Towards large scale aligned carbon nanotube composites: an industrial safe-by-design and sustainable approach

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Abstract. We present the main results demonstrating the feasibility of high surface (> A4 format size) semi-industrial fabrication of composites embedding VACNT in organic matrices. The process of growing VACNT exhibits several advantages regarding safety issues: integrating de facto a safe collecting procedure on the substrate, avoiding additional preparation steps and simplifying handling and protection by impregnation into a matrix. The following steps of the overall process: VACNT carpet functionalization, alignment control and impregnation, can be processed on-line in a closed and safe continuous process and lead to dramatically reduced direct nanotube exposure for workers and users. This project opens the route to a continuous, roll-to-roll, safer, cost-effective and green industrial process to manufacture composites with controlled and aligned greener « black » carbon nanotubes.

1. Introduction

Since their structural identification by Ijima in 1991, Carbon Nano Tubes (CNTs) have remained an exciting material over many years. Their properties are exceptional: stronger than steel, better thermally conductive than diamond, better electrical conductive than copper, blackest material on earth, easy chemical functionalized, faster and frictionless molecule transportation [1]. Industrial production capacity of
dispersed carbon nanotube powder has boomed since 2005, mainly conditioned in masterbatches. The coming of industrial production of Vertically Aligned Carbon Nanotubes carpets/arrays/forests (VACNT) is still at its first stages and is generally considered as the second generation of safer carbon nanotube production [2][3]. Among the different growth processes, CVD methods are the most promising to produce with a high growth rate array/forest or carpet of well-aligned CNTs. The Vertically Aligned CNTs (VACNTs) topology has demonstrated promising properties by combining CNT individual properties and specific arrangement [4]. Recent papers are investigating the embedding of polymers or other matrix materials such as ceramics in the free space between the CNTs in order to fabricate nanostructured multifunctional composites and materials [5][6].

2. Front-end process: VACNT Synthesis by Aerosol Assisted CVD

From an industrial point of view, the main challenges are the control of carbon nanotube characteristics and structure through a safe and low cost process applicable to large surfaces. In this context, Catalytic Chemical Vapour Deposition (CCVD) appears to be a versatile process with great potential. In order to grown VACNT carpet, a carbon source and a catalyst is needed (often Iron, Cobalt or Nickel although other catalysts have been promoted). Two families of CCVD process can be distinguished according to the way the catalyst is engineered:

- The pre-deposition method, which consists of preparing a substrate out of the furnace where nanotubes grow and then synthetize VACNT. Once the catalyst is pre-deposited, the substrate is then submitted to a gas flow of carbon sources. This method has been for years developed for electronic application as it allows a lower synthesis temperature and the patterning of the growth through the patterning of the catalyst layer [7][8]. This method has the disadvantage of a quite slow growth rate and a limitation in the height of the resulting carpets. The addition of water molecules, in a very low quantity, has revolutionized the method leading to a so-called “super-growth” method [9] that can be up-scaled to large surface substrates [10].

- The « co-injection » method which consists of feeding simultaneously and continuously both catalyst and carbon sources in a single step simpler process. Especially, the Aerosol-Assisted CCVD process developed at CEA [11] offers a fast [12] and continuous growth of VACNT directly on various substrates [5][14] with control of nanotube characteristics as density, diameter, length and doping [13].

Although some aspects of the growth process is still not understood, the industrial stakes are now to propose schemes that could be extended for larger surfaces at
mastered costs in safer conditions. In this context, aerosol assisted growth, as illustrated in fig. 1.a, reveals to be the more economical and the safer one.

**Figure 1: Aerosol Assisted CCVD process basics and typical horizontal furnaces configurations**

The synthesis standard procedure has been described previously [11][12]. Briefly, the precursor mixture is composed of 2.5 wt% of ferrocene dissolved in toluene, a composition that was found to be an optimum in terms of growth rate and catalyst efficiency [13]. The resulting solution is nebulized through an injection generator (Kemstream Company, France) associated to an evaporator maintained at 200°C. The temperature is typically fixed at 850°C. The aerosol is carried out by a gas flow of 1 L.min⁻¹ of argon. Moreover we have demonstrated, in laboratory furnace configurations (small and short reactors (external diameter of 1.9 cm and length of 45 cm)), that the process is robust and allows a large control of VACNT carpet characteristics such as:

- Nanotube length ranges from few microns to several millimeters and depends directly on the synthesis duration [5][14];
- Nanotube density [3] ranges from $10^9$ to more than $10^{10}$ CNTs per cm², according to the iron concentration;
- Nanotube diameter can be reduced by the use of additional gas (H₂) [16];
- At last, nanotube structure can be changed by the use of different additional gas (NH₃ etc ..) [17].

Growth is also possible on many other substrates (Quartz, Si, Stainless steel, …) [12] or even flexible fiber substrates [5][15] by adding in the same process a pre-deposition step of catalyst barrier layer.

3. Scale-up of VACNT growth through Aerosol Assisted-CCVD process

3.1. First step: growth of VACNT in laboratory equipment in horizontal configuration
Syntheses were performed in a laboratory set-up equipped with a quite large reactor (55 mm internal diameter), which is introduced in a 1 m long tubular and horizontal furnace.

![Figure 2: VACNT growth on intermediate substrate in an horizontal furnace. (a) VACNT on quartz substrat with STM view of the carpet size, (b) on carbon fiber cloths with STM typical arrangement in aligned ribbons](image)

Squared or rectangular flat quartz or silicon or metal substrates of 5x10 cm2 were placed in the reactor and synthesis is operated at 850°C from precursor solutions of ferrocene (2,5 wt%) in toluene. In addition, growth was also performed on woven carbon fibers exhibiting sizes of 5 x 30 cm. In the case of metal substrates and carbon fiber cloth, a previous treatment is performed consisting in depositing a ceramic oxide barrier layer in order to prevent catalyst diffusion in the substrate [15]. Figure 2 shows the growth on both quartz substrates (a) and carbon fiber cloths (b), with respectively SEM observations. Both substrates are homogeneously covered by a dark layer, which corresponds of carpet of aligned CNT perpendicularly aligned to the quartz substrate surface or to aligned CNT arranged as ribbons along the carbon fiber axis. Therefore, with this quite large experimental set-up, it is possible to homogeneously cover quite large substrates, which are interesting for R&D studies.

3.2. Second step: growth of VACNT in commercial equipment, transposition to vertical configuration

Synthesis on circular silicon wafers of 100 mm diameter (78.5 cm² surface) was performed in a vertical CVD set-up (MC-100 commercial equipment, ANNEALSYS company, Montpellier, France), keeping the substrate in a rotating motion. This set-up is usually used for metals, alloys, oxide and nitride compound layer deposition. We obtain a homogeneous covering of the whole Si substrate by a black layer (figure 3 a)). SEM and TEM observations indicate that this layer is composed of well aligned
and clean carbon nanotube carpets (figure 3 b)) made of multi-walled carbon nanotubes (Figure 3 c)) as in the horizontal configuration. Alignment has been checked by SEM (Figure 3 b) and CNT length is homogeneous all along the substrate surface (figure 4).

This successful synthesis demonstrates that we obtain VACNT of the same characteristics that in horizontal lab furnace, while both temperature and gaz flow is different. Moreover, VACNT growth on moving substrates (rotating), opens the road to roll-to-roll VACNT industrial process.

![Figure 3: a) 100 mm Si substrate homogeneously covered by VACNT, b) SEM characterisation of the VACNT carpet c) TEM images of multiwall nanotubes](image)

![Figure 4: Homogeneousness of the VACNT carpet's height (nanotubes length) all along the substrate](image)

3.3 Design of a new semi-industrial batch-to-batch pilot-plant

We designed a new pilot furnace to allow the semi-continuous production of 12 inches wafer scale or A4 format sheets, to up-scale the growth process for larger surfaces and industrial scales. A prototype equipment was therefore built in a vertical configuration for production of VACNT on large substrates such as silicon wafers exhibiting a diameter of 300 mm (706.8 cm² surface).

Synthesis are performed from toluene/ferrocene precursor solution, in Ar atmosphere at pressures varying between up to 1000 mbar and at temperatures
between 800 and 850 °C on immobilized silicon substrates. The prototype equipment based on vertical configuration and on immobilized substrate enables the homogeneous formation of VA-MWCNT carpets covering homogeneously the whole surface of the Si substrate (Figure 5 (a)) similar to the ones obtained both in horizontal configurations on laboratory equipment and at intermediate scale.

SEM observations (using a SEM-FEG Zeiss Ultra 55 electron microscope) performed on the cross section of the Si substrates at 11 cm from the edge of the Si wafer (Figure 5 (b-c)) reveal the formation of a carpet of well aligned CNT exhibiting a thickness of 200μm for a synthesis duration of x min using a 2,5 wt.% solution of ferrocene dissolved in toluene. After dispersion in alcohol of the CNT carpet collected on the Si substrate at the same position (11cm from the edge of the substrate), CNT morphology and size are obtained from transmission electron microscopy (TEM Philips CM 12) and confirm that carpet is composed of multi-walled CNT with a mean external diameter of x nm and exhibit the cleanliness of the samples with very few by products (Figure 5 (d)).

Moreover, carbon structure has been studied by Raman spectroscopy (Renishaw Invia Reflex, l=532 nm) at the same position (11cm from the edge of the substrate). Recorded spectrum (Figure 5 (e)) exhibit the 2 strong D and G bands (at ~ 1354 cm⁻¹ and ~ 1582 cm⁻¹ respectively) commonly observed for CNT structures. The resulting ID/IG intensity ratio is about 0.27 which is lower than the one reported for aligned MWCNT raw samples synthesized by CVD [1, 2] which is about 0.4 and is significantly lower than the ones generally reported for MWCNTs produced by CVD.
[18]. Thus these analyses confirm the good structural quality of the well aligned multi-walled CNT carpet obtained at the surface of the large Si substrate in our prototype equipment.

4. Back-end process: impregnation, and membrane thinning

Our approach is to use and keep vertically aligned carbon nanotubes carpets in order to evaluate their properties in applications such as:

- Energy system electrodes: the use of VACNTs is electricity storage devices such as ultra-caps, batteries or solar systems is of great interest [19];
- The fact that VACNT can be grown on flexible substrates such as carbon fibers [15], is of great interest for lighten composite material and make them electrically and thermally conductive [16]
- Other exceptional examples are given in the field of environment where one will benefit from both chemical and nanofluidic properties of nanotubes in applications ranging from CO2 sequestration and water desalination [22].

We developed several processes to engineer raw VACNT and fabricate an intermediate product such as an electrode, a composite material or a membrane. For each process, we adopted classical industrial processes, coming from either mechanical or microelectronics industries that could lead to a continuous implementation.

Functionalization, coating or impregnation of VACNT carpet are processes to treat individual nanotubes external surfaces and to fill the space in between the nanotubes to fabricate a dense composite material made of aligned nanotubes in a polymeric matrix.

- In particular, diazonium chemistry in aqueous media was shown to be a powerful tool to graft nanotubes [23]. The grafting phase is obtained by pure chemical protonation of diazonium that serves as a seed for polymer growth. Thickness is easily controlled by the treatment duration and the process is easy to handle and eco-friendly.

The objectives of the coating can be manifold:

- coating can protect from individual nanotubes release during the process [20];
- Functionalization to add a functionality to the composite;
- Allow the removal of substrate by maintaining nanotubes;
- The coating can also be useful as a sub layer in order to improve the link between the impregnation matrix and carbon nanotubes.
Impregnation step consists of filling, without any porosity, the space in between the nanotubes by different polymerization methods. Several polymers have been tested, from PS (polystyrene), PMMA (Poly-methyl methacrylate), epoxydes, PET and other specialties polymers. It has been proven that we can impregnate thick carpets of more than 1 mm in thickness without any detectable porosity or crack (figure 6.a).

![Image](Image)

*Figure 6: Complete impregnation of a thick VACNT carpet (a) side impregnation 1 mm nanotubes with of epoxy (b) top of the carpet*

At the end of the process, Chemical Mechanical Polishing (CMP) was used to thin the composite, laser ablation to engineer the carpet [24] and plasma treatment was used to open nanotubes caps (figure 6.b) in a membrane fabrication context. At the end we were able to extend and chain all the steps of the process continuously as illustrated in figure 7, leading to the fabrication of the current biggest VACNT membrane.

![Image](Image)

*Figure 7: global process illustration allowing us to realize the current biggest VACNT membrane (70 microns of thickness)*

5. **Sustainability and Safe-by design approach**

We adapted the process to replace chemical species such as toluene, which is recognize as CMR, by alternative solvents coming from green sources. We tested three different green oils:
| Source          | Chemical Formula | Density (g/ml) | Molecular weight (g.mol⁻¹) | Vaporisation temperature (°C) |
|-----------------|------------------|---------------|---------------------------|-------------------------------|
| Toluene         | C₇H₈             | 0.867         | 92.14                     | 111                          |
| Camphor oil     | C₁₀H₁₆O          | 0.992         | 152.23                    | 204                          |
| Palm oil        | C₁₆H₃₂O₂         | 0.8527        | 256                       | 350                          |
| Eucalyptus Oil  | C₁₀H₁₈O₂         | 0.913         | 154.25                    | 175                          |

*Table 1: Alternative green Carbon sources for VACNTs*

Figure 8 illustrates the surprisingly good quality of nanotubes obtained by these sources, in particular Camphor Oils, which is already observed in case of dispersed nanotubes [25]. We tested the same mix of ferrocene in these oils (2.5 %w) and proceeded as in a classical synthesis. In this case VANCNT growth rate has been observed as higher than with Toluene/ferrocene reaching up to 200 microns/min.

*Figure 8: VANCNT made from Camphor oil, Alignment and cleanliness observed by SEM*

As already mentioned, one of our motivation is to be able to design a complete fabrication process starting from chemical products to final product without any manipulation, transportation or manual treatment, thus avoiding any exposure (expect of course in the case of maintenance).
In this objective, it appears that AACVD is certainly the safest process as it exhibits many advantages in regards to more classical fluidized-bed-type dispersed nanotubes processes that multiply steps to produce final clean nanotubes.

- Nanotubes in carpets are Non Volatile, Homogeneous in length, clean (less than 4% catalyst content)
- The process is operated in classical room condition (no clean room needed), at ambient pressure, with the use of liquid precursor (easy to handle).
- The fact that the growth occurs on a substrate, allows a direct collection, no sorting neither cleaning steps are needed
- Nanotubes in carpets are easier to store, to manipulate and finally to disperse in case we want to get dispersed nanotubes with this process
- We keep the alignment all along the process
- VACNT carpets can then be directly coated or impregnated to encapsulate CNTs, reducing any further direct exposure.

In order to evaluate and improve safety aspects, we collected residues during the CMP thinning phase. Indeed, by principle, all other phases of the global process, growth, functionalization, impregnation or laser steps do not release any residues. For the thinning step, we never observed by SEM any individual NTCs alone, they are always encapsulated in big polymers particles and often in bundles (« big » particles > 500 microns in Figure 10).

5. Perspectives and Conclusions

We present the main results obtained within the framework of the French program NaWaA4, which aimed at demonstrating the feasibility of high surface (> A4 format size) industrial fabrication of composites embedding VACNT in organic matrices. The process of growing VACNT exhibits several advantages regarding safety issues: integrating de facto a safe collecting procedure on the substrate, avoiding additional preparation steps and simplifying handling and protection by impregnation into a matrix. The following steps of the overall process: VACNT carpet functionalization, alignment control and impregnation, can be processed on-line in a closed and safe continuous process and lead to dramatically reduce direct nanotube exposure for employees and users. We collected sample and residues all along the process and found only large composite particles (of size > 100 nm) made of nanotubes into polymer, which are less toxic than volatile CNT powders. This project opens the route to a continuous, roll-to-roll, safer, cost-effective and green industrial process to manufacture composites with controlled and aligned greener «black» carbon nanotubes.

Acknowledgments.
This work has been supported by the French National Agency (ANR) in the frame of its technological Research NANO-INNOV/RT program (NaWaA4, project N°ANR-09-NIRT-05). Within the framework of the project, the author wants to thanks:

- Julien Cambedouzou, Denis Petermann, Pascale Launois from Université Paris Sud/Laboratoire de Physique des Solides
- Sebastien Pacchini and Christina Villeneuve from CNRS/LAAS (toulouse)
- Sebastien Roussel from Pegas-tech
- Jacques Cinquin, Stéphane Bechtel and Amélie Darfeuille from EADS-IW
- Nicolas Debski for Raman Analysis
- Thomas Gabard for synthesis on pilot

This work has also been supported by the SAPHIR European project (SAfe and Integrated Nanomanufacturing). Authors want to thank Frédéric Schuster for fruitful discussions and CEA’s Materials transverse program financial support.

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