CARBON NANOSTRUCTURED MATERIALS – I

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

This chapter provides an overview of current research on different carbon-based nanostructured materials. Carbon nanostructures are regarded as artificially composed structures with nanometer size and nanostructures modifications of carbon have attracted the attention of many researchers since early 1990s following their discovery. Since that time, the number of discovered structures is rapidly increasing. The existing definitions, concepts and notions about the mechanisms of formation and transformations of carbon nanostructures have been considered in the present review.

The crystal structure of all discovered allotropic modifications of carbon is different. The carbon-based nanostructured materials considered here include graphenes, family of fullerenes in a crystalline form, their derivatives, as well as carbon nanotubes, carbon nanocones, carbon nanohorns, carbon nanofibers, nanocraters, nanoscale carbon toroidal structures and others. Fullerene C_{60} is the most abundant, least expensive and, therefore, most thoroughly studied member of all-carbon hollow-cluster materials. In this overview we also have reviewed various approaches for making endohedral, exohedral fullerenes and fullerenes of substitution. A plethora of novel materials such as functionalized fullerene and nanotube derivatives or nanocomposites has been discussed

here. The carbon nanostructures provide an important means for making advanced composite materials with polymers. In this review, the topics of doped carbon nanostructures and combined nanostructures (fullerenes in the nanotube or the peapod structures, metal inside fullerenes etc.) are not discussed in detail, due to the vastness of this subject.

This review gives the present status of research in this fast moving field by researchers actively contributing to the advances and demonstrates the unique crystal structures of nanostructured carbon modifications as well as approaches to their classification.

1. Introduction

For carbon chemistry and technology, the end of the 20^{th} century was marked by significant scientific and technological progress, which led to the establishment of novel types of nanosized carbon, perspective for developing novel carbon nanomaterials.

Nanostructured carbon-based materials (nanostructured modifications of carbon, NMC) may be defined as those materials whose structural elements (clusters, crystallites or molecules) have dimensions in the range of 1÷100nm. All allotropic modifications of carbon are formed on the nanometer-scale independently of the method of their synthesis. The term "nanostructured modification of carbon" is deeply embedded in the chemical and physical literature and it is used to a great extent as applied to fullerenes, nanotubes and similar structures.

These carbon-based nanomaterials and nanostructures play an increasingly pervasive role in nanoscale science and technology and are thus described in some depth. The discovery of fullerenes has stimulated further research and humanity has concentrated considerable attention to the nanoscale world. With their appearance the terms "nanoparticle", "nanocluster", "nanocomposite," "nanochemistry," "nanotechnology", "nanoengineering", etc. have came into wide use.

Two allotropic forms of carbon as diamond (Figure 1 (a)) and graphite (Figure 1 (b)) are well known. In diamond each carbon atom is covalently bonded to four other carbon atoms to give a tetragonal unit and each atom is sp^3-hybridized. The C-C bond length in diamond is 1.545 Å. The diamond lattice consists of two interpenetrating fcc lattices, displaced along the body diagonal of the cubic cell by one quarter of the length of the diagonal, the lattice constant is equal to $a = 0.3354$ nm for diamond. In graphite the carbon atoms are arranged in parallel layers of interconnected hexagonal rings. Each carbon atom is connected to three others in the layer by covalent bonds and is sp^2-hybridized. The distance between adjacent carbon atoms in the plane is 1.421 Å. The sheets are separated from each other by a distance of 3.35 Å. The crystal structure of graphite is described by hexagonal lattice with lattice constants a = 0.2461 nm, c = 0.6708 nm.

In 1967 the synthesis of elusive third (linear) allotropic form of carbon with sp-electron coupling carbyne (Figure 1 (c)), the analysis of its structure, some of its physical and chemical properties were considered by scientists at the Institute of

Organoelement Compounds, Russian Academy of Sciences (Korshak et al,1978; Kudryavtsev et al, 1993).

Bochvarand Galpern (1973)from Russia and earlier Osawa in Japan (Osawa, 1970; Yoshida and Osawa, 1971)had done the prediction of possible existence of spherical molecules of carbon (carbododecahedron C_{20} and carbo-s-icosahedron C_{60}) on the basis of quantum-chemical calculations (Figure 1 (d)). According to purely theoretical exercises, these molecules, by virtue of closed atomic shell and aromaticity, were supposed to be tolerant and possess chemical stability.

The discovery of fullerenes in 1985 led to a new field of study and a new material class of pure carbon that is significantly different from other forms of carbon, diamond and graphite. Kroto, et al (1985) in the Rice University synthesized the spherical carbon molecules C_{60} and C_{70} by laser irradiation of graphite disks in the helium jet. They also estimated the stability of every fullerene isomer up to C_{70}, using Huckel molecular orbital theory. These molecules get their name fullerenes in honor of American architectural modeler Richard Buckminster Fuller (1895-1983) who built the geodesic dome from pentagons and hexagons. In 1996 the Nobel Prize in Chemistry had been awarded to H.W. Kroto, R.F. Curl, R.E. Smalley for their key role in the discovery and further investigation of fullerenes (Curl and Smalley, 1991; Curl and Smalley, 1988; Curl, 1992; Smalley and Haufler, 1993; Smalley, 1997; Curl and Haddon, 1993; Kroto, 1988; Kroto, 1992; Kroto et al, 1991Other fullerenes were discovered shortly afterwards with more and fewer carbon atoms, ranging from 20 up into the hundreds, though C_{60} remains the easiest to produce.

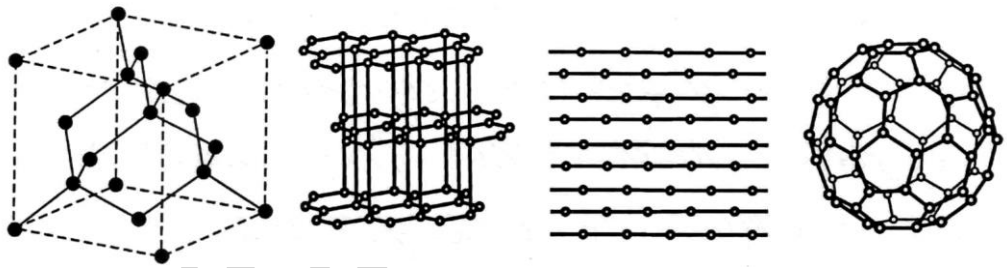


Figure 1. The allotropic forms of carbon: diamond (a), graphite (b), carbyne (c) and carbo-s-icosahedron (d).

In 1990 Kratschmerand others suggested and developed the method of fullerenes production by graphite evaporation in the electric arc in the helium atmosphere (Gao et al, 1992; Taylor et al, 1990; Krätschmer and Huffman 1992; Krätschmer et al, 1990a; Krätschmer et al, 1990b; Parker et al, 1992; Meijer and Bethune, 1990

Since beginning of the 21st century the explosion in both academic and industrial interest in these nanostructured materials has arisen from the remarkable variations in their fundamental properties, the chemical and physical properties of NMC have been a hot topic in the field of research and development and are likely to continue to be for a long time.

2. Graphene

In recent years physicistsGeim andNovoselov have made important experimental discovery of graphene – a one-atom-thick sheet of carbon atoms arranged in a honeycomb pattern that boasts outstanding mechanical and electronic properties (Geim and Novoselov, 2007; Geim, 2009)

In 2010 these researchers have won the Nobel Prize in Physics. Geimand Novoselovhave worked out the rudimentary method to separate graphite into its constituent graphene sheets and this team showed that not only single sheets of graphene could be isolated, but they remain particularly stable even at the room temperature (Novoselov et al, 2004

The reasons for discovering graphene so late are mainly (Castro Neto et al, 2009): 1) graphene was expected to be unstable in the free state before its discovery; 2) no experimental tools existed to detect the one-atom-thick graphene.

Graphene represents an allotrope of carbon (Jiao et al, 2009; Heyrovska, 2008; Suenaga and Koshino, 2010; Novoselov et al, 2007; Luo, 2010; Gass, 2008; Girit et al, 2009) whose structure is monolayer-thick sheets formed by hexatomic cyclic molecules (HACM) of sp^2-bonded carbon atoms (Figure 2). At the formation of bonds between molecules the hexagonal free spaces (interstices) are formed by intermolecular bonds in the space. These free spaces remain unshaded as shown in Figure 2.

The hexatomic cyclic molecules of graphene after formation in the different conditions are combined into clusters under the action of decreasing temperature. The one-atom-thick planar sheets can be built up on the condition of absence in clusters of molecules containing other number of carbon atoms.

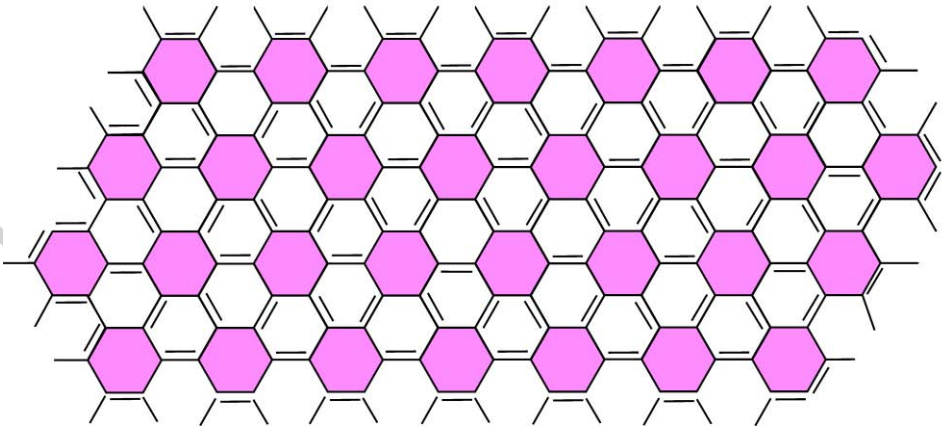


Figure 2. The sheet of graphitized graphene with unpaired boundary bonds (hexatomic carbon molecules are indicated by shaded regions, intermolecular free spaces are shown by unshaded regions).

The energy state of each hexatomic molecule in the cluster is shown in Figure 3. The carbon-carbon bond length in HACM of graphene is about 1.424 Å (Castro Neto et al,

2009; Jiao et al, 2009; Heyrovska, 2008, which is analogous to similar bonds in the molecule of benzene.

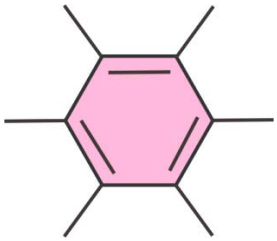


Figure 3. The hexatomic cyclic molecule in graphene with the marked covalent bonds formed during the process of cluster formation.

The mechanism of graphene formation is illustrated in Figure 4. As a result of HACM ordering in the cluster (i.e. the formation of planar honeycomb hexagonal net from hexatomic molecules) with decreasing temperature and at the annealing the double intramolecular bonds in HACM (Figure. 4 (a)) transform into intermolecular double bonds (Figure 4 (b)) that harden the frame of graphene lattice and reduce the overall energy of system. In the course of such transformation six π-electrons of the hexatomic molecule have the doubling of intermolecular σ-bonds. As this takes place, each hexatomic cycling void (HACV) gains three alternating double bonds.

The distinctive geometric feature of these HACV voids, as compared with the molecules, is the fact that each hexagonal void has three common sides with other three voids.

In respect to energy this is reflected in the fact that each conjugated bond can give only one π-electron to the hexagonal void. For this reason, at its outer conjugacy each HACV has in its cycle half number of electrons of the original HACV (or benzene molecule).

In addition, at the HACV clustering each boundary molecule has one unpaired electron, by which it can form a covalent bond with atoms of different elements and molecules of compounds (Figure 4 (a)).

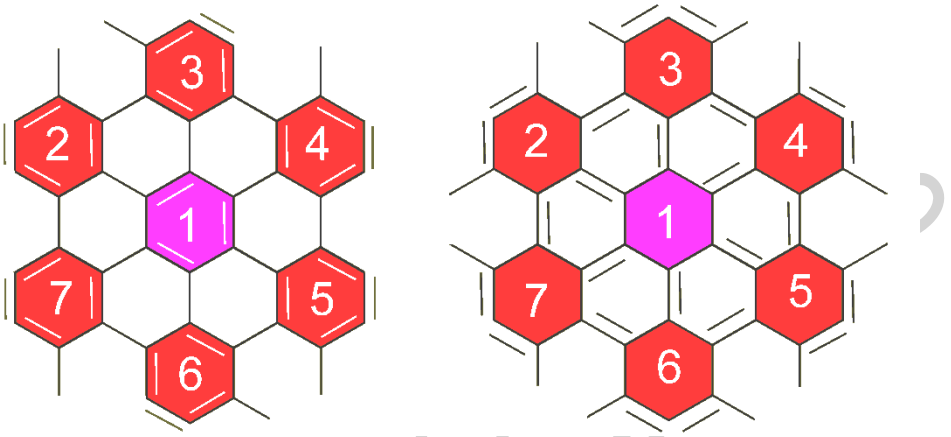
During the course of the molecules ordering in the cluster the number of unpaired electrons in the boundary molecules is doubled that allows to add a double amount of reagents. A similar realignment (in connection with this) gives the lowering of the total energy of the system (Figure 4 (b)). As the number of molecules in the graphene cluster increases, the contribution of boundary molecules to the energy state of graphene decreases and becomes negligibly small in the real crystals.

Thus, at the equal overall energy state of carbon atoms in the graphene, there is an inequality between the hexagons in the graphene sheet due to the existence of HACM molecules and HACV voids. The intramolecular bonds formed by the σ-electrons (1.42 Å) should be longer than the intermolecular bonds (1.40 Å), formed by σ and π-orbitals.

The HACM stability can be explained also by the fact that each atom in the HACM is linked to other two atoms of molecule skeleton by two σ bonds and intermolecular bond

comprises one σ-electron and one π-electron bonds, which is somewhat weaker than the two σ-electron bonds.

Hence, at the external equivalence of atomic bonds in the graphene net and energy equivalence of the carbon atoms the HACM molecule retains its individuality owing to the fact that its constituent each carbon atom is fixed in the hexatomic molecule skeleton by two σ-electron bonds, which it forms in the molecule structure with neighboring atoms. In addition, all voids are combined into one large system of voids.



(a) (b)

Figure 4. The ordering mechanism of heptamolecular cluster consisting of hexatomic carbon molecules: cluster with six unpaired electrons (a), graphene with twelve unpaired electrons (b).

It should be also pointed out that (when all electrons are paired in the molecule structure) the number of electrons per each HACV void is odd.

The odd number of electrons in the HACV assumes some paramagnetism of each void that leads to the sufficiently large polarizability of graphene layers; it manifests itself as the Van-der-Waals forces at the interaction between the layers and the adsorption of gaseous molecules and other substances.

3. Fullerenes and Their Derivatives

(Bubnov et al, 1994; Eletskii and Smirnov, 1993; Eletskii and Smirnov, 1995; Mordkovich, 2000; Heiney et al, 1991a; Heiney et al, 1991b; Dresselhaus et al, 1996; Taliani et al, eds., 1992; Sokolov et al, 1993; Hirsch, 2005; Vol′pin, 1993; Osip′yan et al, 1997; Sokolov, 1999; Konarev et al, 2000; Konarev et al, 1999; Zarubinskii et al, 1999; Scott et al, 2002; Howard et al, 1992; Scott, 2004; Churilov et al, 2002; Krätschmer, 1995; Li et al, 2001; Wilson et al, 1992; Savin et al, 1997; Fischer, 1993; Fischer and Heiney, 1993; Heiney, 1992; Stephens, 1992; Cheng et al, 1992; Sprik et al, 1992; Smalley and Yakobson, 1998; Parker et al, 1992; Bubnov and Laukhina, 1995; Grushko et al, 2007; Krätschmer, 2006; Tsetkova et al, 2011; Stankevich and Sokolov, 2004 Sokolov, 2007; Martín et al, 2006; Osawa ed., 2002; Kadish and Ruoff, ed., 2000;

Langa and Nierengarten, eds., 2007; Margadonna, ed., 2011; Zubov, 2004; Prato, 1997; Mejer and Bethune, 1990; Dikiy and Kabo, 2000; Kroto and Walton, eds., 2011)

Fullerenes are spherical, caged molecules with 20 or more carbon atoms located at the corner of the polyhedral structure consisting of hexagonal and pentagonal rings as the basis of an icosohedral symmetry closed cage structure. Each molecule contains 2 (10 + *n*) carbon atoms (*n* is the number of hexagons). The most stable spherical forms of fullerenes are formed if the pentagons are separated by no more than one hexagon (the rule of isolated pentagons).

The derivatives of fullerenes are formed by addition of atoms, molecules, ions, radicals and other types of particles to the fullerene molecule. In this case, these particles can be connected both on the outside of the fullerene molecule (exocompounds) and inside (endocompounds).

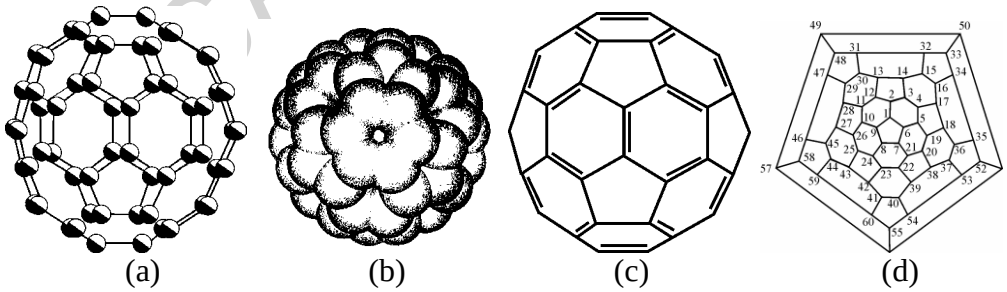
Fullerene-like substances are spherical molecules that differ from the fullerenes by the chemical composition, the skeleton structure and the presence of defects. These materials include fulleroids, heterofullerenes, homofullerenes and other spherical structures.

The homofullerenes are spherical molecules whose structure is composed of atoms of any one chemical element (except carbon).

The heterofullerenes are spherical molecules formed by partial replacement of carbon atoms in the fullerene cage by atoms of other chemical elements.

The fulleroids are fullerene-like materials as homofullerenes, heterofullerenes, norfullerenes, secofullerenes, because they resemble fullerenes in structure but substances are composed of defective fullerene molecules. Among these defects is usually the appearance of additional atoms in the fullerene structure, the skeletons with a deficit of carbon atoms or with broken links.

Fullerenes are usually denoted as follows: fullerene C_{60}, C_{70}, C_{84}, C_{240}, C_{540}, etc. (index is the number of carbon atoms). For convenience the three-dimensional structure of spherical molecules of fullerene is illustrated diagrammatically (Figure 5).



(a) (b) (c) (d)

Figure 5. The schematic representation of the C_{60} fullerene molecule: ball and stick model (a); model in the form of the electron cloud (b); model showing the double bonds(c); Schlegel diagram with numbered carbon atoms (d).

The distinctive feature of the fullerenes molecules structure is their sphericity. Completeness of the elementary structural unit of fullerenes as compared with the broken bonds of carbon atoms on the surface of crystals and infinite number of clusters of atoms in carbyne, graphite and diamond, is responsible for their unique capability to dissolve in liquids. This property of fullerenes is used for their extraction, separation and purification. Fullerene is the only one known soluble form of carbon.

The characteristic feature of the temperature dependence of the solubility of fullerene C_{60} molecules in certain solvents is its extremality over the temperature range $310< T< 313$K. The heat capacity of the solution has a maximum at these temperatures. The enthalpy of dissolution of C_{60} varies from 0.5 (in benzene) to 14.4 kJ / mol (in 1,2-dichlorobenzene). It is believed that two phases with different in sign temperature coefficients of solubility and different enthalpies of dissolution exist in the solution.

The highest dissolution of C_{60} has been observed in solvents belonging to the aromatic hydrocarbons and their derivatives. The evident solubility has been noted in solvents whose molecules contain atoms with undivided pairs of p-electrons (N, O, S), as well as being powerful donors of π-electrons (as for instance in CS_2).

Recent works of research group of N.S. Anikina (Institute for Problems of Materials Science of NAS of Ukraine, Kiev, Ukraine) have demonstrated that the existing correlation between the solubility of C_{60} and the electron-donor force of solvents is indicative of charge-transfer interaction with the formation of complexes of donor-acceptor type between molecules of solvent and C_{60}.

The dissolution of C_{60} is proportional to the density of π-electrons of carbon atoms that are in the ortho- and para-positions of the benzene ring of the solvent. According to the relationships of mesomeric effect, the electron-donor groups, that replace hydrogen of benzene ring, cause an increase of the π-electron density in the ortho- and para-positions.

Aromatic solvents with electron-acceptor substituents of hydrogen contributing to the *p*-electron density in the meta-positions and to the decrease in the ortho- and para-positions have low dissolving power in relation to the C_{60}.

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synthesis and molecular structure of fullerene halides and this structure is refined by X-ray investigation of monocrystals].

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together with theoretical studies of hydrogen storage on carbon materials, types of carbon materials with potential for hydrogen storage].

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155. Matysina Z.A., Schur D.V., Zaginaichenko S.Yu. (2003). Transition of Cs3C60 crystals with Rb impurity to the superconducting state. *Carbon* 41 (7), 1369-1373 [This paper presents elaboration of statistical theory of phase transition in fullerides of alkali metals to the superconducting state and comparison of calculation results with experimental data].

156. Rao A.M., Eklund P.C., Hodeau J.L., Marques L., Nunez-Regueiro M. (1997). Infrared and Raman studies of pressure-polymerized C60. *Phys. Rev*. B55 (7), 4766-4773 [This paper discusses the room-temperature infrared and Raman spectra for the pressure-induced C_{60} polymers and C_{60} photopolymer and presents comparison of these spectra with vibrational spectra obtained from molecular dynamical calculation for C_{60} dimer].

157. Sundar C.S., Sahu P.Ch., Sastry V.S., Rao G.V.N., Sridharan V., Premila M., Bharathi A., Hariharan Y., Radhakrishnan T.S., Muthu D.V.S., Sood A.K. (1996). Pressure-induced polymerization of fullerenes: a comparative study of C60 and C70. *Phys. Rev*. B53 (13). 8180-8183 [This paper presents investigation of polymerization of solid fullerenes C_{60} and C_{70} subjected to high pressures and high temperatures and associated changes in their structure].

158. Sundqvist B. (2004). Polymeric fullerene phases formed under pressure. In: *Fullerene-Based Materials*. Springer Berlin/ Heidelberg 109, 85-126 [This is an overview of structures, pressure-temperature phase diagrams of C_{60} and C_{70} and of their physical properties under high pressure].

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163. Lee G.D., Wang C.Z., Yoon E., Hwang N.M., Ho K.M. (2010). The role of pentagon-heptagon pair defect in carbon nanotube. *Appl. Phys. Lett*. 97 (9), 093106-093106-3 [This paper discusses the role of pentagon-heptagon (5-7) pair defects in carbon nanotubes as the center of vacancy reconstruction].

164. Heinmann R.B., Evsyukov S.E., Koga Y. (1997). Carbon allotropes: a suggested classification scheme based on valence orbital hybridization. *Carbon* 35, 1654-1657 [This paper describes the classification scheme of known structural versions of carbon materials based on definition of hybridization degree of carbon atoms].

165. Belenkov E.A. (2003). Classification of carbon structures. *Hydrogen Materials Science and Chemistry of Carbon Nanomaterials*, 731-735 [This paper demonstrates the classification scheme of existing variety of structural updatings of carbon and predicts new carbon allotropes based on definition of structural states and hybridization states of carbon atom].

166. Schur D.V., Zaginaichenko S.Yu., Matysina Z.A. (2008). The special features of formation of carbon nanostructures, their classification and site on the state diagram of carbon. In: *Carbon Nanomaterials in Clean Energy Hydrogen Systems*, Springer, 67-83 [This work describes the peculiarities of formation of low-temperature carbon structures and regions of existence of high-temperature structures and presents areas of these structures on the P-T diagram and gives theory of phase transformations in carbon crystals].

167. Haddon R.C. (1992). Electronic structure, conductivity and superconductivity of alkali metal dopes C60. *Acc. Chem. Res*. 25, 127-133 [This work discusses progress in the preparation and characterization of conducting and superconducting solids and films based on alkali metal doped fullerenes].

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169. Belenkov E.A., Ali-Pasha V.A. (2011). Investigation of carbon phases from sp2±δ- hybridized atoms with three-dimensional rigidly bound structure. *Russ. Phys. J*. 53 (12), 1280-1285 [This paper presents calculations of cluster structures of new carbon phases of 3D graphite synthesized by polymerization and carbonization of hydrocarbon molecules].

Reviews and Books

Ajayan P.M. (1999). Nanotubes from carbon, *Chem. Rev.* 99(7), 1787-1800. [Important paper about synthesis techniques of pure nanotubes, study of structure-topology-property relations in nanotubes, ideal structure of nanotube, a host of remarkable properties and practical applications].

Akasaka T., Nagase Sh. (2002). *Endofullerenes: a New Family of Carbon Clusters*, Springer, 308 p. [It contains a review of current research work on endohedrally doped fullerenes including classification according to atoms encapsulated into fullerene, structural, electronic and dynamical properties of endofullerenes].

Baranowski B., Zaginaichenko S.Yu., Schur D.V., Skorokhod V.V., Veziroglu A. (2008). *Carbon Nanomaterials in Clean Energy Hydrogen Systems – I*, Dordrecht, Netherlands: Springer, 907 p. [This book includes papers on the most recent advances in carbon nanomaterials science, the progress of hydrogen-based science and discusses the role of hydrogen and carbon nanomaterials in the energy field].

Bottani E.J., Tascon J.M.D. (2008). *Adsorption by Carbons*, Amsterdam, Netherlands: Elsevier, 742 p. [This book covers important aspects of adsorption by various carbons including the adsorption on fullerenes and carbon nanotubes and presents both basic and applied aspects].

Dai L. (2006). *Carbon Nanotechnology: Recent Developments in Chemistry, Physics, Materials Science and Device Applications*, Elsevier Science, 750 p. [This book presents major classes of carbon nanomaterials, including carbon fiber, diamond, C_{60} and carbon nanotubes; discusses comprehensive treatment from materials chemistry and structure-property to practical applications].

Dresselhaus M.S., Dresselhaus G., Avouris P. (2010). *Carbon Nanotubes: Synthesis, Structure, Properties and Applications*, Berlin: Springer-Verlag, 447 p. [This book is a review of researches in the field of synthesis techniques of different carbon nanostructures, carbon nanotubes growth mechanisms, nanotube electronic structure, electrical, optical, mechanical properties, nanotube spectroscopy and applications].

Dresselhaus M.S., Dresselhaus G., Eklund P. (1996). *The Science of Fullerenes and Carbon Nanotubes: Their Properties and Applications*, New York: Academic Press, 965 p. [This book deals with the fullerene and their derivatives structure, discusses the unique properties and applications, both current and future, of all classes of fullerenes].

Ebbesen T.W. (1997). *Carbon Nanotubes, Preparation and Properties*, Boca Raton, FL: CRC Press, 296 p. [This is a book on results of study of growth mechanisms, structure and morphology of carbon nanotubes and their potential applications].

Endo M., Iijima S., Dresselhaus M.S. (1996). *Carbon Nanotubes*, Pergamon, 202p. [This book gives a comprehensive review of recent research and development in the field of nanoscale materials as carbon nanotubes, their preparation, structure, properties and observation of quantum effects in CNTs].

Francois L. (2008). *The Physics of Carbon Nanotube Devices*, New York: William Andrew Inc., 296 p. [This book explains the experimental and theoretical aspects of carbon nanotube devices including applications in electronics, nanoelectrochemical systems, field-emission, optoelectronics and sensing].

Guldi D.M., Martin N. (2010).*Carbon Nanotubes and Related Structures: Synthesis, Characterization, Functionalization and Applications*, Weinheim, Germany: Wiley-VCH, 562 p., 6 th ed. [This is a book on fundamental research, recent breakthroughs and real-life applications of carbon nanotubes, their controlled chemical functionalization and the latest research on novel carbon-derived structures as graphene, nanoonions and carbon pea pods].

Guldi D.M., Martin N. (2002). *Fullerenes: From Synthesis to Optoelectronic Properties*, Springer, 440 p. [This book discusses the latest developments in disciplines of fullerene research].

Harris P.J.F. (2009). *Carbon Nanotube Science: Synthesis, Properties and Applications*, Cambridge, UK: Cambridge University Press, 314 p, 2nd Edition. [This book is devoted to the structure of carbon nanotubes and related structures, the discussion of synthesis, purification and processing methods, electronic properties and potential applications in a wide range of fields].

Hirsch A., Brettreich M. (2005). *Fullerenes: Chemistry and Reactions*, Weinheim, Germany: Wiley-VCH, 423 p. [This book gives fundamental aspects of fullerenes chemistry and presents chemical properties of this family of molecules].

Kadish K.M., Ruoff R.S. (2000). *Fullerenes: Chemistry, Physics and Technology*, New York: Wiley-Interscience, 968 p. [This book is a guide to the current state of knowledge in the field of fullerenes and presents physical and chemical properties and applications of fullerenes described by chemists, physicists, materials scientists, pharmacologists and chemical engineers].

Langa F., Nierengarten J.F. (2011). *Fullerenes: Principles and Applications*, Cambridge, UK: Royal Society of Chemistry, 650p., 2nd ed. [This book summarizes the basic principles of fullerene chemical reactivity, electrochemistry, light induced processes, fullerenes for materials science, fullerenes and solar cells, multifunctional carbon nanotube materials].

Loiseau A., Launois P., Petit P., Roche S., Salvetat J.P. (2006). *Understanding Carbon Nanotubes: From Basics to Applications*, Berlin: Springer, 571 p. [This book represents the foundations of carbon nanotube science, structural analysis, synthesis and growth, electronic structure, mechanical and surface properties of nanotubes and composites].

Martin N., Giacalone F., Plato M. (2009). *Fullerene Polymers: Synthesis, Properties and Applications*, Wiley-VCH, 332 p. [This book provides different strategies for the synthesis of fullerene-containing polymers, new classification of the different types of fullerene polymers; it covers all aspects from different classes to their synthesis and application in materials science according to their chemical structures].

Marulanda J.M. (2011). *Electronic properties of Carbon Nanotubes*, InTech, 696p. [This book concentrates on fabrication techniques, physical properties including density of states and electronic structures and industry applications of carbon nanotubes].

Melinon P., Maseneli B. (2012). *From Small Fullerenes to Superlattices: Science and Applications*, Pan Stanford Publishing, 350 p. [This book covers predicting models of popular nanostructures as fullerenes, graphene and nanotubes and possible routes for their synthesis; the description at the nanoscale of these new structures and complex architectures that ensue from them, offers an original perspective into these scarcely evoked structures].

Osawa E. (2012). *Perspectives of Fullerene Nanotechnology*, Springer, 400 p. [This book covers main ways of the industrial applications of fullerenes and carbon nanotubes].

Pierson H.O. (1993). *Handbook of Carbon, Graphite, Diamonds and Fullerenes*, New Jersey, USA: Noyes Publications, 419 p. [This book provides a review of science of carbon allotropic modifications, as graphite, diamond and fullerenes, and presents structures and properties of these carbon materials].

Prassides K. (2004). *Fullerene-Based Materials: Structures and Properties*, Berlin, Germany: Springer-Verlag, 283 p. [The present book contains both theoretical and experimental contributions devoted to novel carbon materials like fullerite, fullerene polymers, fullerides, their electronic structure, structural and electronic properties].

Reich S., Thomsen C., Maultzsch J. (2004). *Carbon Nanotubes: Basic Concepts and Physical Properties*, Berlin: Wiley-VCH, 215 p. [The book includes information about the structures and symmetries of carbon nanotubes and provides the description of carbon nanotubes properties based on theoretical and experimental studies].

Reitmeijer F.J.M. (2006). *Natural Fullerenes and Related Structures of Elemental Carbon*, Springer, 317 p. [This book presents experimental and analytical data for C_{60}, larger fullerenes and related structures of elemental carbon existed in interstellar space, meteorites and on Earth].

Saito R., Dresselhaus M.S., Dresselhaus G. (1998). *Physical Properties of Carbon Nanotubes*, New York: World Scientific, 259 p. [This book focuses on the basic principles behind the physical properties of nanotubes and gives the background necessary to understand the recent developments].

Saito S., Zettl A. (2008). *Carbon Nanotubes: Quantum Cylinders of Graphene*, Elsevier Science, 215 p. [This book discusses the development of a variety of synthesis techniques of carbon nanotubes both experimentally and theoretically. It is also devoted to consideration of graphene as a building block of carbon nanotubes].

Stankevich I.V., Sokolov V.I. (2004). Advances in fullerene chemistry, *Russ. Chem. Bulletin*, 53(9), 1824-1845. [A concentrated review of key results obtained in experimental and theoretical studies on fullerene chemistry].

Tagmatarchis N. (2011). *Advances in Carbon Nanomaterials: Science and Applications*, Pan Stanford Publishing, 300 p. [This book provides extensive information on carbon-based nanostructures materials, varied from fullerenes and endohedral metallofullerenes to carbon nanotubes and nanohorns; their exclusive structures and novel properties; gives an insight on the morphology and structure of carbon nanotubes and strategies for chemical functionalization of carbon nanohorns].

Taylor R. (2003). *Chemistry of Fullerenes*, Singapore: World Scientific Publ. Co, 274 p., 3rd.ed. [This book describes all of the known types of reactions, the means of production, purification and properties of fullerenes].

Thilgen C., Diederich F. (2006). Structural aspects of fullerene chemistry - a journey through fullerene chirality, *Chem. Rev*., 106(12), 5049-5135. [This paper contains a comprehensive review of study of different aspects of fullerene chirality and their derivatives].

Tomanek D., Enbody R.J. (2002). *Science and Application of Nanotubes*, New York: Kluwer Academic Publishers, 398 p. [This book represents the state of the art in the field of nanotubes. The main focus is on the relative merits of various techniques used to synthesize nanotubes of carbon and other materials].

Varin R.A., Czujko T., Wronski Z.S. (2009). *Carbons and Nanocarbons In: Nanomaterials for Solid State Hydrogen Storage*, Springer, P. 291-320. [This book chapter provides physi- and chemisorptions of hydrogen on nanostructured carbons, discusses C-H bonds in hydrocarbons and hydrogen storage in ordered fullerenes, carbon nanotubes, nanographites and carbon nanohorns].

Verner R.F., Benvegnu C. (2011). *Handbook on Fullerene: Synthesis, Properties and Applications*, Nova Science Pub. Inc. [The topical research in study of synthesis, properties and applications of fullerene has been presented in this book. The discussed topics include phase-equilibria in the fullerene-containing system, symmetrical features of fullerene structures, metal complex catalysts in the fullerenes chemistry, functionalized nanofullerenes].

Wang Zh. M. (2008). *One-Dimensional Nanostructures*, New York: Springer Science, 329 p. [In this book one dimensional nanostructures, including nanowires, nanotubes and quantum wires, have been regarded as the promising building blocks for nanoscale electronic and optoelectronic devices].

Yellampalli S. (2011). *Carbon Nanotubes – Synthesis, Characterization, Applications*, InTech, 528 p. [This is a book on research results of synthesis methods, processing techniques, characterization and applications of carbon nanotubes].

Yoshimura S., Chang R.P.H. (2010). *Supercarbon: Synthesis, Properties and Applications*, Berlin, Germany: Springer-Verlag, 266 p. [This book is a status report on synthesis, properties and applications of new carbonaceous materials (π-electron materials) with extended π-electron clouds in the solid state, including fullerenes, graphite and carbon nanotubes].

Zaginaichenko S.Yu., Schur D.V., Skorokhod V.V., Veziroglu A., Ibrahimoglu B. (2011). *Carbon Nanomaterials in Clean Energy Hydrogen Systems – II*, Dordrecht, Netherlands: Springer, 539 p. [The book presents papers on current progress in chemistry of carbon nanomaterials and metal-hydrogen systems, technologies for hydrogen storage, carbon nanomaterials processing, energy and environmental problems].

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 researchis 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 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 specialty in 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 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 "Solubility 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