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Production of bamboo-type carbon nanotubes doped with nitrogen from polyamide pyrolysis gas

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ABSTRACT

Bamboo-type carbon nanotubes (BCNTs) doped with nitrogen were produced by catalytic chemical vapor deposition from the effluent gases resulting from pyrolysis of polyamide 6.6. This polymer provides the carbon and nitrogen source and allows to obtain enough hydrogen during its decomposition for the carbon nanotubes (CNTs) production without prior catalyst reduction. The influence of pyrolysis and growth temperatures was studied in order to obtain the best quality CNTs. Transmission electron microscopy, X-ray diffraction, and Raman spectrometry showed that the best results were obtained at 900 °C pyrolysis temperature and 750 °C growth temperature, since the presence of amorphous carbon was negligible and the best crystalline degree was obtained. These BCNTs had from 5 to 20 layers and their arcs of bamboo-like compartments had from 3 to 15 layers. They had 20 nm in diameter and lengths typically on the order of micrometers.

1. Introduction

Carbon nanotubes (CNTs) were first reported by Oberlin at al [1] and were extensively studied after the profound characterization given by Ijima [2], due to its extraordinary mechanical and conductive properties. They are graphitic materials composed mainly of carbon, where the basic units are graphene layers rolled into perfect cylinders. However, there are also CNTs lattices where foreign atoms are inserted, thus modifying their structure and their chemical and physical nature. Some authors have studied CNTs doped with different heteroatoms as boron [3,4], nitrogen [5–7] and others, but among them, the bamboo-type CNTs doped with nitrogen (BCNTs), have particular interest in electronics since they show a higher electron carrier concentration that renders n-type behavior [8–12]. Therefore, the synthesis of these materials is crucial in the semiconductor industry if they want to be used as future building blocks, in nanocomposites and nanoelectronic devices. In fact, their interest is increasing in a variety of electrical engineering applications. The field emission characteristics of BCNTs have also been demonstrated to be better than those of pristine CNTs [13]. Additionally, nitrogen-doped graphitic materials present a high enhancement of the specific electrical capacitance, of great importance in energy storage [14].

Nitrogen atoms can be incorporated into the CNTs lattice trough either in situ methods, using a nitrogen source together with the carbon source, or trough post-treatment strategies [15]. In situ techniques are more commonly reported in recent investigations, with strategies such as dc-arc evaporation [16], thermal chemical vapor deposition (c-CVD) [17–23], and microplasma assisted CVD [24–27]. Previous research references were found for CVD synthesis methods where expensive reagents are used, and sometimes hydrogen as a reaction atmosphere. Moreover, usually they are complex methods and nitrogen–carbon precursor gas stream must be evaporated previously in order to be homogeneous before injecting it into the CVD reactor. Chen and Higgins [28] employed three different kind of mixtures of ferrocene and three different aliphatic diamines (ethylenediamine, 1,3-diaminopropane and 1,4-diaminobutane) in solution, and injected them in a furnace at 800 °C. Katayama et al. [29] evaporated Ni-phthalocyanine and grew BCNTs in two consecutives furnaces at temperatures of 600–850 °C in presence of H_2/Ar. Boncel et al. [30] made use of a mixture well dissolved of toluene and pyrazine, which decomposes into acetylene, hydrogen cyanide and cyanoacetylene at 760 °C, as the carbon and additional heteroatomatic nitrogen precursor along with ferrocene. This feedstock was introduced in a horizontal injection c-CVD furnace at temperatures of 760 and 860 °C. Wong et al. [31] synthesized BCNTs using precursor solutions which consisted of ethanol and aniline, diethylamine, and ethylenediamine, respectively. The premixed solutions were heated to its boiling point before entering the furnace along with iron (II) phthalocyanine when temperature reached 850 °C. Li et al. [32] chose imidazole, as both precursor of carbon and nitrogen, and ferrocene as the catalyst, they were evaporated simultaneously and carried by Ar into a horizontal quartz tube furnace at 850 °C. Villapando-Paez et al. [33] synthesized BCNTs by pyrolyzing a

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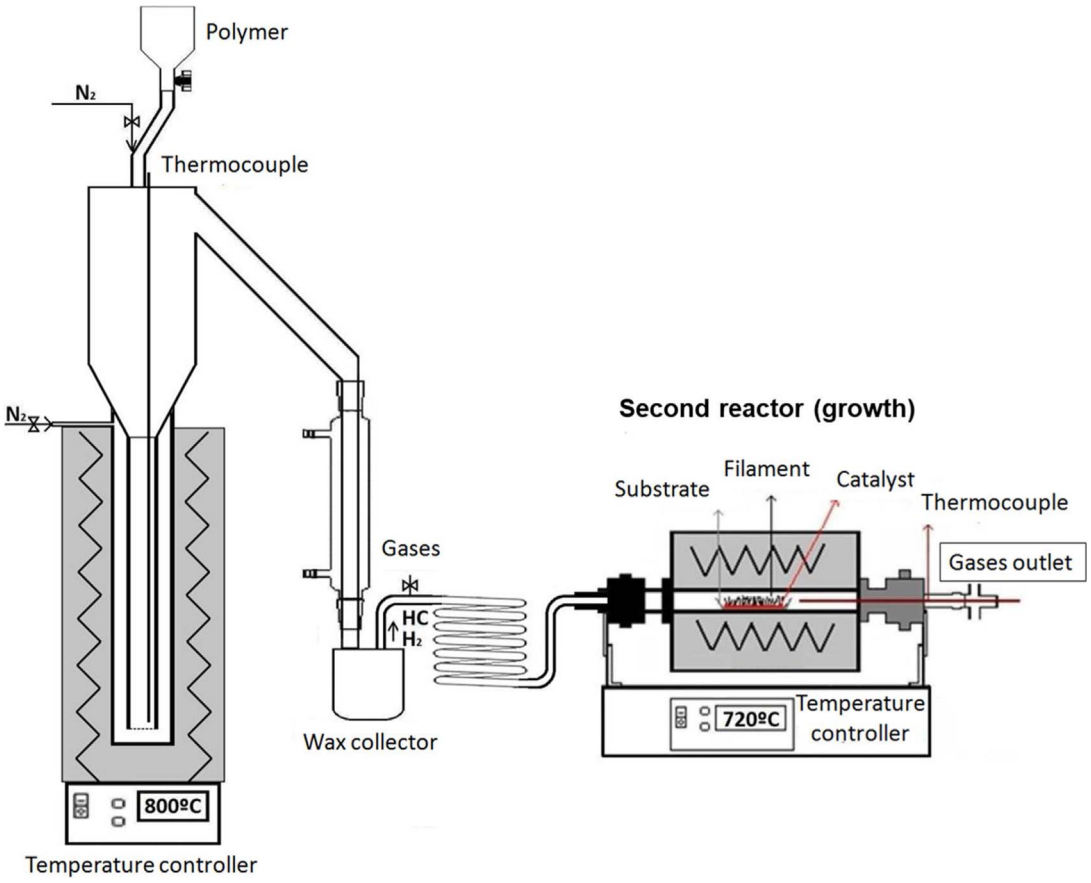

Fig. 1. Diagram of the experimental set-up used for the BCNTs synthesis.

ferrocene/ethanol/benzylamine solution. For that purpose, the solution was first introduced inside an aerosol generator, and the mist produced was directed to a furnace operated at 950 °C. Srivastava et al. [34] pretreated an iron film in NH_3 plasma and introduced acetylene and hydrogen in a tubular microwave plasma enhanced CVD at 600 °C. Lee et al. [35] produced BCNTs with a Ni/Si catalyst dipped in HF solution and treated with NH_3 and acetylene at 950 °C in a quartz reactor. Hao et al. [36] pyrolyzed acetonitrile over MgO supported Fe catalyst in a tube furnace in the presence of hydrogen at 850 °C.

On the other hand, several studies have already shown the viability of different waste plastics pyrolysis gas as a carbon source and hydrogen evolution for the production of CNTs and carbon nanofibers (CNFs). A pyrolysis stream produced in a first reactor (or first half of a reactor) is conducted to a second reactor for filament growth by c-CVD. These studies are mainly focused on the production from polyolefins, polypropylene [37–42] and polyethylene PE [42–45]. Other contribution studies the production of CNT from a mixture of waste polymers, more realistic and economically viable, which consists of a majority of polyolefins with small contribution of polystyrene [37,46], polyvinyl chloride [42,46], PET [47], etc. Borsodi et al. [46] also studied the production of CNTs from a pyrolysis stream of a set of waste polymer mixtures, including one based on polyolefins and 1 wt-% polyamide. However, nothing was reported about its structure with respect to those mixtures without a nitrogen feedstock. Consequently, there are no studies about production of BCNTs from waste polymers to our knowledge.

In view of these circumstances, the aim of this work was to take advantage of the nitrogen content in the structure of some polymers to study the feasibility to grow BCNTs by c-CVD. To this end, the effluent gases from pyrolysis of polyamide (PA) were used, thereby avoiding extra carbon, hydrogen and nitrogen source and without prior reduction of the catalyst. Thus, the process is simplified and the cost is reduced with respect to other methods proposed in the literature. In addition to this, the influence of pyrolysis and growth temperatures was studied to find the proper conditions for the best quality of BCNTs.

2. Material and methods

2.1. Preliminary pyrolysis study at laboratory scale

As a first approximation to know the composition of the effluent pyrolysis gases of PA at different temperatures, a preliminary study of a set of polymer decomposition experiments in a bench-scale reactor was carried out. The PA used was PA 6.6 (Dinalon Natural A3S25-0042, Grupo Repol, Spain). The reactor was a batch horizontal quartz tubular furnace (AOX Euroglass 1600) where around 200 mg of polymer was pyrolyzed at different temperatures, ranging from 600 to 900 °C based on the literature [48–50]. The feeding system of the reactor allows the introduction to the sample to the oven once it is already at the setpoint temperature, which assures to reach the final temperature in a few seconds, simulating a continuous reactor. More details about the apparatus can be found elsewhere [44]. Special attention was paid to obtain nitrogen compounds and hydrogen as decomposition products, since they are required for growing BCNTs.

Gases and volatile compounds evolved in the thermal process were collected in a Tedlar® bag and analyzed by gas chromatography. On the one hand, a Shimadzu GC-14A gas chromatograph equipped with a thermal conductivity detector (TCD) was used, with a Supelco carbosieve SII (4 m × 1/8) column to value mainly hydrogen, and with a concentric Alltech CTR I column (6 ft × 1/8 in. and 6 ft × 1/4 in. for the inner and outer columns, respectively) to value mainly CO and CO_2. On the other hand, the light hydrocarbons were analyzed in a Shimadzu GC-17A gas chromatograph with a Supelco capillary Alumina-KCl Plot column (30 m × 0.32 mm) in split injection and a flame ionization