Synthesis of carbon nanofibers and nanotubes using carbon disulfide as the precursor

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The synthesis of carbon nanofibers and nanotubes by a thermal chemical vapor deposition technique using carbon disulfide as carbon source and iron as the catalyst is reported. The nanofibers present a poor graphitisation stage and we find the existence sulphur incorporated in the nanofibers. We show an example of an atypical behaviour of the electrical characteristic against temperature of a nanofiber film that might be related to the existence of sulfur.

Keywords: Carbon nanofibers and nanotubes; thermal chemical vapor deposition, sulfur.

En este trabajo se reporta la síntesis de nanofibras de carbono empleando la técnica de descomposición térmica de vapores químicos empleando disulfuro de carbono como fuente de carbono y hierro como catalizador. Se encuentra que las nanofibras están en una etapa inicial de grafitización y la existencia de azufre en su estructura. Se presenta un ejemplo de comportamiento anómalo de la característica eléctrica como función de la temperatura de películas delgadas de este tipo de nanofibras que podría estar relacionado con la existencia del azufre.

Descriptores: Nanofibras y nanotubos de carbono; descomposición térmica de vapores químicos; azufre.

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1. Introduction

Carbon nanotubes and nanofibers have resulted very interesting materials owing to their unique physical properties. Due to their electronic and mechanical properties and by their hollow structure, many potential applications have been proposed; such as nanometer-sized electronic devices, composites with other materials and for hydrogen storage [1]. For this reason we consider important to explore new routes for the synthesis of carbon nanotubes and nanofibers. Many techniques have been developed for these purposes, for example by arc-discharge, laser ablation and by thermal chemical vapor deposition (CVD) [2]. CVD has particularly resulted a valuable method to grow carbon nanotubes and nanofibers due to its versatility in the use of a great variety of carbon precursors and catalysts. In this work we report the synthesis of carbon nanotubes and hollow nanotubes by the CVD method using iron as a catalyst and carbon disulfide (CS$_2$) as the carbon source, the important finding is the production of a high yield of nanofibers with an excess of sulfur in the reaction.

2. Experimental section

The experimental details of the CVD system used for the synthesis have been published elsewhere [3], in this work the only difference is the change of the carbon source (CS$_2$). Briefly, as the source of the iron a 120 mM solution of Fe(NO$_3$)$_3$.9H$_2$O in ethanol was prepared and spin-coated on fused quartz and silicon substrates which were placed at the center of an horizontal quartz tube furnace. The tube was purged with argon and the temperature was raised to 900 °C under an argon flow of 126 sccm, then the flow of argon was switched off and replaced by pure hydrogen (450 sccm, 5 minutes) directly into the tube furnace. After this process, the hydrogen flow is reduced to 88 sccm and passed through a bubbler containing 20 ml of carbon disulfide during a period of 60 minutes. At the final of this stage, the flow of hydrogen through the bubbler is switched off and pure argon (126 sccm) is introduced directly into the tube furnace. Finally, the furnace is switched off and cooled to room temperature under the argon flow.

Material characterization was performed using a scanning electron microscopy (SEM JEM5600), X-ray diffraction (Siemens D5000) and infrared spectroscopy (Nicolet 510P). An electron microscope copper grid was gently placed on the substrate sample to collect carbon nanofibers for high resolution electron microscopy (HRTEM) observations using a JEOL 2010 FasTem analytical microscope equipped with EDS and GATAN Image Filter (GIF) facilities.

3. Results and discussion

In Fig. 1a a SEM image of the sample grown on the fused quartz substrate is presented: long and entangled nanofibers can be observed. An overall view of the SEM and TEM images show nanofibers with diameters ranging from 50 nm to 500 nm and some nanofibers are as long as 0.5 mm. Some
of the structures show uniform diameter and others with nonhomogeneous morphology show several waistlines as is illustrated in Fig. 1b. The image contrast indicates that the nanotubes with uniform diameter are hollow (Fig. 1c); meanwhile we did not find an irrefutable evidence of the hollow nature of the nanofibers with non uniform diameter; a further electron diffraction study has been performed at different morphologies, however this part of the structural characterization remains under study. Closer observation shows that some nanotubes with uniform diameter have elliptical segments producing interconnected compartments (Fig. 1c) and HRTEM indicates a poor graphitization stage of their walls, such as is observed in Fig. 1d.

In the X-ray diffractogram, taken in the whole sample on the quartz substrate (Fig. 1a), we can not identify any peak associated to a crystalline graphitic phase, but a shoulder observed at low diffraction angles in the broad peak can be approximately fitted to a Lorentzian peak centered at \(2\theta \sim 25.1^\circ\) (Fig. 2), which can be associated to a disordered carbon with a \((002)\) spacing of \(d \sim 3.54\,\text{Å}\), similar to that found for carbon nanotubes obtained by other methods [4]. This fact is also consistent with HRTEM analysis, where a highly defective graphitization stage is observed (Fig. 1d). In this XRD the existence of the hexagonal phase of FeS can also be identified. This compound is formed on the substrate with the reaction of the iron catalyst and sulfur from the decomposition of \(\text{CS}_2\).

Due to the high content of sulfur in the reaction, one important issue is to determine whether sulfur is incorporated in the nanofibers. For this purpose, a local nanoprobe was focused on a nanotube in order to obtain an elemental analysis by EDS (square on Fig. 3a). The analysis showed that the atomic ratio of sulfur in relation to carbon is \(S/C = 0.25/99.75\%\) at (Fig. 3b). On the other hand, from the hollow morphology of the nanotube showed in Fig. 3a is evident that there is not diffraction contrast observed inside of the nanotube due to the presence of Fe or any compound of iron. This issue is corroborated by the elemental chemical analysis obtained by EDS where no traces of Fe are present inside of this particular nanotube. An elemental mapping was performed in GIf mode using K-Carbon (284 eV) and L\(_{23}\) - Sulfur (165 eV) edges respectively. The images filtered at carbon and sulfur edges from the EELS spectrum are shown in Fig. 3: in (c) the image corresponds to a nanotube mapped at K-Carbon edge (the holey carbon film is also observed clearly because of the presence of carbon) and in (d) the image corresponds to mapping at the sulfur L\(_{23}\) edge; in this case just the nanotube is observed and the gray brightness contrast depends on the sulfur presence at the surface of the tube, therefore, the contrast intensity of the zone depends on the sulfur accumulation in a particular zone of the sample. Although sulfur appears along the nanotube, the white arrows in the image show that the sulfur is non-uniform distributed on the fiber surface. It is not conclusive the presence of S inside of the hollow surface tubes. The elemental chemical analysis by EDS or EELS technique must be performed at cross section view of the nanotube, this part of the characterization is under study; however, the GIF analysis results strongly suggest that the sulfur must be associated at any surface of the tube.

\[\text{FeS}\]
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Figure 3. (a) STEM micrograph from a single nanofiber and (b) its corresponding EDS microanalysis, where it is possible to observe the C and S peaks. (c) Image filtered at carbon edge using a GIF spectrometer for other nanofiber and (d) the corresponding image filtered at sulfur edge.

Figure 4. (a) HAADF image from a hollow nanotube. A high intensity zone is observed at the edge of the tube. (b) EELS spectrum from the brightest zone shows the presence of Fe in the particle.

Figure 5. IR spectrum of the as grown nanofibers on silicon substrate. The peaks labeled Si-C (612 cm$^{-1}$) and SiO$_2$ (small peak at 1100 cm$^{-1}$) correspond to the substrate.

Alternatively, it is possible to observe particles with high brightness obtained by HAADF technique, where the image contrast strongly depends on the Z number of the sample compounds. This result confirms the presence of an iron chemical phase at some edges of the nanotubes (Fig. 4). The HAADF image shows the hollow nature of the tube and the corresponding EELS spectrum in diffraction mode taken at the nanoparticle zone corroborates that this particle corresponds to an iron compound which could be the hexagonal phase of FeS identified by X-ray diffraction (Fig. 2).

In an attempt to see the sulfur bonds, in Fig. 5 we present an IR spectrum of a sample grown on a silicon substrate. For carbon-sulfur polymers, the following bands have been reported: S-S stretching modes (473, 462, 425 cm$^{-1}$), C=S stretching modes (1155, 1070 cm$^{-1}$) [5] and features associated to C-S stretching modes located between 600-900 cm$^{-1}$ [6]. On this base, we tentatively assign the following bands in the IR spectrum to: S-S stretching (450 cm$^{-1}$), C-S stretching (800 cm$^{-1}$) and C=S stretching (shoulder around 1150 cm$^{-1}$) modes. We believe that due to the poor graphitization stage there are many carbon dangling bonds that react with sulfur to have C/S bonds, or perhaps the existence of great quantities of sulfur in the reaction provokes the poor graphitization of the fibers [7].

On the other hand, the precise role of sulfur in the synthesis of carbon nanotubes and nanofibers is not clear to date, but it has been reported that it works as a promoter, mainly leading to a high yield and quality of nanotubes [8]. Other reports raise the importance of sulfur in the arc-discharge method to have filled nanotubes with metals [9]. In some experiments using iron as a catalyst, the high yield of carbon nanofibers by adding sulfur have been explained invoking the VLS (vapor-liquid-solid) process [7]. Within this model sulfur reacts with iron forming the eutectic phase at 988°C, more sulfur produce the liquefaction of the catalyst particle enabling the VLS process and then the gas phase of the precursor can dissolve and decompose more efficiently in the liquid catalyst. But sulfur in excess moves the melting point above the eutectic, decreasing the production of good quality nanofibers and nanotubes. In other studies [10] the reconstruction of catalyst surface has been adjudicated to sulfur at low coverage making the surface more active and provoking the rupture of carbon-carbon bonds, carbon atoms then diffuse through the solid and the growth of carbon nanofibers in the rear part of the catalyst particle is attained. Higher coverage of sulfur can eventually form a bulk compound which inhibits completely the catalytic activity of the particle [10].

The results obtained in this work indicate the production of high yield of carbon nanofibers and hollow nanotubes using a precursor with high content of sulfur and that some sulfur is incorporated in the structure of the nanofibers. We believe that this material might have novel physical and chemical properties. As an example, in Fig. 6 we present the electrical resistance against temperature characteristic curve of a thin film of carbon nanofibers on glass substrate [11]. It is evident an anomaly around 273 K that may be related to charge
trapping enhanced by the functionalization with sulfur; but this issue deserves further investigation.

4. Conclusions

The synthesis of carbon nanofibers and nanotubes doped with S using CVD technique via CS$_2$ as carbon source and iron as catalyst is reported in the present work. The morphology structures correspond to waistline bending nanofibers and hollow straight multiwall nanotubes. However the graphitization stage of the nanotubes by this technique generates highly defective walls. The presence of S at the external surface of the nanotubes is corroborated by image filter using energy loss spectroscopy. This result promises a novel functionalization technique in order to decorate MWNCT with metal nanoparticles to obtain hybrid materials with application in gas sensors avoiding the use of thiols molecules. The profile of the electrical resistance as function of temperature has an anomaly around 273 K, we believe this effect could be related with the presence of sulfur on the carbon nanofibers.

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