

Microstructural Characterization of Large Area C₆₀ Films Obtained by Conventional Microwave Oven Irradiation

Jacobo Martínez-Reyes¹, Lucía Graciela Díaz Barriga-Arceo², Luis Rendón-Vázquez³,
Reynaldo Martínez-Guerrero⁴, Néstor Romero-Partida⁴, Eduardo Palacios-González⁵,
Vicente Garibay-Febles⁵, Jaime Ortiz-López¹

¹National Polytechnic Institute (IPN), ESFM, UPALM, Mexico City, Mexico

²National Polytechnic Institute (IPN), ESIQIE, UPALM, Mexico City, Mexico

³Facultad de Ciencias, UNAM, Mexico City, Mexico

⁴ROMFER S.A. de C.V., Mexico City, Mexico

⁵IMP-Molecular Engineering Program, Mexico City, Mexico

Email: jacobomartinezreyes@gmail.com, luchell@yahoo.com

Received August 14, 2012; revised August 28, 2012; accepted September 5, 2012

ABSTRACT

In the present work the synthesis of C₆₀ 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 C₆₀ 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 C₆₀ ordered in FCC structure and the elemental composition and atomic bonding state can be determined by analyzing the energy with the electron microscope by Electron Energy-Loss Spectroscopy (EELS), technique allowed confirm all the phase C₆₀ 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 5×10^{-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 C₁₀H₁₆O 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 $\text{CuK}\alpha$ ($\lambda = 1.54 \text{ \AA}$). The sample were observed with two instruments a Scanning Electron Microscope SEM/FIB NOVA 200 (with point resolution of 1.7 \AA) and High Resolution Transmission Electron Microscopy FEI Tecnai G-20 to 200 kV with resolution of 1.9 \AA . 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

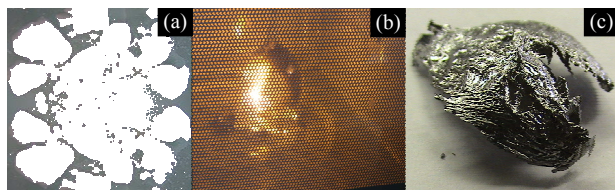


Figure 1. (a) Terpenoid $\text{C}_{10}\text{H}_{16}\text{O}$; (b) Synthesis in microwave oven; (c) Carbon thin films.

absorbing material [32,33]. The average film surface is in the range from 2 to 12 cm^2 (**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 $2 \text{ cm} \times 2 \text{ cm}$ [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 C_{60} 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 crowned by other well defined low intensity peaks, corresponding to lower symmetry phases C_{60} 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

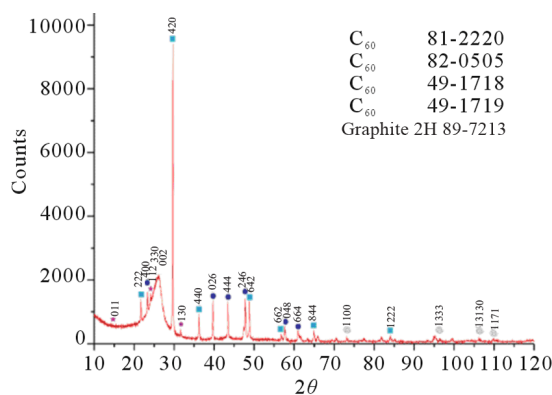


Figure 2. XRD pattern carbon thin film.

Table 1. Phases of the diffraction pattern of carbon film.

Name	Charter Number	Crystalline Structure	Lattice Parameter (Å)	Space Group	Percentage of Phase (%)
C ₆₀ ^a	81-2220 82-0505	Face-centered cubic	a = 14.16	Fm $\bar{3}$ m	82.7
C ₆₀ ^b	49-1718	Orthorhombic	a = 9.56 b = 8.87 c = 8.34	-	4.1
C ₆₀ ^b	49-1719	Monoclinic	a = 10.27 b = 7.80 c = 9.49 $\beta = 92.4$	-	2.5
Graphite 2H ^c	89-7213	Hexagonal	a = 2.464 c = 6.711	P63/mm C	4.1
C ₇₀ ^d	50-1363	Rhombohedral	a = 9.92 c = 26.51	R $\bar{3}$ m	6.6

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

performed (**Figure 3(c)**) by Electron Dispersive Spectroscopy (EDS). The sample is mainly composed by carbon (93.88% at) and oxygen (6.12% at).

3.4. High-Resolution Transmission Electron Microscopy-Electron Energy Loss Spectroscopy

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 C₆₀ (**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 11] and zone axis from plane (0 4 $\bar{4}$).

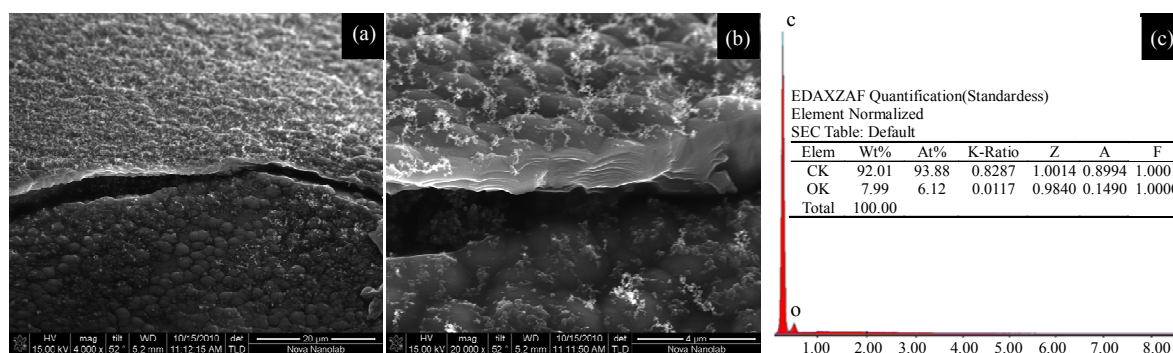


Figure 3. (a) SEM micrographs of the carbon film; (b) Thickness of carbon film; (c) EDS-carbon film.

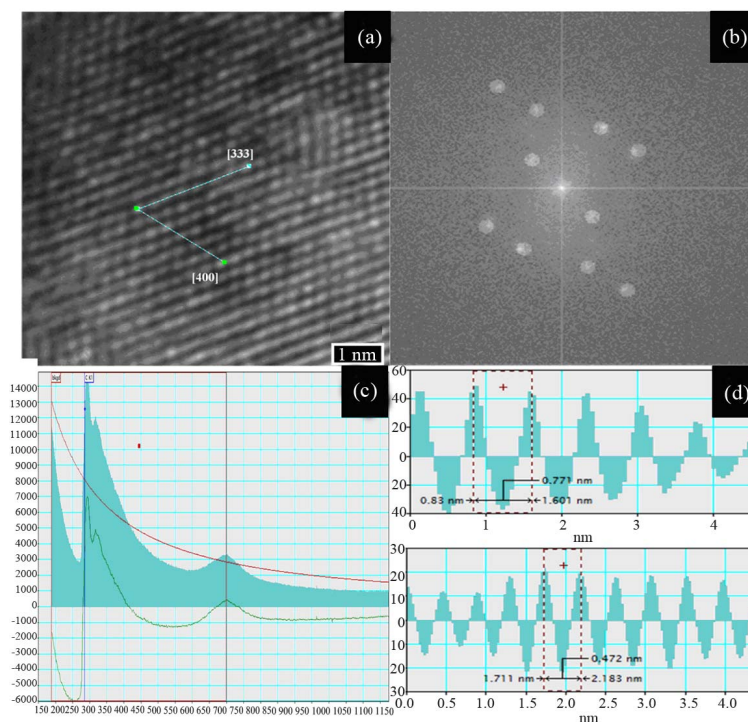


Figure 4. (a) Bright field electron HRTEM carbon films; (b) Fast Fourier transformation; (c) EELS spectra. The spectra show the π^* and σ^* peaks in the carbon K-edge; (d) Histogram of the measuring the diameter of the molecule C₆₀.

The buckyball molecule diameter was also measured using the D.M, It was found that molecule diameter value was 6.83Å and corresponds to C₆₀ 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 C₆₀ 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 C₆₀ cluster [43-46], the hump at 296 eV in the region of the carbon K-edge this is characteristic of the C₆₀ 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 C₆₀ and a peak at 530 eV assigned to oxygen.

REFERENCES

- [1] T. D. Burchell, "Carbon Materials for Advanced Technologies," Pergamon Press, New York, 1999, p. 85.
- [2] R. Schnupp, R. Kühnhold, G. Temmel, E. Burte and H. Ryssel, "Thin Carbon Films as Electrodes for Bioelectronic Applications," *Biosensors and Bioelectronics*, Vol. 13, No. 7-8, 1998, pp. 889-894. doi:10.1016/S0956-5663(98)00057-8
- [3] C. Chen and Z. Lou, "Formation of C₆₀ by Reduction of CO₂," *The Journal of Supercritical Fluids*, Vol. 50, No. 1, 2009, pp. 42-45. doi:10.1016/j.supflu.2009.04.008
- [4] A. H. Jayatissa, T. Gupta and A. D. Pandya, "Heating Effect on C₆₀ Films during Microfabrication: Structure and Electrical Properties," *Carbon*, Vol. 42, No. 5-6, 2004, pp. 1143-1146. doi:10.1016/j.carbon.2003.12.058
- [5] Z. B. Zhou, R. Q. Cui, Q. J. Pang, G. M. Hadi, Z. M. Ding and W. Y. Li, "Schottky Solar Cells with Amorphous Carbon Nitride Thin Films Prepared by Ion Beam Sputtering Technique," *Solar Energy Materials and Solar Cells*, Vol. 70, No. 4, 2002, pp. 487-493. doi:10.1016/S0927-0248(01)00086-1
- [6] R. F. Xiao, "Growth of Large Fullerene C₆₀ Crystals and Highly Oriented Thin Films by Physical Vapor Transport," *Journal of Crystal Growth*, Vol. 174, No. 1-4, 1997, pp. 821-827. doi:10.1016/S0022-0248(97)00051-1
- [7] A. G. Dall' Asén, M. Verdier, H. Huck, E. B. Halac and M. Reinoso, "Nanoindentation on Carbon Thin Films Obtained from a C₆₀ Ion Beam," *Applied Surface Science*, Vol. 252, No. 22, 2006, pp. 8005-8009. doi:10.1016/j.apsusc.2005.10.008
- [8] P. Milani, M. Ferretti, P. Piser, C. E. Bottani, A. Ferrari, A. Li Bassi, G. Guizzetti and M. Patrini, "Synthesis and Characterization of Cluster-Assembled Carbon Thin Films," *Journal of Applied Physics*, Vol. 82, No. 11, 1997, pp. 5793-5798. doi:10.1063/1.366446
- [9] S. M. Mominuzzaman, T. Soga, T. Jimbo and M. Umeno, "Camphoric Carbon Soot: A New Target for Deposition of Diamond-Like Carbon Films by Pulsed Laser Ablation," *Thin Solid Films*, Vol. 376, No. 1-2, 2000, pp. 1-4. doi:10.1016/S0040-6090(00)01189-5
- [10] A. I. Oreshkin, R. Z. Bakhtizin, J. T. Sadowski and T. Sakurai, "Epitaxial Growth of C₆₀ Thin Films on the Bi(0001)/Si(111) Surface," *Bulletin of the Russian Academy of Sciences: Physics*, Vol. 73, No. 7, 2009, pp. 883- 885. doi:10.3103/S1062873809070065
- [11] M. Rusop, X. M. Tian, T. Kinugawa, T. Soga, T. Jimbo and M. Umeno, "Preparation and Characterization of Boron-Incorporated Amorphous Carbon Films from a Natural Source of Camphoric Carbon as a Precursor Material," *Applied Surface Science*, Vol. 252, No. 5, 2005, pp. 1693-1703. doi:10.1016/j.apsusc.2005.03.215
- [12] P. R. Somani, S. P. Somani and M. Umeno, "Planer Nanographenes from Camphor by CVD," *Chemical Physics Letters*, Vol. 430, No. 1-3, 2006, pp. 56-59. doi:10.1016/j.cplett.2006.06.081
- [13] A. del V. Turina, M. V. Nolan, J. A. Zygodlo and M. A. Perillo, "Natural Terpenes: Self-Assembly and Membrane Partitioning," *Biophysical Chemistry*, Vol. 122, No. 2, 2006, pp. 101-113.
- [14] B. D. Steinberg, E. A. Jackson, A. S. Filatov, A. Wakamiya, M. A. Petrukhina and L. T. Scott, "Aromatic π-

- Systems More Curved than C₆₀. The Complete Family of All Indenocorannulenes Synthesized by Iterative Microwave-Assisted Intramolecular Arylations,” *Journal of the American Chemical Society*, Vol. 131, No. 30, 2009, pp. 10537-10545. [doi:10.1021/ja9031852](https://doi.org/10.1021/ja9031852)
- [15] M. Kumar and Y. Ando, “Carbon Nanotubes from Camphor: An Environment-Friendly Nanotechnology,” *Journal of Physics: Conference Series*, Vol. 61, 2007, pp. 643-646. [doi:10.1088/1742-6596/61/1/129](https://doi.org/10.1088/1742-6596/61/1/129)
- [16] M. Kumar, T. Okazaki, M. Hiramatsu and Y. Ando, “The Use of Camphor-Grown Carbon Nanotube Array as an Efficient Field Emitter,” *Carbon*, Vol. 45, No. 9, 2007, pp. 1899-1904. [doi:10.1016/j.carbon.2007.04.023](https://doi.org/10.1016/j.carbon.2007.04.023)
- [17] S. M. Mominuzzaman, M. Rusop, T. Soga, T. Jimbo and M. Umeno, “Nitrogen Doping in Camphoric Carbon Films and Its Application to Photovoltaic Cell,” *Solar Energy Materials and Solar Cells*, Vol. 90, No. 18-19, 2006, pp. 3238-3243. [doi:10.1016/j.solmat.2006.06.037](https://doi.org/10.1016/j.solmat.2006.06.037)
- [18] S. M. Mominuzzaman, M. Rusop, T. Soa, T. Jimbo and M. Umeno, “Rearrangements of Hybridized Bonds in Nitrogen Incorporated Camphoric Carbon Thin Films Deposited by Pulsed Laser Ablation,” *The 5th International Conference on Mechanical Engineering ICME 2003*, Dhaka, 26-28 December 2003, pp. 1-4.
- [19] S. Kar and S. Chaudhuri, “Optical Properties of Diamond Films Deposited by Low Temperature Microwave Plasma CVD from Camphor,” *Materials Letters*, Vol. 58, No. 24, 2004, pp. 3029-3033. [doi:10.1016/j.matlet.2004.05.035](https://doi.org/10.1016/j.matlet.2004.05.035)
- [20] G. Kalita, M. Masahiro, H. Uchida, K. Wakita and M. Umeno, “Few Layers of Graphene as Transparent Electrode from Botanical Derivate Camphor,” *Materials Letters*, Vol. 64, No. 20, 2010, pp. 2180-2183.
- [21] T. K. Ishii, “Handbook of Microwave Technology: Applications,” Academic Press, Cambridge, 1995, pp. 1-337.
- [22] A. T. Ohns and D. F. Arne, “Engineers’ Handbook of Industrial Microwave Heating,” IET, London, 1998, pp. 1-232.
- [23] D. Bogdal, “Microwave-Assisted Organic Synthesis: One Hundred Reaction Procedures,” Elsevier Science, Amsterdam, 2005, pp. 1-214.
- [24] A. Lew, P. O. Krutzik, M. E. Hart and A. R. Chamberlin, “Increasing Rates of Reaction: Microwave-Assisted Organic Synthesis for Combinatorial Chemistry,” *Journal of Combinatorial Chemistry*, Vol. 4, No. 2, 2002, pp. 95-105. [doi:10.1021/cc010048o](https://doi.org/10.1021/cc010048o)
- [25] C. O. Kappe and D. Dallinger, “Controlled Microwave Heating in Modern Organic Synthesis: Highlights from the 2004-2008 Literature,” *Molecular Diversity*, Vol. 13, No. 2, 2009, pp. 71-193. [doi:10.1007/s11030-009-9138-8](https://doi.org/10.1007/s11030-009-9138-8)
- [26] K. J. Rao, B. Vaidhyanathan, M. Ganguli and P. A. Ramakrishnan, “Synthesis of Inorganic Solids Using Microwaves,” *Chemistry of Materials*, Vol. 11, No. 4, 1999, pp. 882-895. [doi:10.1021/cm9803859](https://doi.org/10.1021/cm9803859)
- [27] A. Stadler, B. H. Yousefi, D. Dallinger, P. Walla, E. Van der Eycken, N. Kaval and C. O. Kappe, “Scability of Microwave-Assisted Organic Synthesis. From Single-Mode to Multimode Parallel Batch Reactors,” *Organic Process Research & Development*, Vol. 7, No. 5, 2003, pp. 707-716. [doi:10.1021/op034075+](https://doi.org/10.1021/op034075+)
- [28] R. Martínez-Palou, “Microwave-Assisted Synthesis Using Ionic Liquids,” *Molecular Diversity*, Vol. 14, No. 1, 2010, pp. 3-25. [doi:10.1007/s11030-009-9159-3](https://doi.org/10.1007/s11030-009-9159-3)
- [29] Committee on Microwave Processing of Materials: An Emerging Industrial Technology, Commission on Engineering and Technical Systems, National Research Council, “Microwave Processing of Materials,” Publication NMAB-473, National Academy Press, Washington DC, 1994, pp. 1-149.
- [30] J. A. Menéndez, E. J. J. Pérez, E. Ruisánchez, J. M. Bermúdez and A. Arenillas “Ball Lightning Plasma and Plasma Arc Formation during the Microwave Heating of Carbons,” *Carbon*, Vol. 49, No. 1, 2011, pp. 339-351. [doi:10.1016/j.carbon.2010.09.010](https://doi.org/10.1016/j.carbon.2010.09.010)
- [31] A. Versteegh, K. Behringer, U. Fantz, G. Fushman, B. Jüttner and S. Noack “Long-Living Plasmoids from an Atmospheric Water Discharge,” *Plasma Sources Science and Technology*, Vol. 17, No. 2, 2008, pp. 1-8. [doi:10.1088/0963-0252/17/2/024014](https://doi.org/10.1088/0963-0252/17/2/024014)
- [32] J. Phillips, C. C. Luhrs and M. Richard, “Review: Engineering Particles Using the Aerosol-through-Plasma Method,” *IEEE of Plasma Science*, Vol. 37, No. 6, 2009, pp. 726-739. [doi:10.1109/TPS.2009.2016969](https://doi.org/10.1109/TPS.2009.2016969)
- [33] E. A. Dawson, G. M. B. Parkes, P. A. Barnes, G. Bond and R. Mao, “The Generation of Microwave-Induced Plasma in Granular Active Carbons under Fluidised Bed Conditions,” *Carbon*, Vol. 46, No. 2, 2008, pp. 220-228. [doi:10.1016/j.carbon.2007.11.004](https://doi.org/10.1016/j.carbon.2007.11.004)
- [34] F. Ravani, K. Papagelis, V. Dracopoulos, J. Parthenios, K. G. Dassios, A. Siokou and C. Galiotis, “Graphene Production by Dissociation of Camphor Molecules on Nickel Substrate,” *Thin Solid Films*, Vol. 527, 2013, pp. 31-37. [doi:10.1016/j.tsf.2012.12.029](https://doi.org/10.1016/j.tsf.2012.12.029)
- [35] N. R. Serebryanaya, “Reference Pattern Production for Superhard Pressure-Induced Phases of Fullerite C₆₀,” International Center for Diffraction Data, Power Diffraction File (PDF-2), No. 49-1717.
- [36] N. R. Serebryanaya, “Reference Pattern Production for Superhard Pressure-Induced Phases of Fullerite C₆₀,” International Center for Diffraction Data, Power Diffraction File (PDF-2), No. 49-1718.
- [37] H.-B. Bürgi, R. Restori and D. Schwarzenbach, “Structure of C₆₀: Partial Orientational Order in the Room-Temperature Modification of C₆₀,” *Acta Crystallographica Section B: Structural Science*, Vol. 49, No. 5, 1993, pp. 832-838. [doi:10.1107/S0108768193004008](https://doi.org/10.1107/S0108768193004008)
- [38] R. Chen and P. Trucano, “Comparisons of Atomic Thermal Motions for Graphite at 300 K Based on X-Ray, Neutron, and Phonon-Spectrum Data,” *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography*, Vol. 34, No. 6, 1978, pp. 979-982. [doi:10.1107/S0567739478002004](https://doi.org/10.1107/S0567739478002004)
- [39] D. L. Dorset and M. P. McCourt, “Automated Structure Analysis in Electron Crystallography: Phase Determination with the Tangent Formula and Least-Squares Refinement,” *Acta Crystallographica Section A: Foundations of Crystallography*, Vol. 50, No. 3, 1994, pp. 287-292.

- [40] M. Stöhr, T. Wagner, M. Gabriel, B. Weyers and R. Möller, "Binary Molecular Layers of C₆₀ and Copper Phthalocyanine on Au (111): Self-Organized Nanostructuring," *Advanced Functional Materials*, Vol. 1, No. 3, 2001, pp. 175-178. [doi:10.1002/1616-3028\(200106\)11:3<175::AID-ADFM175>3.0.CO;2-L](https://doi.org/10.1002/1616-3028(200106)11:3<175::AID-ADFM175>3.0.CO;2-L)
- [41] A. Goel, J. B. Howard and J. B. Vander Sande, "Size Analysis of Single Fullerene Molecules by Electron Microscopy," *Carbon*, Vol. 42, No. 10, 2004, pp. 1907-1915. [doi:10.1016/j.carbon.2004.03.022](https://doi.org/10.1016/j.carbon.2004.03.022)
- [42] S. Jun-Yeo, R. Pode, J. Sun-Ahn and H. Min-Kim, "Study on the Size of Fullerene (C₆₀) Aggregates in Solution by Photoluminescence and HRTEM Measurements," *Journal of the Korean Physical Society*, Vol. 55, No. 1, 2009, pp. 322-326. [doi:10.3938/jkps.55.322](https://doi.org/10.3938/jkps.55.322)
- [43] P. L. Hansen, P. J. Fallon and W. Krätscher, "An EELS Study of Fullerite C₆₀/C₇₀," *Chemical Physics Letters*, Vol. 181, No. 4, 1991, pp. 367-372. [doi:10.1016/0009-2614\(91\)80086-D](https://doi.org/10.1016/0009-2614(91)80086-D)
- [44] S. Muto, G. Van-Tendeloo and S. Amelinckx, "High-Resolution Electron Microscopy of Structural Defects in Crystalline C₆₀ and C₇₀," *Philosophical Magazine, Part B*, Vol. 67, No. 4, pp. 443-463. [doi:10.1080/13642819308207685](https://doi.org/10.1080/13642819308207685)
- [45] C. C. Ahn, "Transmission Electron Energy Loss Spectrometry in Materials Science and the EELS Atlas," Wiley-VCH Verlag GmbH & Co. KGaA, 2004, pp. 1-455.
- [46] W. Grogger, F. Hofer, G. Kothleitner and B. Schaffer, "An Introduction to High-Resolution EELS in Transmission Electron Microscopy," *Topics in Catalysis*, Vol. 50, No. 1-4, 2008, pp. 200-207.