CARBON NANOSTRUCTURED MATERIALS – II

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Contents

1. Introduction
2. Features of carbon nanostructures formation
3. Methods of synthesis, extraction and separation of carbon nanostructures
4. Separation and purification of endofullerenes
5. Polymerization method
6. Fullerene polymer composites
7. Methods for synthesis of other carbon nanostructures
8. Production of hydrocarbons by pyrolysis method
9. Synthesis of non-carbon nanotubes
10. Methods of assessment and identification of CNM
11. Prospects for practical applications of fullerenes and fullerene derivatives
12. Fullerenes as promising material for hydrogen storage application
13. Classification of carbon modifications
Glossary
Bibliography
Biographical Sketches

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 sp²- to sp³-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/cm³.

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 H₂ 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.
Gas-phase carbon fibers are synthesized by pyrolysis of hydrocarbons with a volatile catalyst. Their structure resembles the multilayer carbon nanotubes 1-15 \( \mu \)m 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\textendash}20 \( \mu \)m 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 \( \mu \)m 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 context: diamond-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.
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 (CH₄, C₂H₂, C₆H₆) 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 sp³ and sp² co-ordinations and mainly is composed of sp³-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/cm³. 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 sp²-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 sp²- and sp³-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 has density of 1.8±1.9 g/cm³. 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).](image-url)
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 fullerene 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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Bibliography


5. Cowlard F.C., Lewis J.C. (1967). Vitreous carbon – a new form of carbon. J. Mat. Sci. 2 (6), 507-512. [This is one of the earliest papers on the structure of different forms of carbon, including a new form as vitreous carbon and some their properties as strength, hardness, resistance to corrosion, porosity, etc.].

6. Harris P.J. (2004). Fullerene-related structure of commercial glassy carbons. Phil. Magaz. 84 (29), 3159-3167. [This is the paper proposed the structure model of low temperature and high-temperature glassy carbons].


11. Krätschmer W., Huffman D.R. (1992). Fullerites: new form of crystalline carbon. Carbon 30 (8), 1143-1147. [This is a research reporting on the methods of fullerenes and fullerites synthesis and some of their properties].


17. Taylor R., Langley G.J. (1994). Formation of C\(_{60}\) and C\(_{70}\) by pyrolysis of naphthalene. In: Recent advances in the chemistry and physics of fullerenes and related materials. *Proceedings of Electrochem. Society* 94-24, 68-79. [Following intramolecular dehydrogenation, authors of this work show that the species for which n=6 and n=7 are precursors to [60]- and [70]-fullerene respectively].


19. Conley N.R., Lagowski J.J. (2002). On an improved pyrolytic synthesis of [60]- and [70]-fullerene. *Carbon* 40 (6), 949-953. [This paper provides discussions on fullerene yields and on mechanism by which fullerenes C\(_{60}\) and C\(_{70}\) are formed in pyrolysis].


23. Pat. 5581503 US, Int. Cl.CO1B 31/00. Fullerene compound, manufacturing method and use/ Mitani T., Suzuki K., Ahn J., Iwasa Y.-Publ. 22.12.98. [Patent describes the dissolution of fullerene in solvents, the formation of stable fullerene cluster compounds].

24. Pat 5876684 US, Int. Cl. CO1B 31/00. Methods and apparati for producing fullerenes/ Withers J.C., Loutfy R.O.-Publ. 03.03.94. [This patent presents the fullerene synthesis by subjecting a carbon source (as carbon particulate or liquid or gaseous hydrocarbons) to an intense, heat generating means].

25. Smalley R.E., Hauffer R.E. (1993). Electric arc process for making fullerenes. Pat. 5227038 US, Int. Cl. CO1 B31/00/ Rice William Marsh University. – Publ. 13.07.93. [This invention provides method of generating fullerenes by vaporizing carbon with the heat from an electric arc and then condensing a soot from which fullerenes may be recovered].

26. Pat. 5510098 US, Int. Cl. CO1B 31/00. CVD method of producing and doping fullerenes/ Chow L.: University of Central Florida.-Publ. 23.05.96. [This patent presents the fullerenes formation in the CVD chamber and method of using fullerenes to enhance properties of rubber composites].

27. Pat. 2086503, US, Int. Cl. CO1B 31/00. Procedure of industrial production of fullerenes / Petric V.I.-Publ. 10.08.97. [Patent presents the production and separation of formed fullerenes by arc electric discharge in argon].

28. Namikata T. (1993). Carbon clusters. Pat. 05-97416 JP, Int. Cl. CO1 B31/02/ Asahi Chemical Ind. – Publ. 20.04.93. [This work provides an analysis of high purity carbon clusters production with the excellent productivity].

29. Howard I.B., Mckinnon I.T. (1992). Manufacture of fullerenes. Pat. 92-20622 WO, Int. Cl CO1 B31/00/ Massachusetts Institute of Technology. – Publ. 26.11.92. [This is information on the process of fullerene production in the hydrocarbon flames, the growth of the hydrocarbon precursors of fullerenes].
30. Taylor R.: Hochst A.G. (1995). Process for the preparation of fullerenes. Pat. 95−06001 WO, Int. Cl. CO1 B31/02/—Publ. 02.03.95. [This patent presents the fullerenes production from coal, isolation process of fullerenes in macroscopic quantities and their chromatographic separation on alumina].


32. Kakiuchi C., Nakayama Y. (1995). Method and apparatus for collecting fullerene C_{60}. Pat. 07-33419 JP, Int. Cl. CO1 B31/02/ Ritsumeikan. —Publ. 03.02.95. [This patent points out method and device for the yield of carbon fullerenes].

33. Hayahara S. (1995). Manufacture of carbon clusters. Pat. 07-61804 JP, Int. Cl. CO1 B31/02/ Daiichi Nenryo Kogyo. —Publ. 07.03.95. [This patent presents new technique which can be employed for the efficient production of carbon clusters].

34. Withers I.C., Loutfy R.O. (1994). Method and apparatus for the manufacture of fullerenes. Pat. 94-04461 WO. Int. Cl. CO1 B31/00/ Materials and Electrochemical Research Corp. —Publ. 03.03.94. [This patent relates to a method and device for the continuous production of carbon black with a high fullerene content].

35. Sugioka T. (1993). Manufacture of fullerenes. Pat. 05-70115 JP, Int. Cl. CO1 B31/00/ Koatsu Gas Kogyo. —Publ. 23.03.93. [This patent provides description of process for the mass-production of fullerene from carbon soot produced by the heating of surface of solid carbon at a high temperature in inert atmosphere under reduced pressure].


38. Diederich F., Ettl R., Rubin Y., Whetten R.L., Beck R., Alvarez M., (1991). The higher fullerenes: isolation and characterization of C_{70}, C_{84}, C_{90}, C_{94} and C_{70}O, and oxide of D_{5h}-C_{70}. Science 252, 548-551. [This paper discusses the production of a variety of molecules larger than C_{60} and C_{70} in total amount of 3 to 4 % by weight and the isolation of solid C_{70}, C_{84}, C_{90} samples by repeated chromatography on neutral alumina].

39. Ajie H., Alvarez M., Anz S.J., Beck R.D., Diederich F., Fostiorpoulous K., (1990). Characterization of the soluble all-carbon molecules C_{60} and C_{70}. J. Phys. Chem. 94 (24), 8630-8633. [This paper demonstrates results with high yield of production of new forms of molecular carbon (C_{60} and C_{70}) and their complete separation by column chromatography on alumina].


41. Lieber C.M., Chen C.C. (1994). Preparation of fullerenes and fullerene−based materials. Solid State Phys. 48, 109-148. [This chapter is a review on the preparation, isolation and characterization of fullerene clusters, including the purity of C_{60}, the properties of solid C_{60} and methods for preparing metal-dopes C_{60} solids].


44. Van der Biest O.O., Vandeperre L.J. (1999). Electrophoretic deposition of materials. Annu. Rev. Mater. Sci. 29, 327-352. [This review describes numerous applications of electrophoretic deposition of materials including coating production, free-standing objects, laminated or graded materials, infiltration of porous materials, preparation of electrophoretic suspension, etc.]


50. Liu S., Sun S. (2000). Recent progress in the studies of endohedral metallofullerenes. Organomet. Chem., 599 (1), 74-86. [This overview presents the recent progress in area of endohedral metallofullerenes in the past years, metals encapsulation into fullerene cage to form mono-, di- and trimetallofullerenes by arc-evaporation technique].

51. Kikuchi K., Suzuki S., Nakao Y., Nakahara N., Wakayabashi T., Shiromaru H. (1993). Isolation and characterization of a new metallofullerene La@C_{82}. Chem. Phys. Lett. 216 (1-2), 67-71. [This paper gives description of isolation of metallofullerene LaC_{82} from the carbon soot by two-step liquid chromatographic method and comparison of IR absorption spectra between LaC_{82} and C_{82} empty fullerene].

52. Maeda Y., Matsumaga Y., Wakahara T., Takahashi S., Tsuchiya T., Ishitsuka M.O., Hasegawa T., Akasaka T., Liu M.T., Kokura K., Horn E., Yozu K., Kato T., Okubo S., Kobayashi K., Nagase S., Yamamoto K. (2004). Isolation and characterization of a carbene derivative of La@C_{82}. J. Am. Chem. Soc. 126, 6858-6859. [This work shows the structure of La@C_{82}(Ad) by ESR, MS and UV-vis-NIR spectroscopies and reports X-ray crystallographic characterization of endohedral monometallofullerene derivative].


54. Shinoara H., Yamaguchi H., Hayashi N., Sato H., Ohkohchi M., Ando Y., Saito Y. (1993). Isolation and spectroscopic properties of scandium fullerenes (Sc_2@C_{84}, Sc_2@C_{82}, and Sc_2@C_{84}). J. Phys. Chem. 97 (17), 4259-4261. [This paper shows the results of separation and isolation of discandium fullerenes from various hollow fullerenes using a two-stage high-performance liquid chromatography].

56. Yamamoto K., Funasaka H., Takahashi T., Akasaka T. (1994). Isolation of an ESR-active metallofullerene of La@C_{60}. J. Phys. Chem. 98 (8), 2008-2011. [This paper demonstrates separation of La@C_{60} isomer by an efficient single-stage chromatographic process].


58. Meier M.S., Selegue J.P. (1992). Efficient preparative separation of C_{60} and C_{70}-gel permeation chromatography of fullerenes using 100% toluene as mobile phase. J. Org. Chem. 57, 1924-1926. [This paper shows the method of purifying fullerenes to obtain a preparation enriched in a fullerene of selected molecular weight].

59. Klute R.C., Dom H.C., McNair H.M. (1992). HPLC separation of higher (C_{84+}) fullerenes. J. Chromatogr. Sci. 30, 438-442. [This paper presents the isolations of higher fullerenes above C_{84} (in addition to C_{60}, C_{70}, C_{76}, C_{78}, C_{84}) using high performance liquid chromatography procedure].

60. Stevenson S., Dorn H.C., Burbank P., Harich K., Haynes J., Kiang C.H., Salem J.R. (1994). Automated HPLC separation of endohedral metallofullerene Sc@C_{2n} and Y@C_{2n} fractions. Anal. Chem. 66 (17), 2675-2679. [This paper describes an automated rapid separation of metallofullerenes from empty-cage fullerenes utilizing two polyurethane chromatographic columns 500 and 1000Å in series].


63. Diener M.D., Smith C.A., Veirs D.K. (1997). Anaerobic preparation and solvent free separation of uranium endohedral metallofullerenes. Chem. Mater. 9 (8), 1773-1777. [This paper demonstrates the production of films of C_{60}, C_{70} and M@C_{60} by subliming fullerenes from arc-produced soot onto a mass spectrometry target].


65. Krätschmer W., Huffman D.R. (1992). Fullerites: new form of crystalline carbon. Carbon 30 (8), 1143-1147. [This is one of the earliest papers on the structure of solid fullerene and fullerite and some their properties].

66. Talyzin A.V., Dubrovinsky L.S., Le Bihan T., Jansson U. (2002a). In situ Raman study of C_{60} polymerization at high pressure high temperature conditions. J. Chem. Phys.116 (5), 2166-2174. [This work presents study of C_{60} polymerization in the pressure range 10-27 GPa and temperatures up to 830 K].


68. Bennington S.M., Kitamura N., Cain M.G., Lewis M.H., Wood R.A., Fukumi K., Funakoshi K. (2000). In situ diffraction measurement of the polymerization of C_{60} at high temperatures and pressures. 1. Phys.: Condens. Matter. 12 (28), L451-L456. [This is a paper on study of polymerization process of fullerene C_{60} and dynamics of phase transformations at temperatures 300-1100 K].

phases of \( \text{C}_{60} \), created in the range 1-9 GPa and up to 1100K and polymeric forms of \( \text{C}_{70} \) and their physical properties under high pressure and presents pressure-temperature phase diagrams of \( \text{C}_{60} \) and \( \text{C}_{70} \).

70. Blank V.D., Buga S.G., Dubitsky G.A., Serebryanaya N.R., Popov M.Yu., Sundqvist B. (1998). High pressure polymerized phases of \( \text{C}_{60} \). *Carbon* 36 (4), 319-343. [This is an overview of phase transformations and structures of polymeric phases of \( \text{C}_{60} \) in the pressure range up to 20 GPa and at temperatures up to 2300K; paper presents pressure-temperature diagram and discusses physical properties of various phases.]

71. Rao A.M., Eklund P.C., Hodeau J.L., Marques L., Nunez-Regueiro M. (1997). Infrared and Raman studies of pressure-polymerized \( \text{C}_{60} \). *Phys. Rev. B* 55 (7), 4766-4773. [This paper discusses the room-temperature infrared and Raman spectra for pressure-induced rhombohedral, tetragonal, orthorhombic \( \text{C}_{60} \) and presents comparison of experimental spectra with the vibrational spectra from a first-principles molecular calculation for \( \text{C}_{60} \) dimer and infinite chain of polymerized \( \text{C}_{60} \).]

72. Blank V.D., Dubitsky G.A., Serebryanaya N.R., Mavrin B.N., Denisov V.N., Buga S.G., Chernozatskii L.A. (2003). Structure and properties of \( \text{C}_{60} \) and \( \text{C}_{70} \) phases produced under 15 GPa pressure and high temperature. *Physica B* 339 (1), 39-44. [This work discusses the high-temperature high-pressure treatment of fullerenes \( \text{C}_{60} \) and \( \text{C}_{70} \) and production of three-dimensional polymerized \( \text{C}_{60} \) and \( \text{C}_{70} \) phases, analyzes formation of superhard phases with high elastic properties.]

73. Szwarc H., Davydov V.A., Plotianskaya S.A., Kashevarova L.S., Agafo nov V., Céolin R. (1996). Chemical modifications of \( \text{C}_{60} \) under the influence of pressure and temperature: from cubic \( \text{C}_{60} \) to diamond. *Synth. Metals* 77 (1-3), 265-272. [This paper presents transformations of solid \( \text{C}_{60} \) as a function of pressure and temperature.]


75. Horikawa T., Suito K., Kobayashi M., Oshima R. (2005). High-pressure synthesis of superhard material from \( \text{C}_{60} \). *Jpn. J. Appl. Phys.* 44 (5 A), 3141-3146. [This gives information on properties (hardness of \( \text{C}_{60} \) in the temperature range 165-800°C and the pressure range 10-15 GPa).]


79. Wang C., Guo Z.X., Fu S., Wu W., Zhu D. (2004). Polymers containing fullerene or carbon nanotube structures. *Prog. Polym. Sci.* 29, 1079-1141. [This is a review paper on many living polymerization methods introduced into the preparation of the polymer fullerenes and synthesis of polymeric CNTs, their unusual mechanical, electrical, magnetic and optical properties and a broad range of potential applications.]


presents various synthetic approaches to making polymeric composites with novel methods of microstructuring these materials into aligned or patterned forms.


86. Ivanovskii A.L. (2002). Non-carbon nanotubes: synthesis and simulation. *Russ. Chem. Reviews.* 71 (3), 175-194. [This review discusses the main methods for synthesis of non-carbon nanotubes and some of their properties, analyses the electronic structures of these objects and compares the results of experimental and theoretical studies along these lines].


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97. Harris P.J.F. (1999). Carbon Nanotubes and Related Structures: New Materials for the Twenty-First Century, Cambridge: Cambridge University Press, 293p. [This monograph covers most aspects of carbon nanotube research as well as discussing related structures such as fullerenes in 9 chapters and provides an excellent bibliography at the end of each chapter].


110. Haddon R.C. (1993). Electronic structure, conductivity and superconductivity of alkali metal doped C_{60}. *Pure & Appl. Chem.* 65 (1), 11-15. [This paper discusses experiments on the ability of fullerenes to accept electrons and qualitative explanations for their extraordinary electron affinity].

111. Tanigaki K., Zhou O. (1996). Conductivity and superconductivity in C_{60} fullerides. *J. Phys.* 6 (12), 2159-2173. [This paper presents the specific features of C_{60} fullerides from the viewpoint of their electronic properties and structure].


118. Frechet J.M.J., Thompson B.C. (2008). Polymer-fullerene composite solar cells. *Angew. Chem.* 47, 58-77. [This review discusses the most effective solar cells made from bicontinuous polymer-fullerene composites and advances in the understanding of the complex interplay between the active layer morphology and electronic properties].


127. Cataldo F., Iglesias-Groth S. (2010). Characterization of hydrogenated fullerene mixture of C_{60}H_{x} and C_{60}H_{14}. Fullerenes, Nanotubes and Carbon Nanostructures 18 (2), 97-106. [This paper presents an analysis of hydrogenated mixture of fullerenes by liquid chromatographic analysis, electronic absorption, FT-IR spectroscopy and thermal analysis].


133. Endo M., Strano M.S., Ajayan P.M. (2008). Potential applications of carbon nanotubes. Topics Appl. Phys. 111, 13-61. [This is a review paper on applications of various kinds of carbon nanotubes, both existing commercial uses and feasible nanotubes applications].


nanotubes including hydrogen storage media, energy storage and energy conversion devices, nanosized semiconductor devices, etc."


142. Rao S.G., Huang L., Setyawan W., Hong S. (2003). Large-scale assembly of carbon nanotubes. *Nature* 425, 36-37. [This work shows efforts focused on tackling the controlled assembly of carbon nanotubes and presents strategy for large-scale assembly of ordered nanotubes for devices as computer chips and sensor arrays to be produced industrially].


149. Saito Y., Uemura S. (2000). Field emission from carbon nanotubes and its application to electron sources. Carbon 38, 169-182. [This is a review paper on properties of purified carbon nanotubes favorable for field emitters and application results of nanotube field emitters].


155. Pirio G., Legagneux P., Pribat D., Teo K.B., Chhowalla M., Amaratunga G.A., Milne W.I. (2002). Fabrication and electrical characteristics of carbon nanotube field emission microcathodes with an integrated gate electrode. Nanotechnology 13 (1), 1-4. [This is a report on the fabrication process of field emission microcathodes which use carbon nanotubes as the low-voltage field emission source].

156. Rincon P. (2007). Super-strong body armour in sight. BBC News, Published 23.10.2007. [This work presents research results of carbon nanotubes and fibers properties and their applications as a new super-strong material at the production of body armor for military and law enforcement].

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
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