Microstructural Characterization of Large Area C$_{60}$ Films Obtained by Conventional Microwave Oven Irradiation

Jacobo Martínez-Reyes$^1$, Lucia Graciela Díaz Barriga-Arceo$^2$, Luis Rendón-Vazquez$^3$, Reynaldo Martínez-Guerrero$^4$, Néstor Romero-Partida$^4$, Eduardo Palacios-González$^2$, Vicente Garibay-Febles$^5$, Jaime Ortiz-López$^1$

$^1$National Polytechnic Institute (IPN), ESFM, UPALM, Mexico City, Mexico
$^2$National Polytechnic Institute (IPN), ESIQIE, UPALM, Mexico City, Mexico
$^3$Facultad de Ciencias, UNAM, Mexico City, Mexico
$^4$ROMFER S.A. de C.V., Mexico City, Mexico
$^5$IMP-Molecular Engineering Program, Mexico City, Mexico
Email: jacobomartinezreyes@gmail.com, luchell@yahoo.com

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ABSTRACT

In the present work the synthesis of C$_{60}$ produced in a conventional microwave oven from the decomposition of camphor resin is reported. The polycrystalline structure of the sample was determined by X-Ray Diffraction (XRD), the sample showed several phases, the main phase corresponds to fullerene C$_{60}$ ordered in a Face-Centered Cubic structure (FCC), with two more structures: one orthorhombic system and the other the monoclinic system coexisting also with graphite 2H phase. It was observed in a Scanning Electron Microscopy (SEM), that the sample formed thin films of stacked carbon. Whereas in a High Resolution Transmission Electron Microscopy (HRTEM), measurements in Bright Field mode revealed that the main phase of the material is C$_{60}$ ordered in FCC structure and the elemental composition and atomic bonding state can be determined by analyzing the energy with the electron microscope by Elesctron Energy-Loss Spectroscopy (EELS), technique allowed confirm all the phase C$_{60}$ established with XRD observations.

Keywords: Microwave-Assisted Synthesis; Carbon Film; Fullerene

1. Introduction

Carbon thin films are important for the development of applications due to the physicochemical properties [1-5]. Several methods are currently used for the preparation of carbon films such as: the condensation of steam to carbon, magnetron sputtering, mechanical peeling, chemical vapor deposition, physical vapor deposition [6-11] among others. In these methods the films are obtained in temperature conditions at ranges of 950°C - 1250°C with different energies from 100 to 1000 eV at pressure from 1 to $5 \times 10^{-7}$ Tor using inert atmospheres or carbon gases as control atmospheres, flowing in a continuous way to obtain small area films with thicknesses from 500 nm to 10 microns and crystalline or amorphous structure [12], making this synthesis expensive. Comparing the chemical precursors used in the synthesis of carbon films, it was observed that organic resins present more advantages than the inorganic precursors because some of these resins are environment friendly that is why camphor resin was chosen [13-15]. It is important to mention that camphor C$_{10}$H$_{16}$O resin has been successfully used in carbon nanomaterial synthesis and also in carbon films [16-20]. Therefore the Microwave Assisted Synthesis (MAOS) [21-28], is a cost-effective alternative technology which reduces the impact on the environment by saving energy, being able to produce materials and microstructures that cannot be performed by other methods. The aim of this work was to find the synthesis and microstructural of carbon films to characterization them carbon films by microwave radiation a resins of commercial camphor.

2. Experimental Details

2.1. Microwave Oven Preparation

The plate was removed from the microwave oven and the samples were placed in a position where the microwave radiation reaches the maximum. Determinations of maximum and minimum points were done as reported in literature [29]. Resin sample were located in one of the points where microwave radiation has one maximum.

2.2. Sample Preparation

For this work 250 mg of camphor Sigma-Aldrich were
placed in a Florence flask because it was observed that this glass result better than Pyrex glass under the same radiation condition (Figure 1(a)). The flask volume was 250 ml; the glass container with camphor was located inside a commercial SANYO microwave oven with a frequency of 2450 MHz. The sample was heat treated to the maximum power (1480 Watts) for 5 minutes. Until a carbon film was observed through the microwave oven windows. During the heat treatment, the temperature was measured by using an Infrared Thermometer Cole Palmer Mod.800-323-4340 with LCD display, with a temperature range of −18°C to 900°C (Figure 1(b)).

2.3. Sample Characterization

The film sample were characterized by X-Ray Diffraction in a Siemens D-500 diffractometer using CuKα (λ = 1.54 Å). The sample were observed with two instruments a Scanning Electron Microscope SEM/FIB NOVA 200 (with point resolution of 1.7 Å) and High Resolution Transmission Electron Microscopy FEI Tecnai G-20 to 200 kV with resolution of 1.9 Å. Also the sample was analyzed by electron energy loss spectroscopy (EELS) for quantitative chemical determination and detail about the e-type vibrations resolution @ 20 to 200 kV. The micrographs were analyzed using Digital Micrograph Software version 3.7 for GMS 1.2 Gatan Company.

3. Results and Discussion

3.1. Sample Obtained

The temperature of the substrate and the structure of the deposited species are the major factors for growth of the carbon thin film which depend on the wavelength of the microwaves and the reaction volume, these factors control the atomic mobility on the surface and determining the physical characteristics of the deposited films such as: microstructure, composition and structure. This is because carbon atoms when exposed to microwave radiation, the temperature can increase rapidly by dielectric heating [30,31], the mechanism responsible for the polarization or the effect Maxwell-Wagner due to the free electrons in the carbon. It is known that different allotropes or organic precursor upon heating to different degrees in a microwave field depend on its structure and composition for this reason are considered microwave absorbing material [32,33]. The average film surface is in the range from 2 to 12 cm² (Figure 1(c)), obtaining films of high surface area compared with the literature that a macroscopic level the average size of the area of the films is reported 2 cm × 2 cm [34].

3.2. X-Ray Diffraction Patterns

The diffraction pattern of carbon thin film is shown in Figure 2. In this pattern many phases were observed and they were identified using a reference database cards ICDD PDF-2 Release 2003 [35-39].

It was observed that the well-defined peaks in this pattern correspond to the highly ordered crystalline structures. In this pattern those peaks are thin and correspond to main phase of the sample which is C₆₀ fullerene molecule ordered in a face-centered cubic structure which is the phase of higher symmetry. In this pattern a broad peak, in the range between 15 and 26 degrees can be observed, this peak is crowded by other well defined low intensity peaks, corresponding to lower symmetry phases C₆₀ ordered in orthorhombic and monoclinic structures. Another phase observed was the hexagonal 2H graphite phase. It can be noticed that the presence of these phases may be caused by the difference in temperature in the container and between the sample and glass substrate. A summary of the observed phases is shown in Table 1.

3.3. Scanning Electron Microscope and Electron Dispersive Spectroscopy

In Figure 3(a) the scanning electron micrograph of carbon film is shown. Since graphite tape may cause confusion with the carbon film, which is commonly used to hold samples, the carbon film was supported on a copper tape.

In Figure 3(b) it was observed that carbon film consists of a series of stacked monolayers. The film thickness was measured using FEI Nova Nanolab analysis and imaging software. The film thickness varies from 140.8 to 523.3 nm. A qualitative chemical composition was

![Figure 1](image1.png)  ![Figure 2](image2.png)

Figure 1. (a) Terpenoid C₁₀H₁₈O; (b) Synthesis in microwave oven; (c) Carbon thin films.

Figure 2. XRD pattern carbon thin film.
Table 1. Phases of the diffraction pattern of carbon film.

<table>
<thead>
<tr>
<th>Name</th>
<th>Charter Number</th>
<th>Crystalline Structure</th>
<th>Lattice Parameter (Å)</th>
<th>Space Group</th>
<th>Percentage of Phase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{60}^+$</td>
<td>81-2220</td>
<td>Face-centered cubic</td>
<td>$a = 14.16$</td>
<td>Fm 3m</td>
<td>82.7</td>
</tr>
<tr>
<td>$C_{60}^+$</td>
<td>82-0505</td>
<td></td>
<td>$a = 9.56$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{60}^+$</td>
<td>49-1718</td>
<td>Orthorhombic</td>
<td>$b = 8.87$</td>
<td></td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$c = 8.34$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$a = 10.27$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$b = 7.80$</td>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$c = 9.49$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{60}^+$</td>
<td>49-1719</td>
<td>Monoclinic</td>
<td>$\beta = 92.4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td>89-7213</td>
<td>Hexagonal</td>
<td>$a = 2.464$</td>
<td>P63/mmm</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$b = 9.92$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$c = 26.51$</td>
<td></td>
<td>6.6</td>
</tr>
<tr>
<td>$C_{70}$</td>
<td>50-1363</td>
<td>Rhombohedral</td>
<td>$a = 2.464$</td>
<td>R 3m</td>
<td></td>
</tr>
</tbody>
</table>

*aReference [37,40], bReference [35], cReference [38], dReference [36].


In Figure 4(a), bright field electron transmission micrograph of sample is observed. From this Figure, it is easy to observe the crystalline behavior of cubic phase $C_{60}$ (Figure 4(b)). Two interplanar distances were measured, using the Digital Micrograph program (D.M).

The direction index associated with those d spacing were [4 0 0] y [3 1 1] and zone axis from plane (0 4 4).

Figure 3. (a) SEM micrographs of the carbon film; (b) Thickness of carbon film; (c) EDS-carbon film.

Figure 4. (a) Bright field electron HRTEM carbon films; (b) Fast Fourier transformation; (c) EELS spectra. The spectra show the $\pi^*$ and $\sigma^*$ peaks in the carbon K-edge; (d) Histogram of the measuring the diameter of the molecule $C_{60}$. 

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The buckyball molecule diameter was also measured using the D.M. It was found that molecule diameter value was 6.83Å and corresponds to C_{60} molecule diameter (Figure 4(d)). The measurement error was 3.95% [40-42].

The possible existence of small fullerenes is strengthened by the observation that the peak of the diameter distribution shifts from 5 to 7 Å and back again with increasing residence time, indicating that the smaller structures is not an artifact of the measurement method.

On the other hand, by the technique of the energy loss spectrum of electrons in the thin film of carbon corresponds to C_{60} in the range of 280 to 295 eV (Figure 4(c)). The peak near 285 eV corresponds to the transition 1S→π*(C-C), while the peak >290 eV corresponds to the transition 1S→σ*(C-H), these transitions are due to the formation of covalent bonds with nearby neighbors polymerized C_{60} cluster [43-46], the hump at 296 eV in the region of the carbon K-edge this is characteristic of the C_{60} molecule and was also identified a peak at 530 eV corresponding to oxygen. The 285 eV peak is indicative of the sp² bonding fraction; the second peak at 287 eV is attributed to molecular structure within the sample; the third at 293 eV is determined by sp³ bonding contributions in the simple.

4. Conclusions

In this work, it was possible to obtain from the pyrolysis of camphor in a conventional microwave oven, a carbon thin film.

The film is polycrystalline and consists of fullerenes arranged in different crystal structures and graphite 2H. This indicates that the sample is formed within the furnace in a gradient of temperatures around 800°C working with maximum power of the oven. The main phase corresponds to fullerene ordered in a face-centered cubic structure. The sample shows oxidation.

The area of the sample is higher than obtained by other techniques and is a function of the precursor container volume ratio 10:1.

The surface of the film consists of several monolayer of carbon molecules stacked carbon, even leading material of varying thickness.

It was identified peak near 285 eV corresponds to the transition 1S→π*(C-C), while the peak 290 eV corresponds to the transition 1S→σ*(C-H), these transitions are due to the formation of covalent bonds with clusters near neighbors polymerized C_{60} and a peak at 530 eV assigned to oxygen.

REFERENCES


