a weaker activity of the catalytic nanoparticles  
456 due to their size increasing with ferrocene concentration [8]. However, in our study, the CNT  
457 diameter remains similar whatever the ferrocene concentration, which implies that the catalytic  
458 particle size remains also the same [8]. In the present range of ferrocene concentration, this size  
459 is mainly governed by temperature, H<sub>2</sub> content and nature of the substrate, all these parameters  
460 being constant here. On the other hand, when the number density of nanotubes increases, the  
461 amount of precursors available per nanotube decreases, in principle in inverse proportion to the  
462 density. This is not exactly what we are observing here since the mass per unit area that is the  
463 product of the two is not constant, but increases. Such result could be rationalized considering  
464 that at very low forest density, not all the carbon precursors impinging the substrate area around  
465 a given CNT (intertube distance is 150 nm) are able to interact with the catalyst particle, but  
466 their proportion increases when the intertube distance decreases. Such effect could explain the  
467 observed variation of growth rate.

468 Regarding the iron content of the VACNT forest, it increases linearly from 0.48 to 8.75 wt.%  
469 with the ferrocene concentration in single injection, and the atomic ratio Fe/C in the forest  
470 appears to be 10 times the Fe/C ratio in the precursors (Fig. S10). It means that the iron  
471 conversion is 10 times higher than the carbon conversion. It should be noted that the  
472 contribution of the catalyst nanoparticles themselves to the iron content is very low as is out of  
473 principle the case for any VACNT forest (see its estimation in Supplementary Data). The iron  
474 incorporated in the material is predominantly found as nanowires encapsulated in the inner  
475 channel as a consequence of the continuous refreshment of the catalyst nanoparticles from the

476 iron-based nanoparticles continuously nucleated in the gas phase [18] in the one-step aerosol-  
477 assisted CCVD process. When the ferrocene concentration is decreased, the percentage of the  
478 CNT inner channel length occupied by the nanowires (Fig. S4 and Table S2) drastically  
479 decreases: it is estimated to be 10 times lower for the optimal concentration of 0.1wt.%  
480 ferrocene as compared to 2.5wt.%, which corresponds to an encapsulation frequency which is  
481 3 times lower.. Since the CNT growth rate is two-fold higher at 0.1wt.% than at 2.5 wt.%, it  
482 means that the acceleration in the refreshment at high ferrocene concentration does not allow  
483 to increase the growth rate but only leads to an increase of the iron content.

484 Iron can be incorporated in the forest also as nanoparticles found outside the nanotubes. This  
485 contribution increases a lot when the ferrocene concentration increases, as observed by SEM  
486 and TEM (Fig. 4) and by others [21,33]. Since TEM observations show that the amount of  
487 external nanoparticles is negligible in the sample obtained at 0.1wt.% ferrocene, then we can  
488 estimate from the TEM analysis of the inner channel (Table S2) that the iron inside the tubes  
489 represents about 2/3 of the total iron content for the sample formed with 2.5wt% ferrocene.  
490 Therefore, external nanoparticles contain at most a third of the iron content. Their presence in  
491 large quantities is due to the large increase, with the ferrocene concentration, of the number  
492 density of iron nanoparticles in the precursor gas flow going towards the substrate through the  
493 carpet. To avoid the formation of such large proportion of by-products in the presence of H<sub>2</sub>,  
494 the ferrocene concentration must be kept lower than 1wt.%.

495 Regarding now the size and crystalline structure of the nanotubes, both TEM and Raman  
496 analysis show that their structure and diameter depend only slightly on the concentration of  
497 ferrocene in the range studied here. The ID/IG ratio of 0.3 indicates a good structural quality  
498 with a low defect density for MWCNTs as observed previously [15,21]. That is why it is not  
499 possible to interpret the large variation in the oxidation temperature with the ferrocene  
500 concentration in terms of variation of the structural properties. Even considering the position of  
501 the G-band, which was found to correlate with T<sub>ox</sub> in the literature [43], it is not possible to  
502 invoke such structure evolution, since here, the G-band position is very stable (Table S1).  
503 Alternatively, the catalytic activity of the iron-based compounds inside the forests during the  
504 TGA was also considered in the literature since it is able to change the kinetic parameters of  
505 the oxidation [19,21,23–25]. In the present case, this second interpretation is strongly supported  
506 by the strong correlation found between T<sub>ox</sub> and iron content in single injection synthesis  
507 (Fig.8c). Also, the highest oxidation temperature (680°C) obtained for the sample with the  
508 lowest iron content is found very similar to the one of VACNT sample freed from iron after a

509 heat-treatment at 2000°C [29]. Moreover, in double injection, the catalytic activity of the iron-  
510 based compounds allows to understand directly the presence of two components in the TGA  
511 graphs. When the ferrocene concentration is very different between the two injection sequences,  
512 two layers are formed with very different iron contents and different oxidation temperatures.  
513 The highest oxidation temperature is close to those obtained with single injection with a similar  
514 low ferrocene concentration. The large variation in oxidation temperature under dry air can be  
515 correlated to the iron content and the double peak observed for sample synthesized by double  
516 injection underlines the localized catalytic role of iron compounds in the oxidation reaction as  
517 mentioned in [25]. It could be used to perform selective oxidation of the carpet top in order to  
518 suppress the layer where the CNTs are entangled and to open the tubes. Also, double injection  
519 experiments offer the possibility to control independently forest density and growth rate while  
520 limiting the iron content. The forest density is determined by the ferrocene concentration in the  
521 first injection sequence while the growth rate depends mostly on the ferrocene concentration in  
522 the second injection sequence.

## 523 **5 Conclusion**

524 Our results show that, in the aerosol-assisted CCVD process, the addition of H<sub>2</sub> in the carrier  
525 gas results in a significant increase in the number density of catalytic nanoparticles, due to its  
526 strong influence on the decomposition kinetics of the ferrocene. As a result, the formation of a  
527 self-organized VACNT forest occurs at a much lower ferrocene concentration than without  
528 hydrogen and a pristine forest of high purity is formed with high catalytic yield at a performing  
529 growth rate. At 800°C, with 30% H<sub>2</sub> in Ar, VACNT forest is formed with only 0.1wt.%  
530 ferrocene (Fe/C=0.007at%), a value 25 times lower than the usual one of 2.5% optimized  
531 without hydrogen. The iron content falls down to 0.5wt.%, so that the catalytic yield is strongly  
532 enhanced by a factor of 20, while the growth rate is improved by a factor of 2 and the crystalline  
533 structure remains of high quality. A forest density of  $5 \cdot 10^9$  CNTs/cm<sup>2</sup> appears to be the  
534 threshold for the self-organization of the nanotubes to occur. This number density increases  
535 with the ferrocene concentration, due to the increase in the number density of catalytic  
536 nanoparticles. The iron content of the forest is directly proportional to the ferrocene  
537 concentration. When it decreases, the frequency of encapsulation of iron nanowires in the inner  
538 channel of the tubes decreases significantly and the oxidation resistance of the samples is  
539 greatly improved, with an increase in oxidation temperature equal to 100°C. Finally, double  
540 injection experiments appear to be an attractive approach in order to optimize independently  
541 the density and the growth rate of the forest, since the density is fixed by the initial ferrocene

542 concentration in the first short injection sequence while the growth rate can be controlled by  
543 the concentration in the second injection sequence.

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547 Raman analysis facilities, respectively.

548

#### 549 **Appendix A. Supplementary data**

550 Supplementary data associated with this article can be found, in the online version, at

551

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