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To cite this article: S Patel *et al* 2013 *J. Phys.: Conf. Ser.* **429** 012053

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Development and optimization of a secure injection CVD process to grow aligned carbon nanotubes on large substrates

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Abstract. Growth of aligned carbon nanotubes (CNT) by a secure injection CVD process on large quartz substrates and carbon fiber (CF) cloths has been reported in this study. Adjustments of CVD setup and synthesis parameters have been achieved to control the CNT growth in terms of homogeneous covering of the substrates and to tailor the length of CNT. Two parameters have been optimized such as the precursor feeding rate per reactor surface unit and the carrier gas flow rate.

1. Introduction

Because of their properties, carbon nanotubes (CNT) have opened window for research on materials improvement. They are potential materials for sensors, electrodes, membranes or composites [1–4]. Recently, lots of studies deal with the introduction of CNT in polymer matrix composites reinforced with carbon fiber (CF) in order to enhance mechanical and electrical properties [5–24]. In general, CNT are dispersed in matrix, then the fibers are impregnated with this modified matrix leading to forming composite materials which are compatible for a further industrial processes [7–9], [11], [13], [15], [16], [20], [22]. However, it is often reported that the presence of CNT increases the viscosity of the polymer inducing a change in the composite process elaboration and a non homogeneous impregnation [20]. To avoid this problem, another route to elaborate composite is to integrate CNT directly on the reinforcement materials. It can be either a deposition of CNT or a direct growth of CNT on the carbon fiber cloth. In this latter case, injection CVD (Chemical Vapour Deposition) process is the process mostly used for a direct growth of CNT. It has been demonstrated that a growth of aligned dense and long CNT is possible in the case of a treatment on carbon fiber performed previously to the growth of CNT [10], [25], [26] . In general, this previous treatment is achieved by a process which is different from CVD process such as PVD (Physical Vapour Deposition) processing two different reactors, thus involving intermediate handling phases which are not compatible in terms of secure process development [10], [26]. Recently, a process consisting in performing the pretreatment in the same CVD reactor through two successive steps has been developed for the growth of aligned CNT [25]. Nevertheless, a current problem concerns the achievement of a homogeneous growth of CNT on large substrates such as flexible carbon fiber clothes. Few papers deal with the growth of CNT on substrates exhibiting sizes over 10 cm. We consider that this size constraint is one of the reasons why there are only few studies on mechanical properties of composites (interlaminar shear strength) reinforced with carbon fiber clothes and more papers exhibiting mechanical properties results obtained on individual carbon fibers (interfacial laminar shear strength) [5], [6], [18], [21], [24]. The CVD process used for the growth of aligned CNT is well-known for flat quartz substrates with sizes above 10 mm* 10 mm. Therefore, it is of particular importance to develop and adjust such processes in order to grow aligned CNT on large fiber cloths and to further study the effect of CNT on the properties of composite materials resulting from aligned CNT covered fiber cloth impregnated with organic matrixes.

In this context, the present paper is focused on the adjustment of the DLI-CVD process to grow aligned CNT on large quartz substrates and CF cloths allowing standard mechanical tests on the final composites. Thus, we have investigated the characteristics of aligned CNT grown in quite big reactor and furnace exhibiting sizes over 1 m in length and 80 mm in diameter. From this study, we have pointed out that two synthesis parameters need to be optimized such as the precursor feeding rate per reactor surface unit and the carrier gas flow rate.

2. Experimental

The aligned CNT synthesis is based on a catalytic chemical vapor deposition process which consists in a catalytic decomposition of a liquid hydrocarbon-based aerosol [27–30]. The aerosol is generated by an injection system (Qualiflow-Jipelec) coupled with an evaporator maintained at 200 °C. The precursor mixture, made of ferrocene (Acros, 99,9%) dissolved in toluene (Merck, 99.9%) is filled in a tank and the resulting solution is nebulized through the injection system which feeds a cylindrical quartz reactor (55 mm internal diameter) introduced in a 1 m long tubular and horizontal furnace. The aerosol is carried by argon flow in the reactor and, the argon carrier gas feeding is separated from the precursor solution tank resulting in a precursor aerosol feeding rate of the reactor independent of the argon flow rate. The growth mechanisms have been detailed previously [27–30] and the set-up has been adjusted for an efficient growth of aligned CNT on carbon fiber [25]. It consists in depositing a silica based sub-layer previously to the CNT growth. This is performed with the same CVD process and in the same CVD reactor, which reduces considerably all intermediate handling steps of materials which is a real challenge for the development of a secure CNT growth process. In order to perform such synthesis, the evaporator is fitted with another injection system similar to the one for the growth of CNT. This injection system is connected with another tank containing a solution of tetraethylorthosilicate namely TEOS, (Aldrich, 99%) (figure 1).

The temperature furnace profile is illustrated in the figure 2 which indicates that the isothermal area (+/- 20°C) starts at 20 cm and finishes at 80 cm from the entrance of the furnace. Our previous results show that the best growth rate of CNT and catalyst efficiency is obtained for a solution of ferrocene diluted in toluene (2.5 wt. %), and pyrolysed at 850°C.
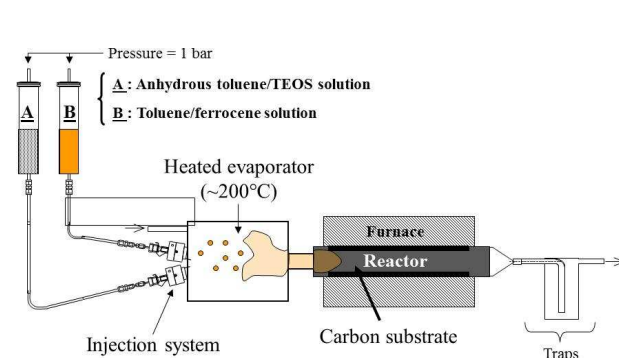

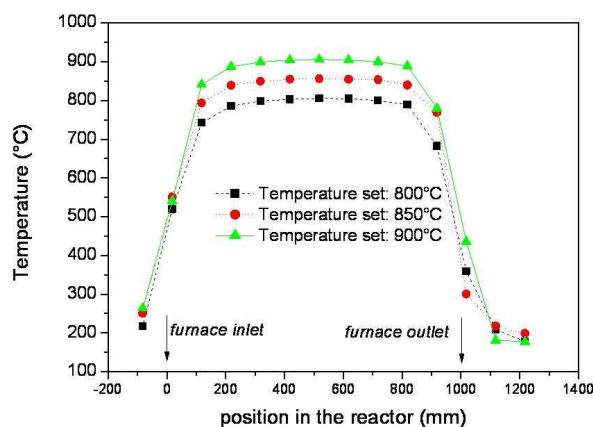**Figure 1.** Experimental setup for both SiO2-based layer deposition and CNT growth [25].

Figure 2. Temperature furnace profile.

Characterizations of synthesized materials are performed with Scanning Electron Microscopy SEM (Carl Zeiss Ultra 55) to observe the morphology and to measure the length of aligned CNT carpets on quartz substrates as well as on carbon fiber cloths. TGA analyses are carried out under air up to 1000°C with a heating rate of 10°C/min in order to assess the iron content in CNT which, in particular, corresponds to iron contained in catalytic particles generating CNT.

3. Results and discussion

2.1 Growth of aligned carbon nanotubes in a long reactor

Castro *et al.* [30] reported studies on synthesis of aligned CNT growth in a short quartz reactor and studied catalyst particle location as well as CNT length along this reactor after CNT growth. Iron-based catalyst nanoparticles are formed by homogeneous nucleation in the gas phase at a location in the reactor where the temperature is optimal for the ferrocene decomposition (826°C), which happens to be before the isothermal area. From this point, nanoparticles carried by the gas flow are deposited gradually on the reactor walls and their surface density decreases. They give rise to aligned CNT growth with efficiency strongly dependent on the temperature profile. CNT growth is optimal in the isothermal area at the temperature chosen to optimize the carbon precursor catalytic decomposition. This dependence explains the inhomogeneity of CNT products along the reactor especially in terms of thickness [30].

Taking into account the aim of the present study which is to grow homogeneously aligned CNT carpet on large fibre cloths, it is important to check, first, that the same phenomena are observed on a longer reactor device same as the one reported in [25]. Therefore, the same procedure as the one reported in [30] has been performed involving the collection of powdered samples on the internal walls of the reactor by decomposing the reactor in 8 distinct areas of 50 mm or 10 mm long each (no substrates were placed in the reactor). The injection of the precursors (solution of ferrocene (2.5 wt.%) diluted in toluene) is performed at 800°C with a feeding rate of 1,5 g/min and with a argon flow rate of 2,5 l/min during 75 min. The aligned CNT carpet thickness (e.g. CNT mean length) have been measured by SEM and the iron content has been measured by TGA for all samples resulting from the collection in each reactor area.
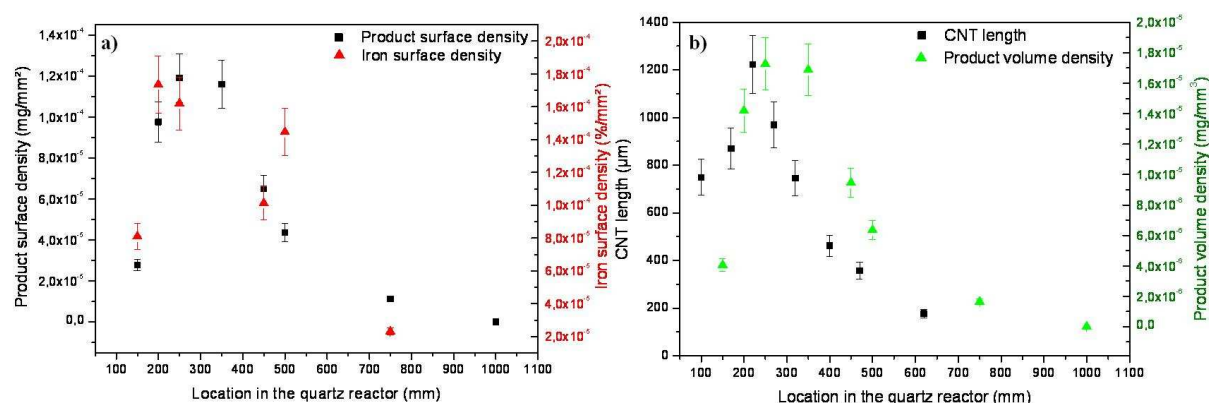

Figure 3. Characteristics of the synthesis products as a function of the location in the quartz reactor (a) surface density of total products and iron, (b) CNT carpet thickness and product volume density (error bar corresponds to the measurement error).

Figure 3 reports the changes of product surface density together with iron surface density (figure 3(a)) as well as the CNT length together with the product volume density (figure 3(b)) both as a function of the location in the quartz reactor. A correlated profile between all these data is shown and the trend is very similar to the one reported by Castro *et al.* [30]. Indeed, the CNT mean length and the iron surface density, as well as both product volume and surface density, increase to reach their maximum at a location of 250 mm corresponding to a 800 +/- 20 °C temperature (beginning of the isothermal area). This temperature is only slightly lower than the decomposition temperature of ferrocene (826 °C) [30], and we can assume, similarly to our previous study [30], that in this area ferrocene is decomposed and numerous iron-based catalyst nanoparticles are suddenly nucleating by homogeneous nucleation. After the 250 mm location, a decrease of CNT mean length and iron surface density, as

well as both product volume and surface density is observed. As a consequence, these results indicate that the phenomena reported by Castro *et al.* [30] in a short reactor are confirmed in a long reactor and that the germination of iron-based catalyst particles occurs always at the same temperature whatever the CVD device and the programmed temperature. Therefore, the growth of aligned CNT can be extended on a much longer area of the internal walls when using a long reactor as compared to a short one.

Besides, it was important to check if these phenomena are similarly occurring on substrates placed in this long reactor since the aim is to synthesize aligned CNT on large and flexible carbon fiber cloths. Therefore, we introduced either several short quartz substrates (20) with sizes of 10 mm*10 mm or 3 large quartz substrates with sizes of 100 mm*50 mm, which width corresponds to the quartz reactor diameter. We observe CNT carpet present on the different substrates put in the reactor and those collected from inner reactor walls for the 8 different areas defined previously along the reactor. First, on substrates we observe the same results mentioned previously namely the decrease of the CNT length along the reactor because of the impoverishment of catalytic particles along the reactor. Moreover, in presence of substrates, CNT length measured from CNT carpet collected from reactor wall in the same area varies from 140 µm to 1.37 mm, depending on the area collected in the circumference of the reactor (figure 4). We suppose that it is the consequence of a disruption of the flow in the reactor due to the presence of the substrates.

In other words, two main phenomena have to be considered for a homogeneous growth of CNT on large substrates which are the impoverishment of catalytic particles along the reactor and the disruption of the gas flow in the reactor. Thus, it is necessary to change the reactor entrance configuration to allow a large homogeneous growth on substrates and powder of CNT growing on the quartz reactor wall to limit the disruption and to limit the rapid reduction of catalytic particles along the reactor.
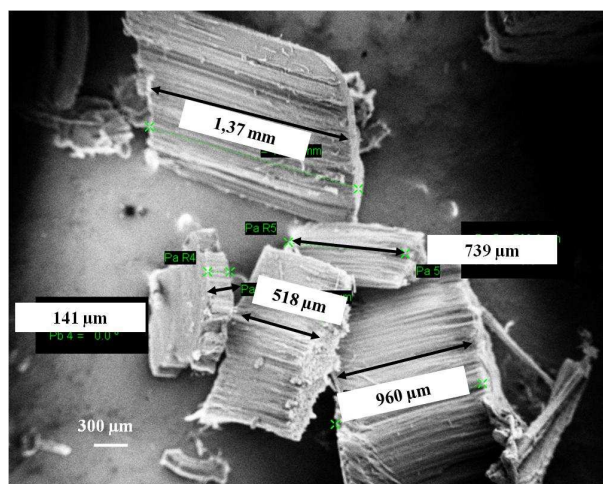

Figure 4. SEM observations of CNT carpet collected from the inner quartz reactor wall.

2.2 Growth of aligned carbon nanotubes on large substrates in a long reactor

2.2.1 Set-up synthesis modifications. To avoid the flow disruption generated by the presence of substrates, the reactor entrance was modified in order to localize the precursor flow only above the substrates. This leads to a decrease of reaction volume by a factor of 2 as compared to the initial configuration of the reactor. This modification plays a role on two parameters: the precursor content per surface unit of the reaction chamber increases as compared to the initial configuration of the reactor which should limit the decrease of iron surface density along the reactor and the precursor flow along the reactor should be less turbulent with low disruption of the flow.

2.2.2 Growth of CNT on large quartz substrates. Before testing this new configuration on carbon fiber cloths, we performed preliminary tests on large quartz substrates. The growth of CNT has been performed on three large quartz substrates (100 mm * 50 mm) placed along the reactor (figure 5) at a temperature of 850 °C during 5 min and with an argon carrier flow rate of 3 l/min and precursor feeding rate of 1 g/min. The temperature was increased as compared to the previous part of the study in order to improve the catalytic yield as reported in the past [31]. The first substrate, located between 40 to 140 mm from the furnace inlet, contains only a thin layer of nanotubes deposited at around 120 mm from the entrance of the furnace which corresponds to a 800°C temperature and is related to the decomposition of ferrocene. This is consistent with the results reported previously, even if the configuration of the reactor has been changed. The part of the quartz substrate located near the reactor entrance is heated at temperatures which are not enough high to achieve the ferrocene decomposition. The second and the third substrates are located in the isothermal area of the furnace (850°C) allowing at the growth of aligned CNT. SEM observations show that on these two substrates the length of CNT is similar, namely around 370 µm +/- 10 µm. As a consequence, this set-up modification enables a homogeneous covering of large flat quartz substrates on an area of 200 mm x 50 mm. This is most probably due to both the precursor content per surface unit of the reaction chamber which is increased as compared to the initial configuration of the reactor and to the precursor flow which is less disrupted, validating thus the set-up modifications adopted.
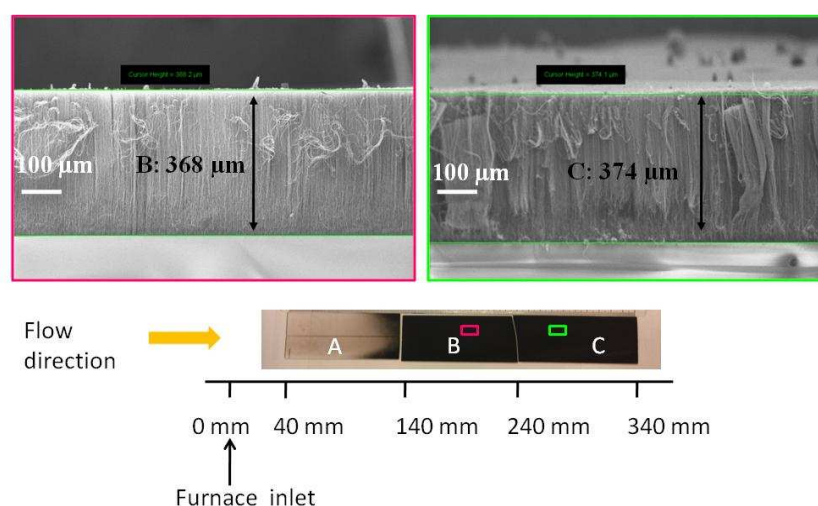

Figure 5. SEM observations of CNT grown on substrates after CVD process adjustment.

2.2.3 Growth of CNT on large carbon fiber cloths. The previous results indicate that the set-up modification enables to get homogeneous CNT growth on flat quartz substrates along a 200 mm long reaction area of the reactor, which means that the CNT synthesis parameters and configuration are optimized. Regarding porous and flexible CF cloth substrates, they exhibit a higher specific surface area as compared to flat substrate, therefore CNT growth conditions need to be adjusted as compared to flat quartz substrates. Moreover, an efficient growth of CNT on CF cloth in terms of alignment and density needs a pre-deposition of ceramic sub-layer on CF as presented in the experimental section. In fact, the feeding rate of ceramic sub-layer precursor (TEOS in this study) and the flow rate of carrier gas have to be adjusted to achieve a homogeneous covering of aligned CNT along the porous CNT cloth (figure 6). Figure 6 shows the influence of carrier gas flow rate which varies from 1 l/min to 10 l/min. For 3 l/min, we have slightly improved the surface covering of CNT on CF cloth as compared to the other flow rates but this is not enough to cover the whole cloth surface. The TEOS feeding rate is then adjusted to 0.1 g/min which involves a homogeneous covering of CF cloth with aligned CNT, as shown in figure 6(c).
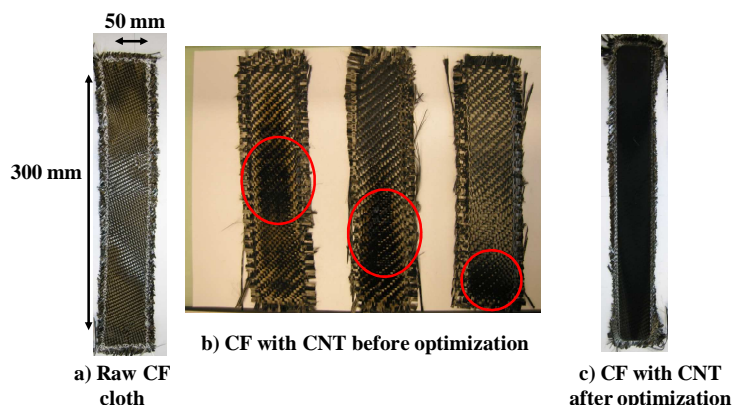
Figure 6. Pictures of carbon cloth (a) raw cloth, (b) cloth without optimization showing CNT on small surface of the carbon fiber cloth, (c) cloth with homogenous growth of CNT on the whole carbon fiber cloth.

The length and the morphology of CNT can be tailored by injection duration of toluene/ferrocene mixture. It is possible to grow either entangled CNT with high density covering the whole CF of the cloth for 3 min precursor injection or long CNT (50 µm mean length), dense and aligned perpendicularly to the CF axis along the CF cloth (200 mm * 50 mm) for 5 min precursor injection as illustrated on figure 7.
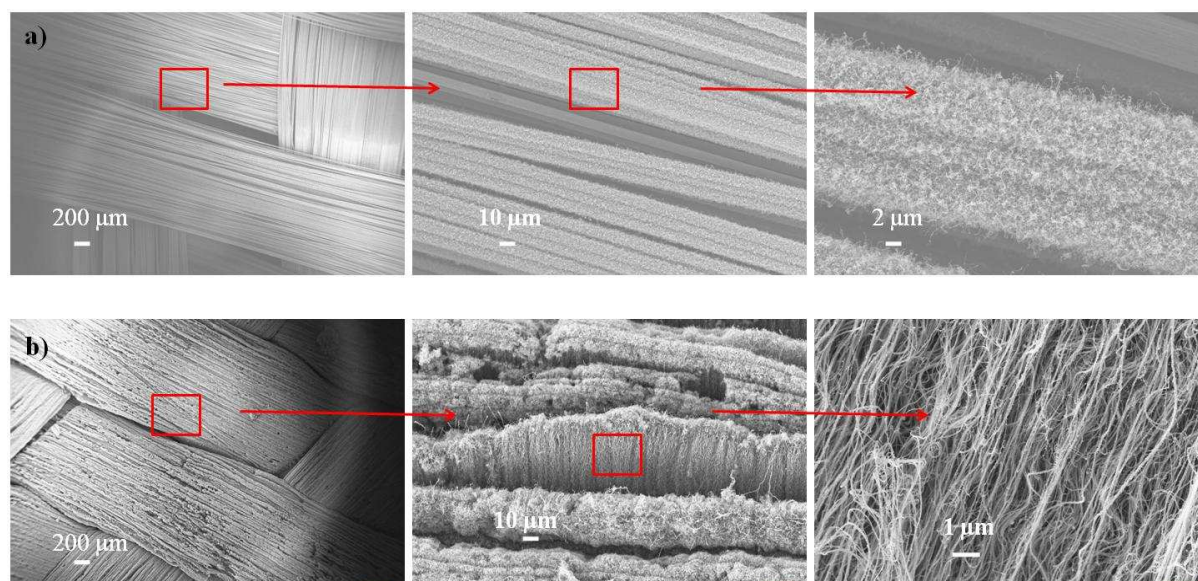

Figure 7. (a) CF cloth with high density of entangled and short CNT covering CF (3 min precursor injection duration) and (b) CF cloth with long dense and aligned CNT covering CF (5 min precursor injection duration).

4. Conclusion
In conclusion, we have demonstrated that the trends regarding vertically aligned CNT growth in small sized CVD reactor are confirmed on larger CVD reactor. Moreover, we have adjusted and optimized the CVD equipment and synthesis parameters in order to achieve a homogeneous covering of large substrates (quartz substrate or carbon fibre cloth with size of 200 mm * 50 mm) by aligned CNT. The length of CNT can be tailored in order to answer to different applications such as membranes or composites. Moreover, growth of CNT on large substrate opens the route to the elaboration of

composite which sizes are compatible with the measurement of mechanical properties such as the interlaminar shear strength.

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