CARBON NANOSTRUCTURED MATERIALS – II

Dmitry V. Schur and **Svetlana Yu. Zaginaichenko**
Institute for Problems of Materials Science of NAS of Ukraine, Krzhyzhanovsky str. 3, Kiev, 03142, Ukraine

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Contents

Summary

After a short introduction to and brief review of the relation between fullerenes, graphite, carbon nanotubes, diamond-like carbon and other nanostructured modifications of carbon or their derivatives, the synthesis methods of various carbon nanostructures, growth mechanisms for carbon nanostructured materials (CNMs) are described. This chapter provides a survey of separation, isolation, purification, characterization and energy storage of CNMs.

The developed methods of synthesis of polymers and composites based on carbon nanostructures have been considered in this general review. It has been shown that different physical, physico-chemical methods, and methods of analytical chemistry are used for evaluation and identification of CNMs. Recent results on growth and study of CNMs arrays are also presented and discussed in this overview. It has been shown that apparently small changes in experimental conditions can result in dramatic changes in the structure of grown CNMs.

The chapter further deals with consideration of the properties of mainly important low-dimensional CNMs as well as important applications of these advanced nanomaterials.

The most conspicuous features of these purified CNMs structures are their extraordinary electronic, mechanical, optical, thermal and chemical properties and characteristics, which pave way to future applications. CNMs have been of great interest both from a fundamental point of view and for future application in the field of nanotechnology and nanoscience.

This review is written to give a consolidated view of the synthesis and properties of carbon-based nanomaterials, with aim of drawing attention to useful available information and to enhancing interest in this new highly advanced technological field for researchers and manufacturing engineers.

1. Introduction

Carbon nanostructured materials (CNM) are nanomaterials including the nanostructured modifications of carbon (NMC) with different degree of disorder (Balandin, 2011) or their derivatives and having qualitatively new properties, operational and functional characteristics. CNM belong to the construction and functional materials.

The related products (or co-products) such as amorphous carbon, soot, fibers and others are formed during the synthesis of nanostructural modifications of carbon and these products cannot be attributed to NMC by their geometric, structural, physical and chemical parameters. They are called *quasi-nanostructured modifications of carbon (QNMC).*

The *amorphous carbon* or free, reactive carbon, according to IUPAC Compendium of Chemical Terminology (International Union of Pure and Applied Chemistry) informally known as the Gold Book, is an allotrope of carbon with the structure that does not have long-range crystalline order; some short-range order can be observed (Fitzer et al, 1995). Its structure is characterized by a large number of defects and has an increased chemical activity. One of the most common ways to characterize amorphous carbon is through the ratio of sp^2- to sp^3-hybridized bonds present in the material.

The *soot* is botryoidal aggregates consisting of spherical particles (Figure 1) formed by carbon polymeric layers with different degree of ordering (from the two-dimensional polycyclic compounds small in size graphite crystals). The density of the substance is 1.76-1.95 g/cm^3.

According to its chemical composition this product consists of mainly carbon, its part is not less than 90 %, and contains up to 5 % of chemisorbed oxygen in the form of carbon-oxygen complexes, up to 1.1 % of sulfur S, up to 0.8 % of molecular hydrogen H_2 and up to 3 % of mineral impurities. The oxygen is predominantly on the surface of the particles and incorporates into the functional groups (COOH, C = O, etc.) connected with the soot carbonic skeleton. Other mixtures are evenly distributed in the carbon black particles.

The QNMC products also include the *graphite-like filamentary structures* such as gas-phase carbon fibers, graphite whiskers, carbon fibers, etc.

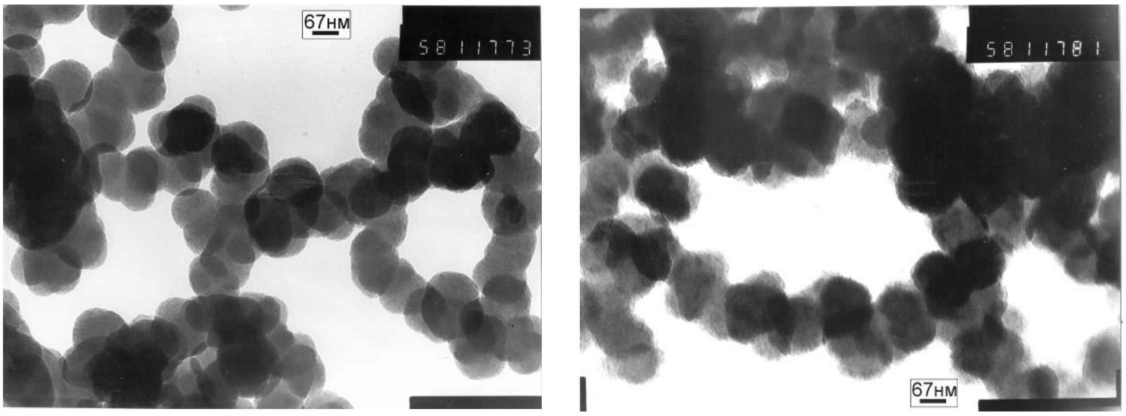

Figure 1. The photomicrographs of soot (transmission electron microscopy) (Schur et al, 2007a).

Gas-phase carbon fibers are synthesized by pyrolysis of hydrocarbons with a volatile catalyst. Their structure resembles the multilayer carbon nanotubes 1-15 μm in diameter (Figure 2). Even a small amount of various additives introduced into the reaction zone of catalytic pyrolysis exerts a substantial effect on the yield, structure and properties of the carbon nanofibers formed.

Graphite whiskers represent the graphene sheet rolled up into a roll with a small angle of taper (with diameters of 5÷20 μm and up to 3 cm in length). Figure 3 shows the Transmission electron microscope (TEM) image of a graphite whisker whose surface is coated with amorphous carbon and soot particles.

Carbon fibers (carbon filaments) are materials of pyrolysis of natural and synthetic fibers consisting of fibers about 5-10 μm in diameter. The carbon atoms are bonded together in crystals that are more or less aligned parallel to the long axis of the fiber. Figure 4 shows the tubular carbon fibers.

Two materials should be mentioned in this contextdiamond-like carbon and glassy carbon, synthesized by technology similar to that described above but which by virtue of their chemical and geometrical parameters can not be attributed to the NMC.

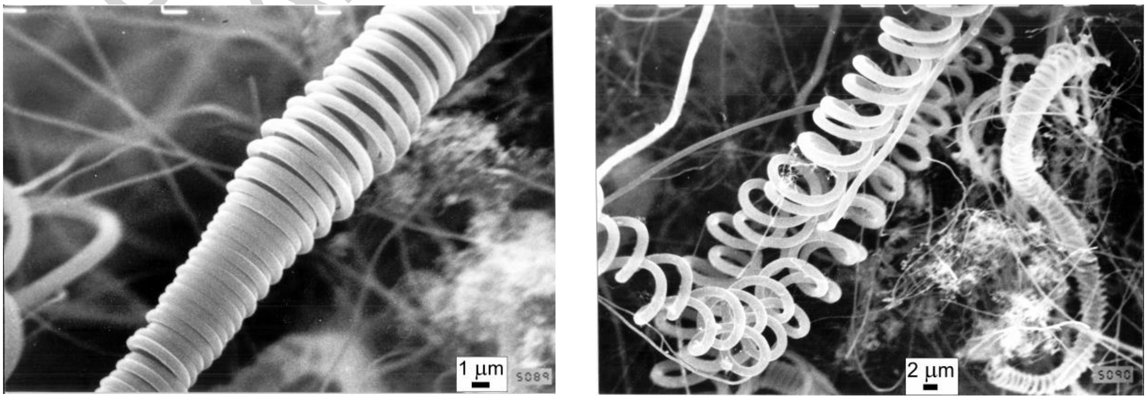

Figure 2. TEM images of the scroll-like gas-phase carbon fibers (Schur et al, 2007a) .

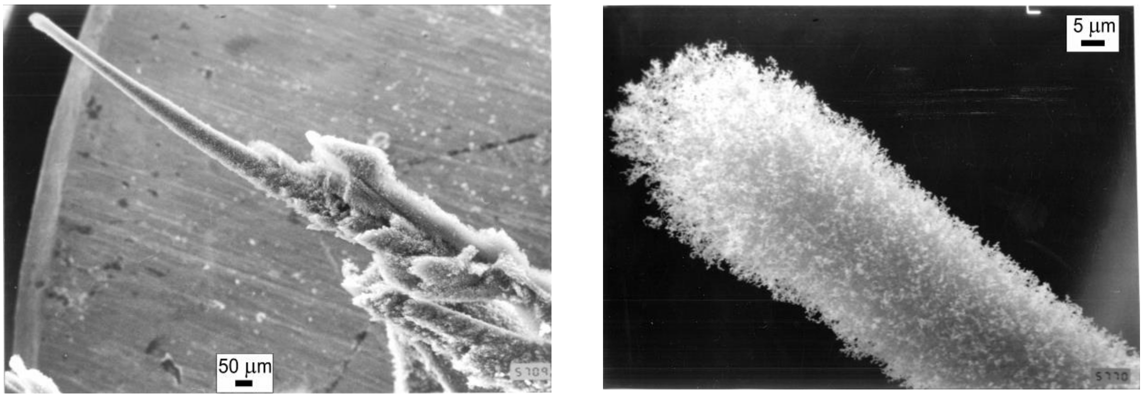

Figure 3. TEM images of the graphite whisker (Schur et al, 2007a)

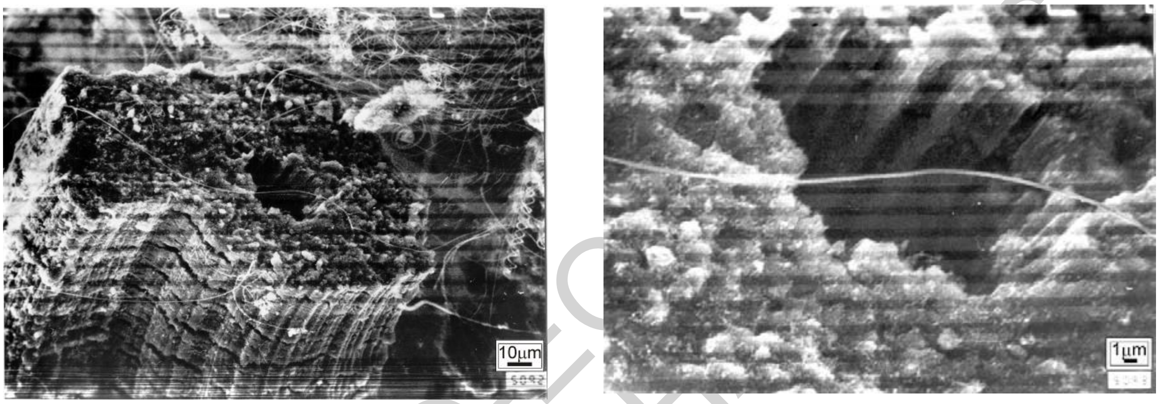

Figure 4. TEM images of tubular carbon fibers (Schur et al, 2007a)

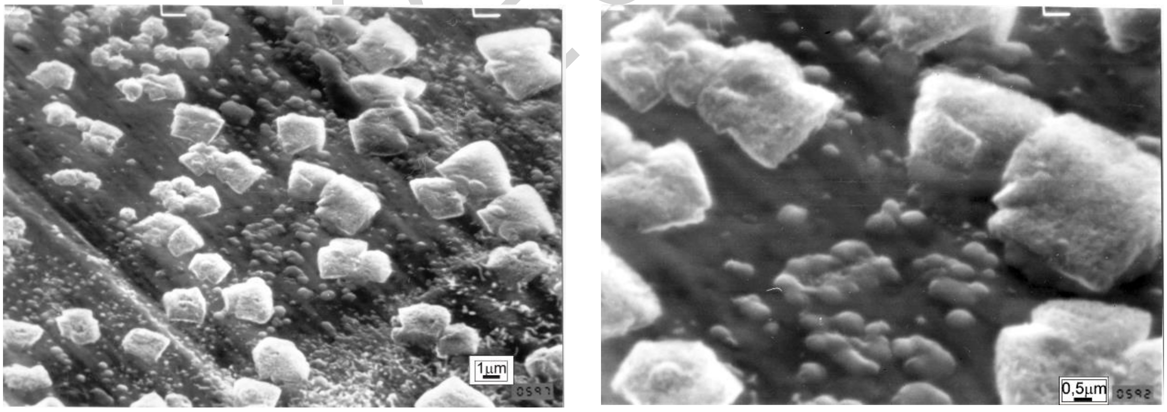

Figure 5. The nano- and microcrystals of diamond in the diamond-like carbon (Schur et al, 2007a)

Diamond-like carbon (DLC) is a metastable amorphous carbon material produced in the form of films by the rapid quenching of the decomposition products of hydrocarbons (CH_4, C_2H_2, C_6H_6) in plasma or under the action of ion beams. The product is amorphous but contains embedded diamond nanocrystals (Figure 5). In general, various forms of DLC can be divided into two broad categories: DLC containing carbon only is called amorphous carbon or amorphous diamond (a-C); DLC containing a mixture of hydrogen and carbon is called hydrogenated amorphous carbon (a-C:H). The DLC material consists of a network of sp^3 and sp^2 co-ordinations and mainly is composed of sp^3-bonded carbon atoms (up to 88%).

Glassy (vitreous) carbon is the product of pyrolysis of polymer-derived carbons (phenol-formaldehyde and furfural resins are used most commonly) consisting of highly, disordered, tightly curled sheets of carbon atoms (graphene layers). Glassy-like carbon has a closed porosity, it is graphitized after 3200 K poorly permeable to liquids and gases and resistant chemically, and its density is 1.45÷1.55 g/cm^3. It is also highly resistant to attack by acids. It is hard and brittle, unlike the soft graphitic forms of carbon and does not revert to these forms at high temperatures (Jenkins and Kawamura, 1971; Cowlard and Lewis, 1967) Recent research (Harris, 2004 has shown that the sp^2-bonded carbon atoms are arranged in planes with a hexagonal symmetry. Non-six-membered rings (pentagons, heptagons) bend the hexagonal carbon planes. As a result of these observations, a model has been proposed for the structure of glassy carbon which consisted of discrete fragments of curved carbon planes, in which pentagons and heptagons have been dispersed randomly throughout networks of hexagons. Such structure model would explain the many interesting properties glassy carbon like low reactivity, high strength and hardness, low density and impermeability.

A similar product is synthesized by pyrolysis of gaseous hydrocarbons. It is made up of randomly tangled fibrous nanostructures, compacted by amorphous carbon; both the sp^2- and sp^3-bonded atoms are present. It is chemically stable and produced in macroscopic quantities. The bulk of the product, heated above the temperature of 2800 K, is graphitized and is a machinable material, polished product and it has density of 1.8÷1.9 g/cm^3. In order to obtain a porous material with a developed surface the amorphous carbon is removed from the semi-finished carbon through ultrasonic treatment in liquid hydrocarbons (Figure 6). Thereafter annealing in an inert medium is carried out at a temperature of 2000÷2500 K.

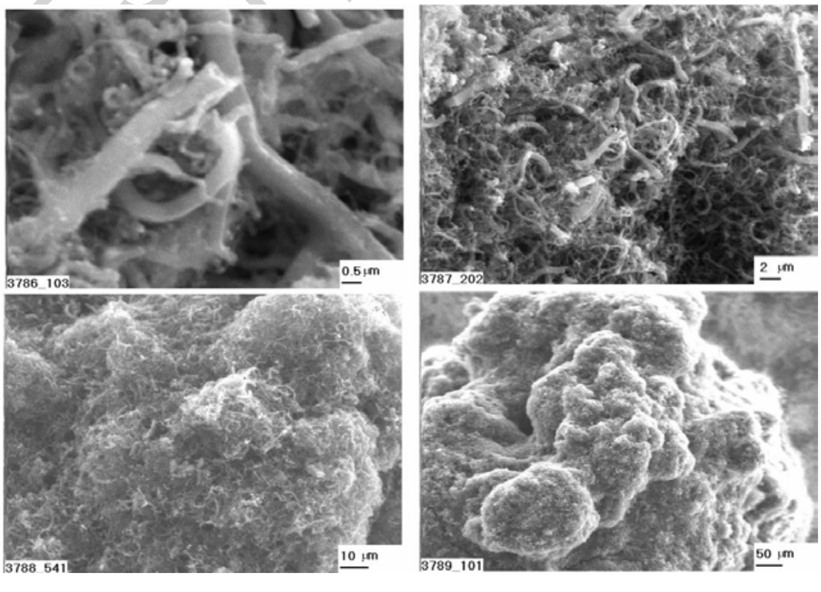

Figure 6. The fiber-based glassy carbon after the ultrasonic removal of amorphous carbon in toluene throughout 1 hour (Schur et al, 2007a).

2. Features of Carbon Nanostructures Formation

Carbon nanostructures have been synthesized with various techniques and these methods produce CNMs with different structures and characteristics. The current general interest is in the development of new techniques for the efficient and selective synthesis of different carbon nanostructures.

In deciding on the method of synthesis of carbon nanomaterials it is necessary to consider the formation features and structure of the synthesizing materials. Carbon nanostructures, including fullerenic materials, are formed in the vapor phase by the interaction of carbon atoms between themselves or with a third body. For the synthesis of a new structure the reagents are obtained by disintegration of carbon or carbon-containing precursor. As this takes place, the interaction of atoms or groups of carbon atoms between each other under certain thermodynamic conditions leads to the formation of nuclei of a prearranged carbon nanostructure (carbyne, graphite, diamond, fullerene and others). Based on experimental data, obtained by research group from laboratory No.67 of the Institute for Problems of Materials Science of National Academy of Sciences of Ukraine (IPMS of NASU) (Schur et al, 2007b&c), on investigation of processes of CNM synthesis by different methods (arc in the liquid and gas, different methods of pyrolysis) using classification of dispersed nanoparticles (Gubin et al, 2005) made by Gubin(Institute of General and Inorganic Chemistry of RAS, Moscow) the sequence of processes of structure formation in carbon nanomaterials has been shown when the system moves from individual atoms through clusters to nanoparticles and further to the bulk samples.

One point appears clearly established – all micro- and macro-amounts of CNM are formed at the stage of nuclei formation, i.e. the product consists of nuclei of various structures. This is the main and essential conclusion drawn from these experimental observations.

The duration of CNM synthesis determines their geometric size, but not the physical-chemical nature which is due to the process thermodynamics at the stage of nucleation. If interaction at the atomic level (nucleation) occurs relatively quickly during a fraction of a second, so minutes and hours are required for the production of macro-size product. To obtain a product of a given degree of dispersion, i.e. material consisting of particles of certain geometrical dimensions and structure, which has certain properties, the technological process of synthesis must be brought to a stop at the definite stage of CNM formation. The term “dispersion” in this case is not quite suited, because it assumes a process of disintegration, i.e. changing from larger to smaller size. In the case of synthesis of carbon nanostructures the process of product formation is aimed in the opposite direction – from the smallest to largest. The nanostructures are produced of the same size, but obtained by different methods (synthesis by precursor and dispersion of macro-size particles of the same synthesis) will have different structures, the surface morphology and hence the properties with the same chemical composition.

The nucleus can be constructed from the chains of varying length and branching, cycles and polyhedrons. Its skeleton can be the carcass, as well as a combination of the enumerated-represented structural element. When the number of atoms in the cluster skeleton (nuclearity) increases the number of ways of their connection increases. At the nuclearity of 20 and above the spherical spatial structure is the most beneficial thermodynamically and geometrically, as observed in the case of fullerene clusters of carbon.

Based on the experimental data and the theoretical calculations we have attempted to formulate the basic rules of stability of polyhedral cluster structures of carbon. Among these are the following postulates: 1) the stable carbon clusters have the form of polyhedra in which each carbon atom has a coordination number 3; 2) carbopolyhedrons, containing only five- and six-membered cycles, are the most stable; 3) the stable carbon clusters are more symmetric; 4) the five-membered cycles in polyhedra must be isolated; 5) the carbo-polyhedron form is to be close to spherical.

In the papers devoted to the theoretical examination of the mechanism of fullerenes growth, it has been assumed that the process goes through the combination of particles from two or three carbon atoms. It has been assumed also that the fullerenes formation occurs at the connection of excited clusters with subsequent separation into two fragments of different masses.

3. Methods of Synthesis, Extraction and Separation of Carbon Nanostructures

The methods of synthesis, extraction and separation of carbon nanostructured materials have been described adequately in literature and therefore in this section we shall only clarify the fundamental moments.

Although the physical chemistry of each fullerene modification in the detailed consideration has its own significant differences, but in the first approximation in generalizing view of this class of materials many common points can be found in all of the fullerene molecules. These points include the formation features of fullerene molecules, solubility in liquids, electrical neutrality of fullerene molecules and the donor-acceptor reactions, their exo- and endoability properties and much more.

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Biographical Sketches

Dmitry V. Schur graduated from Kiev Polytechnical Institute in 1984. He received his Ph. D degree in chemical engineering from Institute for Problems of Materials Science of NAS of Ukraine in 1990. He has served as Chair of the Department of “Hydrogen materials science and carbon nanomaterials” in IPMS from 1993. Much of his research is devoted to the solid-state physics, metal hydrides and carbon nanostructures, hydrogen energetics, hydrogen power installations and fuel cells. Dr. Schur is co-chairperson of Organizing Committee of International Conference “Hydrogen Materials Science and Carbon Nanomaterials” held once in two years from 1987 in Crimea, Ukraine. He has published some 160 papers and 6 books, edited a few volumes “Carbon Nanomaterials in Clean Energy Hydrogen Systems” published in NATO Science Series II: Mathematics, Physics, Chemistry. He is the co-author of monographs “*Carbon Nanomaterials and Phase Transformations in Them*”, 2007, 678 p. and “*Fullerenes – the basis of materials in future*”, 2001, 148 p. (in Russian). He is the member of International Association of Hydrogen Energy from 1992 and member of editorial board of International Scientific Journal “*New materials for electrochemical systems*” from 1998. The results of the twenty-year research of the authors were published as an article, Dmitry V.Schur, Svetlana Yu.Zaginaichenko and T. Nejat Veziroglu "The hydrogenation process as a method of investigation of fullerene C60 molecule" 2015, 40 (6): 2742-2762. In this work, the theory of formation and transformation of spherical molecules was developed. This work was nominated for the Nobel Prize in Chemistry in 2016 by universities of twelve countries (Japan, Canada, USA, Brazil, Italy, China, Egypt, England, Germany, Argentina, South Africa, India). Http://www.lab67.kiev.ua/Itogi2015/itogi2015.html

Svetlana Yu. Zaginaichenko graduated from Dnepropetrovsk National University at specialty of physical metallurgy in 1979. She worked at the physics department of Dnepropetrovsk Metallurgical Institute (1983-1993) and from 1993 she is chief researcher in the Department of “Hydrogen materials science and carbon nanomaterials” in the Institute for Problems of Materials Science of NAS of Ukraine. In 1985 she defended candidate’s dissertation and in 2004 her doctoral dissertation and she is doctor of physical and mathematical sciences, professor. Main field of scientific interest is physical properties of metals, alloys and nanostructured materials on the level of molecular-kinetic idea as well as phase transformations in metal-hydrogen and metal-carbon systems. Prof. Zaginaichenko is co-chairperson of Organizing Committee of International Conference “Hydrogen Materials Science and Chemistry of Carbon Nanomaterials” held once in two years from 1987 in Crimea, Ukraine. She has published some 170 papers and 6 books, edited a few volumes “*Carbon Nanomaterials in Clean Energy Hydrogen Systems*” published in NATO Science Series II: Mathematics, Physics, Chemistry. She is the co-author of monograph “S*olubility of impurities in metals, alloys, intermetallic compounds and fullerites*”, 2006, 514 p. (in Russian). She is the member of International Association of Hydrogen Energy from 1992. The results of the twenty-year research of the authors were published as an article, Dmitry V.Schur, Svetlana Yu.Zaginaichenko and T. Nejat Veziroglu "The hydrogenation process as a method of investigation of fullerene C60 molecule" 2015, 40 (6): 2742-2762. In this work, the theory of formation and transformation of spherical molecules was developed. This work was nominated for the Nobel Prize in Chemistry in 2016 by universities of twelve countries (Japan, Canada, USA, Brazil, Italy, China, Egypt, England, Germany, Argentina, South Africa, India). Http://www.lab67.kiev.ua/Itogi2015/itogi2015.html