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Parametric study on the influence of synthesis variables in the properties of nitrogen-doped carbon nanotubes

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ABSTRACT

Nitrogen doped carbon nanotubes (N-CNT) were synthesized by a Modified Chemical Vapor Deposition method, using pyridine as carbon and nitrogen source, and ferrocene as catalytic agent for the nanotubes growth. The influence of synthesis parameters as the temperature, carrier gas flow rate, concentration of the reactants and preheating temperature over the morphology and physical properties of the N-CNT, were investigated by high-resolution scanning electron microscopy, transmission electron microscopy and X ray diffraction. The statistical analysis for the length of the N-CNT forest revealed that the synthesis temperature and carrier gas flow rate have significantly influenced on the physical properties of the material. The synthesis temperature not only affected the length of N-CNT forest, but also influenced the mass production, as well as, in diameter and the nitrogen content in the nanotubes. This is an important step towards the high yield production of N-CNT for applications in hydrogen storage, electrocatalysts for fuel cells and other electrochemical devices.

Introduction

The exceptional properties of carbon nanotubes, such as good electrical conductivity, chemical and mechanical stability, high thermal conductivity, light weight, and physicochemical compatibility make them an ideal material to be utilized in electrochemical devices [1]. However, in certain applications, it is necessary to modify the nanotubes characteristics to improve their electrochemical properties. One way to enhance such properties is by adding different heteroatoms to their structure (i.e. N, S, B, and Si). Nitrogen atoms have been used as dopant in the carbon structure [2], the so-called nitrogen doped carbon nanotubes (N-CNT) have different potential applications in various areas, such as hydrogen storage [3–5], field emission devices [6,7] and catalysis [8,9]. One of the

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most promising applications is as electrocatalyst for the oxygen reduction reaction (ORR) in fuel cells electrodes [10,11]. The N-CNT can be an efficient candidate as a replacement for expensive catalysts based on platinum, which are commonly used in this reaction [12–14]; however improved synthesis methods need to be achieved to produce doped carbon nanotubes and reach the mass production to meet the future electrocatalysts demand [15,16]. Among the many variety of methods to synthesize CNT, the chemical vapor deposition (CVD) technique is one of the most promising method to produce carbon nanostructures in large quantities, technically scalable and economically viable [17–19]. Nevertheless, the mass production process of N-CNT with the desired structures and properties has been a challenge [20]. Ombaka et al. [21] studied the mass production obtained from three catalyst dissolved in pyridine and acetonitrile, synthesized at 850 °C via CVD. Product yields obtained with pyridine (100–256 mg) were higher than those obtained with acetonitrile (15–30 mg). It is noticeable that although the nitrogen precursor solution influences significantly the materials amount, the product yield is still relatively low. Liu et al. [22] prepared N-CNT (at 850 °C) by the mixture of imidazole and acetonitrile. A systematic study was carried out on the effect of solution injection rate, size of the solution droplet feed to the reactor and the nitrogen concentration on the growth of carbon nanotubes; the results showed that the addition of imidazole increased the N-CNT growth rate and product yield (12–192 mg). Although high length and good quality of nanotubes were obtained, mass production still needs to be improved. Boncel et al. [23] optimized the carbon nanotubes growing conditions by varying the key synthesis parameters such as temperature (660–860 °C), solution composition (ferrocene, toluene and pyrazine) and time of growth; they found that temperature at 760 °C was the optimum value to get very high density of the nanotubes forest and the growth time was proportional to the N-CNT length (10–40 μm). Despite advances in synthesis, it is still necessary to reduce costs and increase product yield. Several studies have been reported to optimize N-CNTs product yield using different types of catalysts [24,25], wherein iron is one of the catalyst that provides a higher mass production. For example, Wang et al. [26] synthesized N-CNT varying the type of transition metal (Fe, Co, Ni or Mn) to catalyze the graphitization of cicyandiamide where Fe yielded the largest tubes. Many efforts have been made to increase the mass production of N-CNT; however, for CVD processes to be economically viable, it is essential to reduce the production costs by using inexpensive materials and optimizing the synthesis parameters.

On the other hand, many studies [27–31] have been done on the effect of temperature on the physical properties of N-CNT. However, few studies had been reported on the synthesis temperature and its correlation to other parameters such as carrier gas flow rate and concentration of the reactants. Although the advance in the synthesis of N-CNT is wide, it is still essential to evaluate the importance of the synthesis parameters and their impact on the main properties and product yield of the carbon nanotubes. Therefore, in this work the production of N-CNT by a Modified Chemical Vapor Deposition method (M-CVD) is highlighted. The microstructure and chemical composition of the samples were analyzed by high-resolution scanning electron microscopy (HR-SEM), transmission electron microscopy (TEM) and X ray diffraction (XRD). The effects of various synthesis parameters such as synthesis temperature, carrier gas flow rate, concentration of the reactants, and preheating temperature were evaluated using an unreplicated 24 factorial design methodology. This parametric study allowed determines the most favorable synthesis parameters in order to reach a high yield production of N-CNT.

Experimental

Synthesis of nitrogen doped carbon nanotubes

N-CNT synthesis was carried out by the M-CVD, the details of the experimental set up and conditions of the synthesis process were previously reported [32]. A brief description is as follows, pyridine (99.5%, Merck) was used as a source of carbon and nitrogen, and ferrocene (98%, Aldrich) as metal catalyst for the nanotubes growth. The molar ratios of low and high pyridine-ferrocene concentration were 1:8 and 1:16, respectively. For the synthesis of pristine carbon nanotubes, only toluene (99.8%, J. T. Baker) and ferrocene were used as carbon source and catalyst, respectively. Vycor tubes (0.7 cm internal diameter and 50 cm length) were placed in a tubular furnace and utilized as growth substrate. Synthesis was carried out by two heating steps; first, the solution was injected by a peristaltic pump and preheated at low temperature (180 and 200 °C) in a home-made heater in order to vaporize the solution; then it was injected into the high temperature tubular furnace using argon as carrier gas. At the end of the process, the furnace was cooled down to room temperature keeping the argon atmosphere. The obtained N-CNT were mechanically removed from the Vycor tube, and then treated with concentrated nitric acid (66.5%, J. T. Baker) during 12 h in order to remove residual iron from the reaction as well as the amorphous carbon. Finally, the treated N-CNT were washed and dried in an oven for 12 h. The analysis was performed varying four synthesis parameters (factors), each of them with two levels high and low, as shown in Table 1. Hence, sixteen experiments were carried out, in order to study the effect of the factors on the physical properties of the N-CNT.

Characterization

A scanning electron microscope Vega 3 Tescan was used to study the morphology of the materials. The images were acquired from different random areas in the sample, in order to assess their typical characteristics. The SEM was also used to determine the elemental composition of the bulk sample by energy-dispersive X-ray spectroscopy (EDS). In addition, a HITACHI SU-8230 high resolution scanning electron microscope and a JEOL JEM-2200FS transmission electron microscope were used to provide high resolution images. For HRTEM analysis, the samples were dispersed by ultrasound in ethanol and placed on a TEM copper grid. The X-Ray diffractograms were obtained in a Bruker D8 advanced equipment, operated at 40 kV and 40 mA. Cu-Kα radiation was used with a wave length $\lambda = 1.5418$ Å.

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