Optimization of CVD processes for the growth of carbon nanotubes with applications in the development of novel polymeric nanocomposites and water purification concepts.

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1. Introduction

Chemical vapor deposition, is considered the most promising method of synthesis of high-purity, good-quality carbon nanotubes, with the possibility of being upscaled [1]. This technique uses hydrocarbon as a carbon source and transition metals as a catalyst. Albeit many studies on the topic have been released recently, an important effort has to be made to relate slight changes in the process parameters to the final properties of the nanotubes, as industrially fabricated CNTs are still quite non-uniform in morphology and properties.

In present work different processes and catalysts have been evaluated towards the obtaining of tailored carbon nanotubes (CNTs) by means of this technique for applications in the development of nanocomposites and water purification concepts.

2. Fabrication process

2.1. Catalyst preparation

Different alumina-supported iron catalysts have been developed in two different forms on silicon substrates:

- As a liquid suspension of iron nitrate, alumina and a molybdenum salt, spin-coated on a substrate. Iron nitrate is oxidized into iron oxide during heating and is finally reduced in the growth process, alumina acts as a placeholder for iron particles and molybdenum as a growth promoter.
- By the deposition of sputtered thin films (500nm of silica, 10nm of alumina and 5nm of iron). By means of the annealing of the samples in a hydrogen atmosphere, the iron film is nucleated, acting like a seed for the growth of the nanotubes when the hydrocarbon gas is decomposed in a high-temperature process [2].

2.2. CVD process

Two kinds of processes have been developed using ethylene or methane as the carbon source.

- In the first process, there is an initial step in which the sample is soaked in hydrogen at 600ºC. Then, the temperature is elevated to 750ºC and a flow of ethylene is introduced during 1h for the growth of the nanotubes.
- In the second process, the sample is soaked in hydrogen at 900ºC to prepare the catalyst. Afterwards, the growth takes place when methane is introduced at the same temperature during 20min.

3. Results

By the combination of these processes and catalysts (and variations of them), CNTs of different dimensions, purity and morphology have been grown and inspected by field emission scanning electron microscopy (FE-SEM).

Attending to the pursued applications in the development of nanocomposites and water purification systems, a process using ethylene and the thin film catalyst have been selected, leading to high-purity vertically-aligned multi-wall carbon nanotubes, shown in figure 1. This combination produced the largest yield of CNTs per process and unit area of the substrate, as nanotubes of more than 1mm long have been obtained, meeting the requirements in volume for the concerned applications.

By means of transmission electron microscopy, the diameter of carbon nanotubes was determined to be between 10nm and 15nm.

For the optimization of this established process, thermogravimetric analysis (TGA) and Raman spectroscopy were of great help to determine the level of impurities.

TGA (figure 2, left) indicates low concentration of amorphous carbon (which is lost in air at 400ºC), as well as low metal catalyst residues [3], having CNTs with a purity near to 98%.

The time of injection of ethylene was varied between 15min and 2h and it was observed that the length of the nanotubes increased, but after 1h the growth was slower and amorphous carbon appeared. From the Raman measurements (figure 2, right) it can be noted that the amount of the impurities increased with the time of growth, as seen from the relation between the intensity of the peaks D and G [4] for the different samples.

In light of these results, it could be said that the nanotubes obtained as explained above are of very good quality, which makes them be expected to work well as an additive for the fabrication of good properties nanocomposites and also for water purification applications.

4. Application of the obtained CNTs

In the field of the refractory bricks, there is an interest in substituting graphite by CNTs by its inclusion in the precursor resins used for its fabrication, which are expected to improve the durability of the final product. Different kind of carbon nanostructures, including the above described CNTs, have been added to a phenolic resin (Bakelite type) and dispersed with the aid of ultrasounds and mechanical stirrers. Research is at the moment at the stage of comparing the properties and performance of nanocomposites fabricated with commercial CNTs with the ones developed during the project at a lab scale.

Elimination of contaminants in industrial wastewater is another field of interest in which CNTs obtained as explained in this work are being applied. For recalcitrant wastewater purification, carbon nanotubes were oxidized in order to enhance their dispersive properties in water by means of different treatments: i) nitric acid/sulphuric acid, ii) nitric acid/hydrogen peroxide and iii) ammonium hydroxide/hydrogen peroxide. Characterization of the obtained products by TPD and XPS demonstrated the selective introduction of functional groups: carboxilic acid, alcohols and ketones, respectively.

In a similar way, obtained CNTs will be used in different concrete applications of interest to industry, including integrated sensors, ropes and slings, domotic tiles and fire-resistant sandwich panels. These cases of study have been proposed in the framework of NANOCIT, an Alliance of Spanish technological centers created with the aim of promoting collaboration in the field of the development of new materials based on the use of carbon nanostructures.

Acknowledgements

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References

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Figures

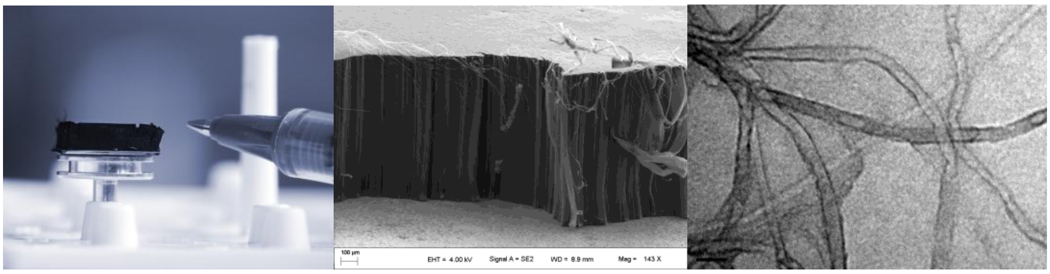

Figure 1. Images of the CNTs obtained at increasing magnification level from left to right. (Photograph, Field Emission Scanning Electron Microscopy and Transmision Electron Microscopy)

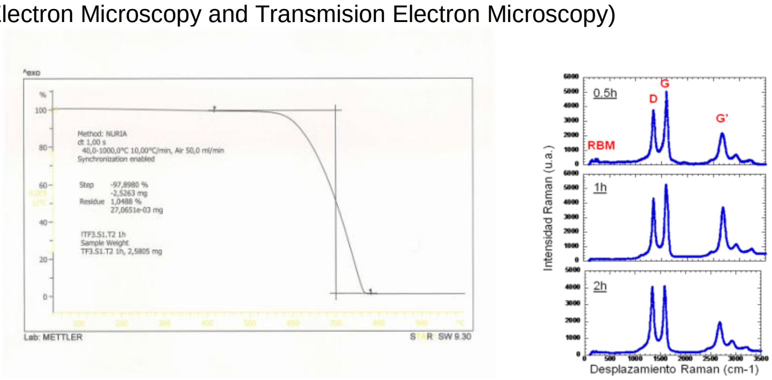

Figure 2. TGA and Raman spectroscopy of the CNTs samples, from which purity was evaluated.