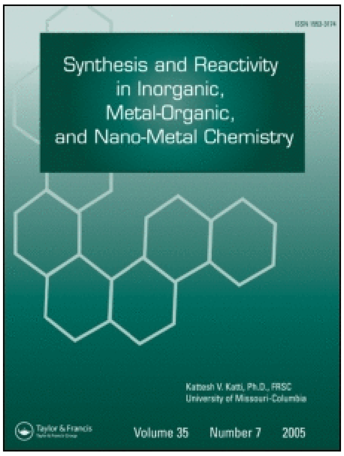
This article was downloaded by: *[Kharisov, Boris]*
On: *17 February 2010*
Access details: *Access Details: [subscription number 919313446]*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597303

Synthesis Techniques, Properties, and Applications of Nanodiamonds

Boris I. Kharisov [a]; Oxana V. Kharissova [a]; Leonardo Chávez-Guerrero [a]
[a] Universidad Autónoma de Nuevo León, Ciudad Universitaria, San Nicolás de los Garza, Nuevo León, México

Online publication date: 16 February 2010

To cite this Article Kharisov, Boris I., Kharissova, Oxana V. and Chávez-Guerrero, Leonardo(2010) 'Synthesis Techniques, Properties, and Applications of Nanodiamonds', Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 40: 2, 84 — 101

To link to this Article: DOI: 10.3109/10799890903555665

URL: http://dx.doi.org/10.3109/10799890903555665

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 40:84–101, 2010

ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.3109/10799890903555665

Synthesis Techniques, Properties, and Applications of Nanodiamonds

Boris I. Kharisov, Oxana V. Kharissova, and Leonardo Chávez-Guerrero
Universidad Autónoma de Nuevo León, Ciudad Universitaria, San Nicolás de los Garza,
Nuevo León, México

Synthesis methods (ion and laser bombarding, CVD, hydrothermal, ultrasonic, electrochemical, and detonation techniques) for obtaining various forms of nanodiamonds (NDs) are generalized. Structure, physical and chemical properties, functionalization of NDs and composites on its basis are discussed, as well as their applications in medicine, electrochemistry, materials chemistry and technology.

Keywords applications, composites, functionalization, nanodiamonds

INTRODUCTION

Carbon takes many different forms, each with its own electronic structure, and has a fantastic range of properties. Nanodiamond (ND) is a new member of nanocarbons, which consist of nano-sized tetrahedral networks. The history of the discovery of ND is unique, since ND synthesis was accidentally discovered in the USSR three times over 19 years starting from 1963 by shock compression of nondiamond carbon modifications in blast chambers.[1] The term *nanodiamond* is currently used broadly for a variety of diamond-based materials at the nanoscale ranging from single diamond clusters to bulk nanocrystalline films.[2] It is generally accepted that *nanocrystalline diamond* (NCD) consists of facets less than 100 nm in size, whereas a second term *ultrananocrystalline diamond* (UNCD) has been coined to describe material with grain sizes less than 10 nm. These differences in morphology originate in the growth process.[3] Closely-related *diamond-like carbon* (DLC) films, according to IUPAC definition,[4] "are hard, amorphous films with a significant fraction of sp^3-hybridized carbon atoms and which can contain a significant amount of hydrogen. Depending on the deposition conditions, these films can be fully amorphous or contain diamond crystallites."

Nanometer sized diamond has been found in meteorites, proto-planetary nebulae and interstellar dusts, as well as in residues of detonation and in diamond films. It is known that primitive chondritic meteorites contain up to approximately 1500 ppm of nanometer-sized diamonds, containing isotopically anomalous noble gases, nitrogen, hydrogen, and other elements. These isotopic anomalies indicate that meteoritic NDs probably formed outside our solar system prior to the Sun's formation (they are thus presolar grains).[5] It appears that some interstellar emission bands in the 3–4, 7–10, and approximately 21 μm spectral regions could originate from NDs.[6]

Diamond thin films have outstanding optical, electrical, mechanical and thermal properties, which make these attractive for applications in a variety of current and future systems. In particular, the wide band gap and optical transparency of diamond thin films make them an ideal semiconductor for applications in current and future electronics. Various aspects on the NDs have been recently emphasized in a series of reviews[7−13] and books,[14,15] in particular such topics as ND preparation by chemical vapor deposition (CVD), NCD film formation from hydrogen-deficient and hydrogen-rich plasma, nanocomposite films, mechanical behavior of NCD films, and field emission characteristics,[16] diamond nanowires and their biofunctionalization of nucleic acid molecules,[17] or use of NCD to study noncovalent interaction.[18] In this review, we have tried to emphasize updated main synthesis and functionalization methods for NDs and their relationship with ND structure and properties.

Received 31 October 2009; accepted 11 December 2009.

This review is dedicated to the 75th birthday (June 13, 2010) of M.Sc. Nadezhda V. Andreeva for her excellent contributions in the development of teaching processes at 23rd School (Moscow, Russia).

The authors are grateful to PAICyT-UANL (project 2009) for financial support, to Professors Guowei Yang (Zhongshan University, Guangzhou, China), Yury Gogotsi (Drexel University, Philadelphia, USA), Masaki Ozawa and Anke Krueger (both from Institut fur Organische Chemie der Julius-Maximilians-Universitat, Wurzburg, Germany), Kian Ping Loh (National University of Singapore), Naomi J. Halas (Rice University, Houston, USA), Kuo Chu Hwang (National Tsing Hua University, Hsinchu, Taiwan), Sergey K. Gordeev (Central Research Institute of Materials, Saint-Petersburg, Russia), as well as to Springer and the American Chemical Society for granted permissions to reproduce images from original publications.

Address correspondence to Dr. Boris Kharisov, Chemistry, A.P. 18-F, Ciudad Universitaria UANL, San Nicolás de los Garza, Monterrey, 52-81-82987496. E-mail bkhariss@mail.ru

SYNTHESIS METHODS FOR NANODIAMONDS

Precursors

NDs can be produced from a series of precursors, among which the CH_4/H_2 mixtures with addition of inert gases, O_2 or N_2 are frequently used. Thus, synthesis of NCD films by using a small amount of simultaneous O_2 and N_2 addition into conventional CH_4/H_2 mixtures.[19] The NCD samples were grown in a 5 kW microwave plasma CVD (MWPCVD) system on large silicon wafers. It was shown that the morphology, microstructure, grain size, crystalline quality and growth rate of NCD films can be tailored by simply adjusting the amount of O_2 and N_2 addition, and with increasing the ratio of addition, the crystal quality of the NCD films is significantly enhanced. Additionally, carbon nanotubes were used as ND precursors,[20] for instance multiwall carbon nanotubes (MWCNTs) served as a precursor to prepare diamond in a pure hydrogen microwave discharge.[21] Also, NDs were easily formed from carbon film containing Si.[22] The growth of diamond and ß-SiC was controllable by adjusting the heating temperature and the proportion of Si. A method for producing a ND, in which a ND was removed from an activated carbon containing the ND, was offered by West et al.[23] A ND fiber (up to 2000 nm) can also be produced by mixing a carbon source, a metal and an acid under conditions, which results in ND formation. Methods of industrial ND synthesis were generalized in a review[24] with attention to aspects of detonation decomposition of powerful mixed explosives with a negative oxygen balance (formation of ultrafine-dispersed diamonds). The most efficient technology of chemical cleaning of diamonds with nitric acid at high temperatures and pressures for producing high-purity NDs was described (other methods see section "Purification of nanodiamonds"). Other ND precursors include fullerenes,[25] graphite, β-SiC, carbide-organic systems, polycarbine, trotyl/hexogen, 1,1,1-trichloroethane, etc.

Hydrothermal Synthesis

Hydrothermal synthesis as any heterogeneous reactions occurring under the conditions of high-temperature/high-pressure ($>100°C$, >1 atm) in aqueous solutions in closed system has a growing interest among the scientists in particular due to a possibility of synthesis of new phases or crystals growth.[26] This technique was also applied for NDs synthesis;[27] thus, available hydrothermal techniques for ND synthesis were reviewed by Nickel et al.[28] The hydrothermal synthesis of diamond was frequently carried out in the silicon carbide-organic compound system.[29,30] Organic matter dissociated in a closed system to generate C-O-H supercritical fluids, known for their high dissolving power and influence on the type of elemental carbon formation. Formed carbon crystallites had typical spectra of sp^3-hybridization, clearly demonstrating the formation of nano-sized diamond crystallites under sub-natural conditions. Among other ND precursors in hydrothermal synthesis, chlorinated hydrocarbons such as dichloromethane and 1,1,1-trichloroethane,[31,32] can be used.

Ion Bombardment

A successful irradiation-induced transformation of MWCNTs to diamond nanocrystals was realized with double ions ($^{40}Ar^+$, $C_2H_6^+$) bombardment.[33] This idea of multi-ion irradiation may also be used for fabricating other nanostructures. The growth of ND under prolonged DC glow discharge plasma bombardment of 1 μm thick polycrystalline CVD diamond was studied by Gouzman et al.[34] It was established that ND formation on diamond started directly. The amorphous carbon/ND composite structure was substantial to the ND nucleation under energetic plasma bombardment. The nucleation of diamond on graphitic edges as predicted by Lambrecht et al. in 1993 was experimentally confirmed by Yao et al.[35] Thus, the precipitation of ND crystallites in upper layers of a film deposited by a 1 keV mass-selected carbon ion beam onto silicon held at 800°C was observed by HRTEM, selected area electron diffraction, and electron energy loss spectroscopy. Molecular dynamic simulations showed that diamond nucleation in the absence of hydrogen can occur by precipitation of diamond clusters in a dense amorphous carbon matrix generated by subplantation. After cluster formation, they can grow by thermal annealing consuming carbon atoms from the amorphous matrix.[36]

Laser Bombarding

Pulsed laser ablation has become an attractive method[37] for the preparation of ND in liquids,[38,39] in liquid-solid interface,[40,41] or solids using carbon powders. Thus, ND were obtained[42] by suspending carbon powders (crystalline flake graphite, microcrystalline graphite or carbon black with particle size less than 10 μm) in a circulating liquid medium (water, alcohols, ketones, ethers, and their solutions or mixtures), bombarding the carbon powders by laser, and further purifying the product to obtain the diamond nanopowders. It was shown that only microcrystalline graphite by laser transformed into diamond (cubic diamond about 5 nm) in the three carbon materials. It also demonstrated that microcrystalline graphite was more advantageous than carbon black and crystalline flake graphite when the laser power density was 10^6 W/cm^2.[43] A theoretical kinetic approach to elucidate the nucleation and growth of nanocrystals with respect to the capillary effect of the nanometer-sized curvature of crystalline nuclei was proposed by Wang et al.[44] on the example of the ND synthesis by pulsed-laser ablating a graphite target in H_2O. The authors predicted the nucleation time, growth velocity, and the grown size of NDs from the proposed kinetic model. Pulsed-laser irradiation of amorphous carbon films in a liquid phase (Figure 1) at room temperature and ambient pressure led to a phase transformation from amorphous carbon to ND (4–7 nm).[45] On the basis of the obtained results, it was concluded that laser irradiation in liquid actually opens a route toward self-assembly of surface micro and nanostructures, i.e., functional nanostructures manufacturing.

The diamond-like carbon films with the highest sp^3 carbon bonding content were obtained at laser fluences of

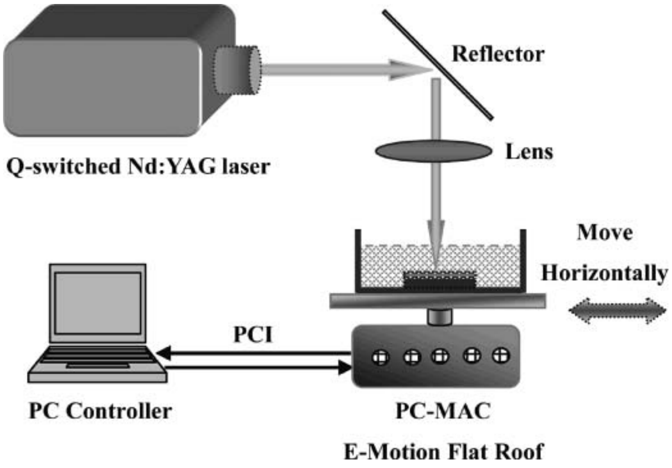


FIG. 1. Schematic illustration of the experimental setup of laser irradiation in liquid.

850 to 1000 mJ/cm^2 by irradiation of the polycarbyne polymer films, coated on silicon substrates, with a pulsed Nd:yttrium-aluminum-garnet laser ($\lambda = 532$ nm) in argon gas atmosphere.[46] Quartz substrates were used as supports in similar experiments ($\lambda = 1064$ nm, $\tau = 20$ ns, $q = 4.9 \cdot 10^8$ W/cm^2) under vacuum ($p = 2.6 \cdot 10^{-3}$ Pa).[47] The effect of low power laser radiation on volume and surface microinclusions of graphite-like carbon during the CVD diamond film fabrication were studied.[48] The simulation calculations showed that laser irradiation accelerates the processes of graphite and non-diamond phase etching.

Microwave Plasma Chemical Vapor Deposition (MWPCVD) Techniques

An important research and industrial method, microwave and millimeter-wave processing of materials,[49−51] in particular diamonds, was reviewed by Lewis et al.[52] CVD techniques, in particular those based on microwave-assisted approach, have become one of the most classic methods in materials production, including various carbon nanoforms, and are well generalized in a series of books.[53−55] The experimental findings providing a basic understanding of the plasma chemistry of hydrocarbon/Ar-rich plasma environment, used for growing ND films, were discussed by Gordillo-Vazquez et al.[56] Both main ND types, NCD and UNCD, were obtained via this route. Among a series of related works, the NCD (40–400 nm) were grown without the help of initial nucleation sites on Ni substrates in a microwave plasma reactor (400 to 600°C) using hexane/nitrogen-based CVD.[57] In a related work, NCD thin films were prepared and characterized with MPCVD.[58] Ultra smooth nanostructured diamond (USND) coatings were deposited by MPCVD technique using He/H_2/CH_4/N_2 gas mixture as a precursor.[59]

Various aspects of CVD applications for ND materials were studied in detail by Butler et al.,[60] in particular the growth and characteristics of NCD thin films with thicknesses from 20 nm to <5 μm containing 95->99.9% diamond crystallites. It was shown that the UNCD was usually grown in argon-rich, H-poor CVD environments, and may contain up to 95–98% sp^3-bonded C. Effect of gas (mixed methane and hydrogen) flow rate on diamond deposition on mirror-polished silicon substrates in a microwave plasma reactor was studied by Chen et al.[61] Microcrystalline diamond thin films were obtained at relatively low gas flow rates (30–300 sccm), while NCD thin films with cauliflower-like morphology were obtained at higher gas flow rates (>300 sccm). This result may be attributed to the enhancement of diamond secondary nucleation arising from the increase in the flux rate of carbon-containing radicals reaching the diamond growth surface.

A series of patents are dedicated to various presentations of microwave equipment for fabrication of distinct diamond forms. Thus, the equipment for MWCVD processing was patented by Nanba et al.[62] The apparatus had a dielectric window for introducing microwave in a vacuum chamber and an antenna part with an edge electrode for introducing microwave in the chamber, wherein the window is sandwiched between the chamber inner surface and the electrode. The apparatus was suitable for forming a large-area high-quality semiconductor diamond film. Another microwave CVD apparatus precisely for preparation of diamond, comprising a globe-shaped discharge chamber and a coaxial antenna for feeding microwave into the chamber, with the antenna tip equipped with a work holder, positioned in the center of the globe, was proposed by Ariyada et al.[63]

Detonation Methods for ND Fabrication

Detonation techniques belong to the most conventional methods[64] for obtaining NDs, in particular at industrial scale. In this respect, we note a series of fundamental reviews of Dolmatov, dedicated to such various aspects of detonation-produced nanodiamonds (DND) as the structure,[65] key properties and promising fields of application of detonation-synthesis NDs,[66] modern industrial methods for their manufacture,[67,68] etc. DND purity is an important problem, which is being continuously studied. In particular, the mechanism of prolonged water washing to remove excessive acidity was described,[69] which was offered to improve essentially the quality of NDs and the stability of their aqueous suspensions by treating them with ammonia water (to an alkalescent medium), followed by heating to 200–240°C under pressure (so called "thermolysis"). Alternative methods to remove materials still unconverted to diamond (details see below) produced[70] with yields up to 60% by firing of high explosive mixtures in water confinement, avoiding the use of inert gas and preventing the oxidation and graphitization of recovered diamonds, various selective oxidation treatments (with KNO_3/KOH, H_2O_2/HNO_3 mixtures) were carried out, leading to light gray ultradispersed diamond aggregates with a yield up to 60%.

Mechanisms of various steps of DND formation have been established. Thus, problems associated with the final stages in the disintegration/purification of DND into monodisperse single-nanodiamond (DSND) particles were critically reviewed by Osawa et al.[71,72] Possible pitfalls that might encounter during the search of industrial application of DSND were identified: low diamond-graphite transition temperature, and abnormally strong tendency of the dispersed primary particles to re-aggregate. The formation kinetics of detonation NDs was proposed by Titov et al.[73] As a conclusion of a series of detonation experiments with ultradisperse diamond in oxygen and oxygen-free media, the diamond cannot be produced immediately behind the wave front. The authors believed that there is a diamond-free zone and zones of diamond formation. Production of NDs with an increased colloidal stability by using an explosion synthesis was patented by Puzyr et al.[74]

Use of Ultrasound

Ultrasonic action during the ND manufacture or its pretreatment has got a certain use in NDs fabrication and compared with other treatments. Thus, carbon materials containing C≡C were irradiated with X-rays, microwave, and/or ultrasonic waves to give varieties of carbon structures, in particular diamond thin film and fine-grain diamond.[75] Diamond microcrystals were prepared (size 6 or 9 μm, yield $\sim$10% by mass) using ultrasonic cavitation of a suspension of hexagonal graphite in various organic solvents at $\sim$120°C and at atmospheric pressure.[76] Thermal processing of ND powder in air at 440–600°C until powder weight loss reached 5–85% led to stable suspensions in water, EtOH and other solvents upon ultrasonic treatment.[77] Effects of pretreatment on the nuclei formation of UNCD on Si substrates were studied,[78] showing that either precoating a thin layer of titanium ($\sim$400 nm) or ultrasonication pretreatment using diamond and titanium mixed powder enhanced the nucleation process on Si substrates markedly. NCD coating using sol-gel technique as an easy coating technique for NCD films was reported by Hanada et al.,[79] making a ND sol for coating by ultrasonic dispersion in water of diamond nanoparticles ($<$10 nm) synthesized by a detonation method, followed by mechanical milling milled with zirconia balls. This technique allowed fabrication NCD films easily at a much lower processing temperature in comparison with conventional diamond coating. Process and apparatus for manufacture of diamond powder in nanometer range by size reduction using ultrasonic agitation was patented by Iijima.[80]

Electrochemical Synthesis of DLC

The first attempt to use electrolysis in the production of carbon structures was made by Namba[81] in 1992, who deposited diamond-like carbon (DLC) films on silicon substrates using ethanol solutions at 70°C. The electrochemical process is dependent on many variables, including temperature,[82] electrolyte, applied potential, current density, distance between electrodes, and the substrate for deposition. The advantages include low cost, low temperature, scalability, endless possibilities for use of precursors, ability to use simple experimental equipment, and the flexibility to produce different structures. Methanol has been used as one of the most used precursors and/or solvents in the reported electrochemical procedures, although DMSO, ethanol, acetonitrile, nitroethane and liquid ammonia were also applied; graphite were used as anodes; silica, nickel foil, SnO_2-coated glass were used as substrates in the synthesis of DLC films. There is a huge variability in the voltage used; it can be set in the range between 2 and 5000 volts, which shows that this so many variables can be modified in order to obtain the desirable surface. Among other experimental reports, Roy et al.[83] produced DLC films using a SnO_2 substrate in an aqueous solution of acetic acid at room temperature and claimed that the substrate had a deficiency in oxygen sites where molecules can be anchored, which promoted the breaking chemical bonds and formation species with sp^2 and sp^3hybridizations. DLC films and nanoinclusions of diamond, graphite, and lonsdaleite phase were prepared[84] from acetylene-saturated liquid ammonia at a temperature of -33°C by potentiodynamic, potentiostatic, galvanostatic, and pulsed deposition methods. The source of carbon was acetylene according to the reaction (1); electrolysis of these solutions resulted in the deposition of a DLC film confirmed. We emphasize that this work contains valuable tabulated information on the electrochemical preparation of diamond thin films.

$$x\,\mathrm{HC} \equiv \mathrm{CH} \rightarrow \mathrm{C}_{2x}(\mathrm{sp}^3 \text{ and } \mathrm{sp}^2) + 2x\,\mathrm{H}^+ + 2x\mathrm{e}^- \qquad [1]$$

Models for Nanodiamond Synthesis

Additionally to the described above (section "Detonation nanodiamonds") DND formation mechanisms, various models of ND synthesis on the basis of experimental results have been offered including softwares. Thus, visualization techniques for modelling carbon allotropes, including NDs, were described by Adler et al.,[85,86] in particular AViz (atomistic visualization package), which is essential for understanding sample geometries. A cold plasma hybrid-fluid-particle approach, agreed with experimental results, was used to describe the deposition of diamond films from pulsed MW discharges.[87] A density functional theory study was presented[88] on changes in band gap effects of NDs (hydrogen terminated diamond-like molecules, diamondoids) depending on size, shape, and the incorporation of heteroatom functionalities. The combination of increasing the size of the ND and push-pull doping are likely to make these materials highly valuable for semiconductor applications. A comparison of several theoretical models that have been proposed to describe the relative phase stability of diamonds and other forms of carbon at the nanoscale was reviewed.[89]

Simulation and bonding of dopants in NCD was reviewed by Barnard et al.[90] using quantum mechanics based simulation methods. It is known that impurities can be introduced into diamond, resulting in materials with unusual physical and

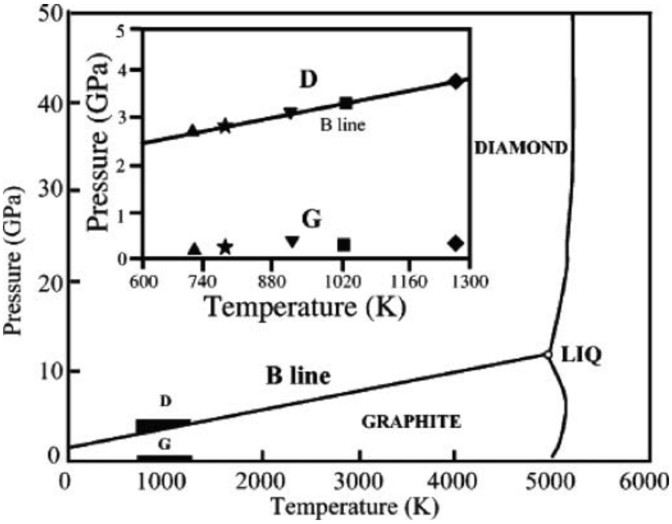


FIG. 2. Carbon thermodynamic equilibrium phase diagram based on pressure and temperature. G region means a metastable phase region of diamond nucleation; D region means a new stable phase region of diamond nucleation by hydrothermal synthesis or reduction of carbide under the nanosize-induced interior pressure conditions. The inset shows the enlarged G and D region.

chemical properties. For electronic applications one of the main objectives in the doping of diamond is the production of *p*-type and *n*-type semiconductors materials. The thermodynamic approach on the nanoscale to elucidate the diamond nucleation taking place in the hydrothermal synthesis and the reduction of carbide (HSRC) supercritical-fluid systems was performed by Wang et al.[91] It was shown that the nanosize-induced interior pressure of diamond nuclei could drive the metastable phase region of the diamond nucleation in HSRC into the new stable phase region of diamond in the carbon phase diagram (Figure 2). 400 MPa was predicted to be the threshold pressure for the diamond synthesis by HSRC in the metastable phase region of diamond. Among other reports, the transformation of NDs into carbon-onions (and vice versa) was observed experimentally and modeled computationally,[92] outlining results of numerous computational and theoretical studies examining the phase stability of carbon nanoparticles and clarifying the complicated relationship between fullerene and diamond structures at the nanoscale.

Purification of Nanodiamonds

The diamonds and NDs, obtained by different methods, contain various impurities, described below. Small amounts of graphitic impurities and other carbon structures in diamond can alter its most important properties,[93] so a grand variety of techniques for their purification has been developed, in particular magnetic,[94] ultrasonic,[95] electrolysis[96] or electric field,[97] or laser,[98] as well as pure chemical methods applying generally strong oxidants (acids, potassium permanganate, chromium(VI) oxide, chromates, mixture of potassium nitrate and KOH, ozone) to oxidize and solubilize impurities. Thus, an oxidative treatment for liquid-phase purification of diamonds in an autoclave at increased temperature (215–250°C) and pressure under the action of MW radiation was patented: in the first stage—with mixture of nitric acid and hydrogen peroxide, in the second stage—with mixture of concentrated nitric, hydrochloric and hydrofluoric acids.[99] Milder ND-purification conditions were also reported, for instance adsorption onto a diamond nanoparticle from a bath of 10–100 g·L^{-1} $(NH_4)_2Ce(NO_3)_6$ or $(NH_4)_2Ce(SO_4)_3$ solution at 30–70°C for 24–48 h, washing with 1.5 vol.% H_2SO_4 3–5 times, washing with water, and vacuum drying at 100–120°C for 12–24 h.[100] A reported gas-phase technique for ND purification and modification consisted in passing a gas mixture, in the form of a dried air and/or oxygen and/or ozone at a pressure up to 0.8 MPa, through an initial material, in simultaneously heating it from 20°C to 550°C.[101] Valuable information on various techniques for diamond purification was critically analyzed and reviewed by Lin et al.[102]

TECHNIQUES APPLIED TO STUDY STRUCTURAL AND ELECTRONIC PROPERTIES OF NANODIAMONDS

In order to study the structure of formed carbon allotropes, in particular the NDs, classic methods, usually used in materials characterization, were applied. Thus, magnetic resonance techniques (EPR and solid state NMR[103]) as powerful non-destructive tools for studying electron-nuclear and crystalline structure, inherent electronic and magnetic properties and transformations in carbon-based nanomaterials, in particular NDs, were reviewed by Shames et al.[104] EPR allows control purity of ultradispersed diamond (UDD) samples, to study the origin, location and spin-lattice relaxation of radical-type carbon-inherited paramagnetic centers, among other possibilities, meanwhile solid state NMR provide information on the crystalline quality, allows quantum estimation of the number of different allotropic forms, and reveals electron-nuclear interactions within the UDD samples under study. Raman spectroscopy of amorphous, nanostructured, diamond-like carbon and ND was reviewed by Ferrari et al.[105] This method was useful in determination of sp^2 carbon phases in nanocrystalline diamond films.[106] Additionally, ND formation and its *in-situ* Raman spectroscopy under the conditions of high static pressures and high temperatures were studied using carbon of different isotopic compounds in the K_2O-Na_2O-Al_2O_3-SiO_2 system and the presence of $NaAlSi_2O_6$, low-melting $K_2Si_2O_5$, and Na_2SiO_3.[107]

The sp^2/sp^3 bonding concentrations of nitrogen-doped amorphous carbon samples and ND films were determined from their soft X-ray absorption spectra.[108] The ND films were synthesized on silicon substrates in a CH_4/H_2 gas mixture by MWCVD. It was shown that ND deposition conditions, such as bias voltage and methane concentration, affect the purity of the film. The stress evolution in NCD films deposited at different temperatures (from 800 to 400°C) was investigated,[109] showing that the intrinsic stress gradually changed from tensile to compressive with decreasing deposition temperature. A comparison study of hydrogen incorporation among nano-, micro-, and polycrystalline diamond films grown by MWCVD was performed by Tang et al.[110] indicating from polycrystalline to NCD film, hydrogen impurity content increases drastically with decrease of grain size. It was suggested that hydrogen incorporated not only into grain boundaries but also into other structural defects of CVD diamond. The electric conductivity and sedimentation stability of aqueous dispersions of ND agglomerates were studied by Koroleva et al.[111] The sedimentation kinetic curves showed two sections of fast and slow sedimentation. Consequences of strong and diverse electrostatic potential fields on the surface of detonation ND particles were reported by Osawa et al.[112] DNDs were also studied by time-of-flight mass spectrometry (TOF MS)[113] showing the formation of singly charged C clusters, C_n^+, with groups of clusters at $n = 1–35$, $n \sim 160–400$, and clusters with $n \sim 8000$. It was established that high C clusters consisted of an even number of carbons while the percentage of odd-numbered clusters is quite low ($\sim$5–10%).

Structural and electronic properties of isolated NDs were reviewed by Raty et al.[114] Using *ab-intio* calculations, it was shown that in the size range of 2–5 nm ND (so-called bucky-diamond) has a fullerene-like surface and, unlike silicon and germanium, exhibits very weak quantum confinement effects. Ultrafast photoluminescence of NCD membranes and films on Si and fused SiO_2 glass, prepared by MWCVD, measured by femtosecond upconversion technique was reported by Preclikova et al.[115] It was established that the photoluminescence dynamics were affected by temperature and ambient pressure. Additionally to the generalized report on the ND surface chemistry,[116] detailed structural investigations of patterned NCD submicrometer-tip arrays, synthesized by conformal coating of the SiO_2 nanowires with 5–10 nm sized ND grains by MWCVD, were carried out by high resolution transmission electron microscopy.[117] Electron field emission of ND emitter arrays was observed with a threshold field of 5.5 V/μm. The structural and chemical analysis of the soot particles produced in a bell jar reactor under $Ar/H_2/CH_4$ microwave discharges employed for NCD film synthesis was reported by Aggadi et al.,[118] showing that the soot was mainly composed of polyhedral graphite particles of roughly 100 nm in size and of smaller particles of the same carbon structure, embedded in graphite crumpled sheets. Chemical bonding study of NCD films prepared by various plasma techniques (MPWCVD and hybrid pulsed laser deposition (HPLD)) were carried out by Popov et al.[119] In case of HPLD samples, the formation of NCD was enhanced by lower working pressures and RF powers; no such influence of the deposition conditions on the bonding structure was observed for the MWCVD films.

SOME PHYSICAL PROPERTIES OF NANODIAMONDS

Stability of NDs was reviewed by Barnard,[120] in particular such aspects as theoretical and computational studies on the relative stability of carbon nanoparticles, phase transitions between ND and graphitic and fullerenic forms of nano-C, coexistence of bucky-diamond and other nano-C phases, stability of diamond nanowires, simulation of transitions of NDs, etc. It was distinguished between the stability of large (5–6 nm) and small (<2.5 nm) particles of nano-C. In an interesting report,[121] the stability of NDs with sizes less or more 4 nm was studied by X-ray coherent scattering areas (CSA) and of sample specific surfaces. Authors supposed that small ND particles exhibited higher activity when interacted with oxygen and "burned out", caused by the heat effect of the carbon oxidation with oxygen (reactions 2–3). As a result of detailed study of ND oxidation with water (Figure 3), it was established that it was impossible to produce NDs with particles of size below 4 nm using the oxidation processes. It was concluded that there is a critical size of the stability of ND particles, namely, about 4 nm. A ND cluster having a size below the critical one becomes unstable and rapidly oxidizes in air or transforms into a particle with graphite-like structure. Additionally, in ND crystallites, exposed to extreme UV radiation, the surface H groups and graphite species were found to prevent graphitization, whose radiation-induced mechanism was discussed, as well as other effects influencing on the stability of ND in radiation conditions.[122]

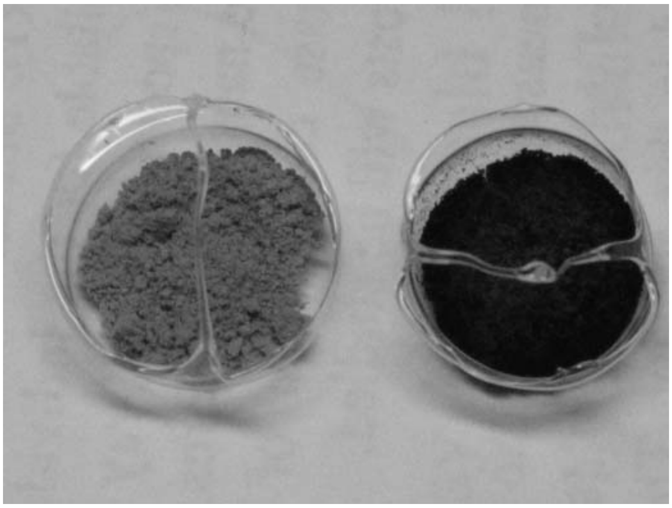


FIG. 3. Initial (left) and oxidized (right) NDs.

$$C + O_2 = CO_2 + 384 \text{ kJ / mol} \quad [2]$$

$$C + 1/2O_2 = CO + 113 \text{ kJ / mol} \quad [3]$$

Nitrogen is a common *impurity* in the crystal of diamond and also one of the predominant elements to affect diamond performance;[123] nitrogen impurity location, related to the luminescent properties of DND, was detected in several detonation DND samples using a combination of TEM techniques,[124] showing that the size and morphology of DND can be modified by temperature treatment. It was suggested[125] on the basis of spectral data and elemental analysis that nitrogen can be mainly in the form of impurity N-centers of different kind inside diamond core of ND particle. Among other impurities in diamonds and NDs, several elements were found in the combustion residues, such as Fe, Ni, Ca, Al, Si, S, Cl, K, Na, Ti, and Mg.[126] It was observed that metal impurities more easily enter into the diamonds, especially Fe-Ni alloy. Non-uniform distribution of impurities in the diamond crystal, especially in the surface region, was the main reason for strength variation in the samples.[127] Additionally, the behavior and influence of cobalt,[128] boron,[129] beryllium and magnesium,[130] and other dopants on diamond and ND properties and reactivity were studied.

Discussing the *solubility* of NDs, it is necessary to mention that bad dispersibility is a major cause that hinders the application of ND severely. In this respect, the techniques allowing increase ND solubility for medical and other applications are being intensively developed. Thus, the method producing a dispersion of a ND particles (clusters having a primary particle diameter of 3–5 nm and produced by a shock compaction method under a H_2 atmosphere at 300–800°C) in organic solvents by disaggregating an aggregate of the diamond particles was proposed by Sakai et al.[131] The formed dispersions did not cause aggregation or precipitation even after six months, and maintains its stable dispersion state. Covalent functionalization of ND, leading to an increased solubility, was carried out by employing several methods,[132] involving, for example, the reaction of acid-treated ND with thionyl chloride followed by reaction with a long-chain aliphatic amine to produce the amide derivative. The products of functionalization produced excellent dispersions in CCl_4 and toluene. By interaction of ND with surfactants such as, for instance, sodium bis(2-ethylhexyl) sulfosuccinate, gives good dispersions in water. Other functionalization techniques resulting enhanced solubility/dispersibility are presented below.

Growth of NDs has been intensively studied as in whole as mechanism of its each steps including the pretreatment of precursors before the reaction and nucleation. Thus, effects of pretreatment on the nuclei formation of UNCD on Si substrates were studied.[133] Either precoating a thin layer of titanium (∼400 nm) or ultrasonication pretreatment using diamond and titanium mixed powder enhanced the nucleation process on Si substrates markedly. Nucleation, growth and low temperature synthesis of diamond thin films were reviewed by Das et al.[134] The important parameters responsible for enhancing the nucleation and growth rates of diamond film were identified and the growth of diamond thin films at low temperatures were discussed.

Various supports/substrates were investigated in respect of diamond nucleation. Thus, studies of diamond nucleation and growth on conical carbon tubular structures showed that the nucleation preferentially occurs at the tips, but only occurs on the sidewalls when they are pretreated with diamond or other powder dispersions, forming a ND coating.[135] It was revealed that the diamond nucleation on the sidewalls may proceed through the formation of diamond nuclei within the walls at subsurface damage sites caused during pretreatment. MWPCVD was used to deposit smooth NCD film on pure titanium substrate using Ar, CH_4, and H_2 gases at moderate deposition.[136] The exceptional adhesion of 2 μm-thick diamond film to the metal substrate was observed by indentation testing ≤150 kg load. This type of materials could be used for aerospace and biomedical applications, avoiding the problem of the different thermal expansion coefficients of thin ND and titanium and its metallic alloys.[137] Nanocomposite films consisting of diamond nanoparticles of 3–5 nm diameter embedded in an amorphous carbon matrix were deposited by means of MWCVD from CH_4/N_2 gas mixtures[138] on different substrates (some of them were pretreated ultrasonically) such as Si wafers, Si coated with TiN, polycrystalline diamond (PCD) and cubic boron nitride films, and Ti-6Al-4V alloy. The growth process seemed to be not affected by the substrate material and the crystallinity and the bonding environment showed no significant differences for the various substrates. A route to high-purity NCD films from C_2 dimers and related mechanisms was investigated[139] by enhancing C_2 growth chemistry in Ar-rich microwave plasmas. C_2 grows ND on diamond surfaces but rarely initiates nucleation on foreign surfaces. The phase purity can be improved by increasing the dominance of ND growth from C_2 over non-diamond growth from CH_x ($x = 0$–3) and large radicals. It was found that growth of ND thin films from hydrocarbon/Ar-rich plasmas was very sensitive to the contribution of C_2 and C_2H species from the plasma.[140] Among other growth studies, the effect of total pressure on growth rate and quality of diamond films prepared by MWCVD was investigated by Li et al.[141] showing that when the total pressure changed from $1.03 \cdot 10^4$ to $1.68 \cdot 10^4$ Pa the growth rate increased from 3 to 16 μm/h. Under a gas pressure lower than that used for growth, a high nucleation density of diamond films on alumina, as high as 10^8/cm^2, and creation of [100]-textured diamond films deposited on alumina was successfully achieved by MWCVD at 800–860°C.[142] NCD films are promising candidates for tribological applications, in particular when deposited on hard ceramic materials such as silicon nitride (Si_3N_4). Thus, MWCVD deposition of NCD was achieved using Ar/H_2/CH_4 gas mixtures on plates and ball-shaped Si_3N_4 specimens either by a conventional continuous mode.[143]

CHEMICAL PROPERTIES AND FUNCTIONALIZATION OF NANODIAMONDS

The structure, solubility, and electronic/magnetic properties of ND vary depending on how the surface carbon atoms are terminated.[144] So, its functionalization with active *biomolecules* is attractive for possible medical applications, among many others. In this relation, different approaches to the surface functionalization of ND, i.e., the key in successful biomedical applications (in particular, biosensing), as well as modification of diamond surfaces with nucleic acids and proteins, were reviewed by Grichko et al.[145] Linear pUC19 molecules with blunt ends, prepared by restriction of the initial ring form of pUC19 DNA, and linear 0.25–10 kb DNA fragments were found to be adsorbed on NDs.[146] The amount of adsorbed linear DNA molecules depended on the size of the molecules and the size of the ND clusters. Size separation (important for passive targeting such as EPR effect in tumor imaging) of ND particles (4 to 25 nm) by use of ultracentrifugation and synthesis of fluorescent ND through the surface chemical modifications for adding requisite functions to NDs such as dispersibility and visibility were reported by Komatsu.[147]

Functionalization of ND with *non-biological organic molecules* includes use of, in particular, amine derivatives, whose attachment leaded to enhanced ND solubility. Thus, ND was covalently functionalized with 1,3-propanediamine to obtain a novel derivative (ND-NH_2) with 29.97% of ND, in which the 1,3-propanediamine molecules were covalently attached to the NDs through amide linkages.[148] This compound dissolves not only in inorganic or organic acidic aqueous solutions, but also in organic solvents such as acetone, CH_2Cl_2, NMP, DMF, DMAc and DMSO; this might be a beneficial base for next study and application of ND in fields of complex electroplating and lubrication. A radio-frequency plasma discharge in vaporized silane coupling agent N-(6-aminohexyl) aminopropyl trimethoxysilane was applied to successfully functionalize the NCD surface with the primary amino group NH_2 as confirmed by using fluorescamine-in-acetone spray as a fluorescence marker.[149] Hydrophobic blue fluorescent ND, easily dispersible in hydrophobic solvents and forming a transparent colloidal solution, was synthesized by covalent linking of octadecylamine (ODA) to the surface of ND particles (reaction 4).[150] This material can be used in those applications where stable dispersions of ND in fuels, polymers or oils are required. Due to the long hydrocarbon chains linked to its surface, the ND-ODA can be easily dispersed in hydrophobic solvents such as benzene, toluene, chloroform, dichloromethane, etc. (Figure 4). At the same time, it is immiscible with water and poorly miscible with polar hydrophilic organic solvents such as DMF, ethanol, methanol, and acetone.

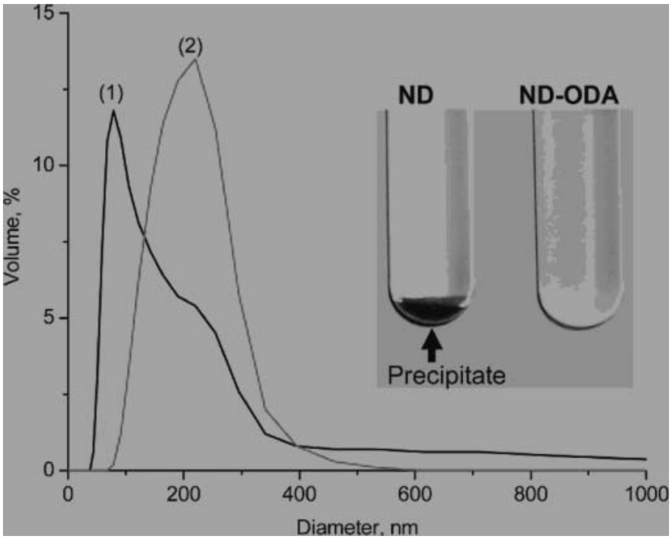
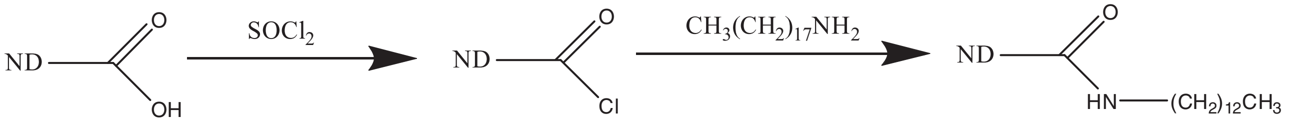


FIG. 4. Particle size of ND-ODA in toluene (1) and chloroform (2); photograph of 0.01% wt. suspensions of ND and ND-ODA in toluene.



(4)

A general procedure to functionalize agglomerating nanoparticles demonstrated on ND was examined by Liang et al.,[151] who reported a new technique to facilitate surface chemistry of nanoparticles in a conventional glassware system offering a beads-assisted sonication (BASD) process to break up persistent agglomerates of NDs in two different reactions (silanization with an acrylate-modified silane (Figure 5a) and the arylation using diazonium salts (Figure 5b) for simultaneous surface functionalization. This allowed for the efficient grafting of aryl groups to the surface of primary diamond nanoparticles yielding stable, homogeneously functionalized ND particles in colloidal solution. Even in media where the original particles were flocculating, an efficient functionalization took place. The latter led to truly dispersed primary nanoparticles with a homogeneous surface termination. In a related work, functionalization of ND particles with aryl organics using Suzuki coupling reactions was demonstrated by Yeap et al.[152] derivatizing hydrogenated ND with aryl diazonium or with boronic acid groups followed by Suzuki cross coupling with arenediazonium tetrafluoroborate salts, in particular in a capillary microreactor (Figure 6). These reactions have general validity to a wide range of organic dyes that have boronic acid or halide functional groups. The dispersion of the ND in organic solvent can be thus improved by coupling hydrophobic aryl groups.

Among classic works on *"inorganic" functionalization* of ND,[153] at least at the first step, we note a suggested technology of ND surface modification,[154] which allowed separation of commercial ND powders into two fractions (differing in size characteristics), each possessing absolutely new properties as compared to the initial powder. Physical and chemical properties of these modified NDs were studied. Analysis of structural and chemical impurities in NDs, polyfunctional surface termination,

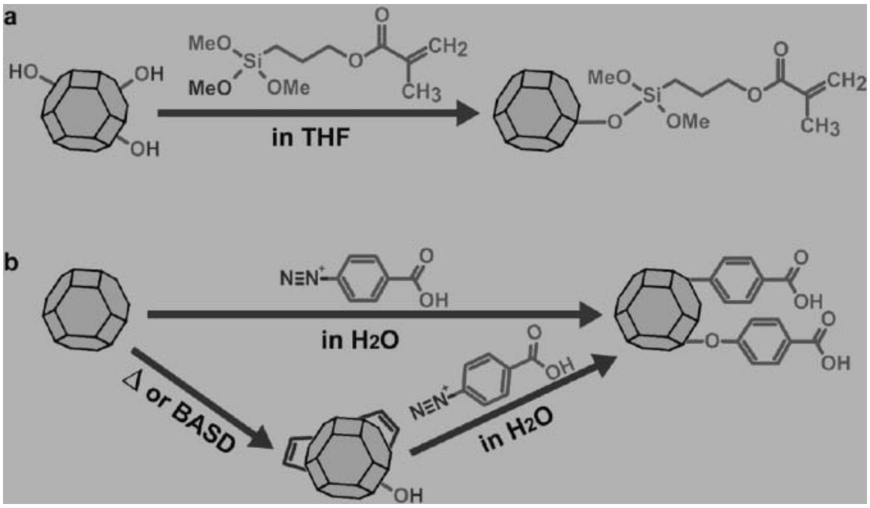


FIG. 5. Surface functionalization of ND. (a) Silanization of ND surfaces. (b) Arylation of NDs by applying aromatic diazonium salts.

agglomeration, and other features that may restrict the ND application in academic research and industrial practice were reviewed by Spitsyn et al.,[155] as well as ND purification and surface functionalization, using a high temperature treatment in gaseous media containing hydrogen and chlorine. The methods for the covalent functionalization of nano size (∼2–10 nm) diamond powders, as well as CNTs, were reviewed by Khabashesku et al.[156] The described methods involved direct fluorination, organic free radical additions, fluorine displacement reactions in fluoro-nanotubes, and fluoro-ND producing amino, hydroxyl, and carboxyl group-terminated derivatives.[157] Thus, the reaction of nanoscale diamond powder with an elemental fluorine/hydrogen mixture at 150–470°C resulted of ND surface fluorination yielding a fluoro-ND with up to 8.6 at. % fluorine content,[158−160] used as a precursor for preparation of the series of functionalized NDs by subsequent reactions with alkyllithium reagents, diamines, and amino acids (Scheme 1), as well as a starting material for the diamond coating on modified glass surface (Figure 7). All functionalized NDs showed an improved solubility in polar organic solvents, for instance alcohols and THF, and a reduced particle agglomeration. The developed method can be extended to ND coating of various substrates, such as quartz, silicon, metals, and other materials.

Additionally to the functionalization reactions above, *graphitization* processes of diamond with emphasis on the low temperature graphitization at 1370–1870 K were described and reviewed by Kunzetsov et al.[161] Some nanocarbons (such

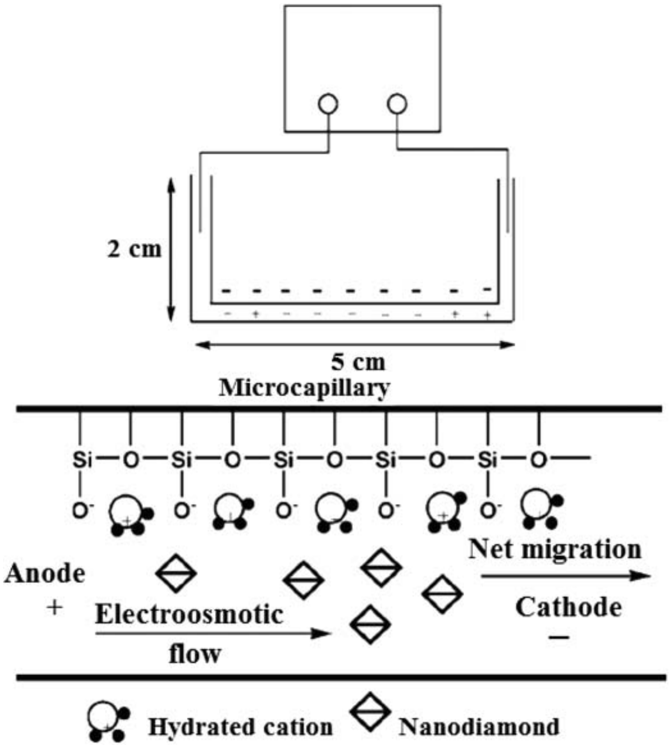


FIG. 6. (Top) Glass microcapillary reactor for Suzuki coupling, (bottom) Schematic showing electroosmotic flow in the glass microcapillary.

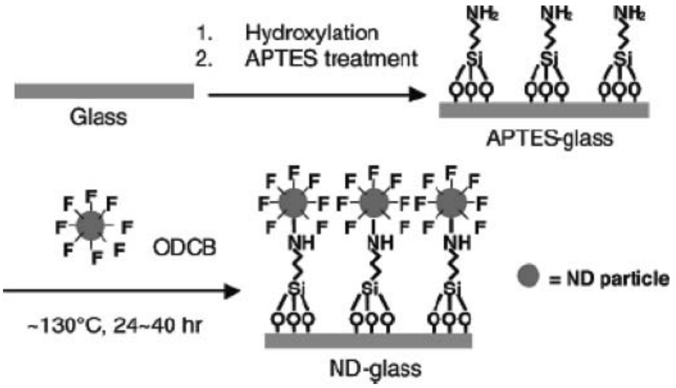
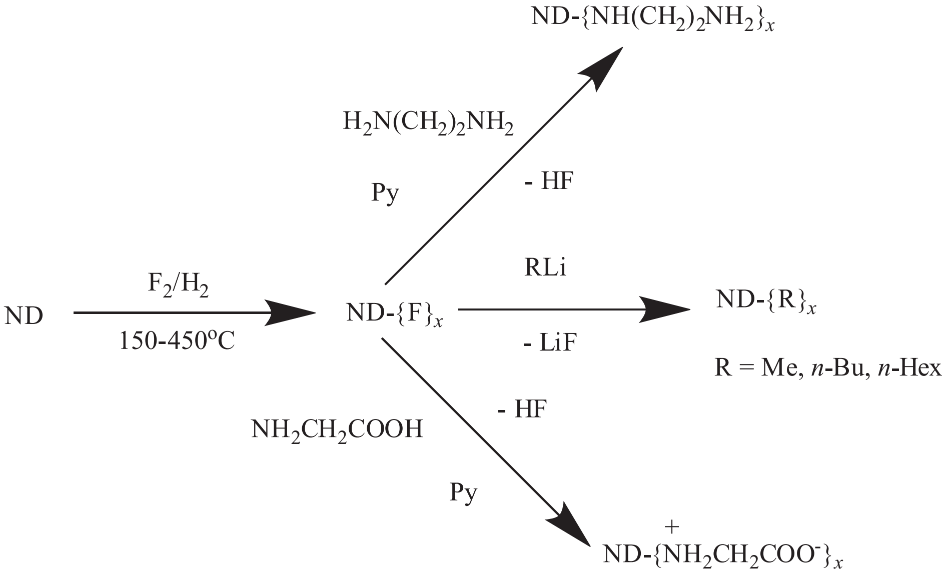


FIG. 7. Reaction steps for coating glass with fluoro-ND. APTES is 3-aminopropyltriethoxysilane, ODCB is 1,2-dichlorobenzene.



SCH. 1. Fluorination and further functionalization of ND with amines and amino acids.

as onion-like carbon (OLC), sp^2/sp^3 nanocomposites, and nanographite) can be thus produced using controlled ND graphitization. A theoretical analysis of the graphitization of a ND in the metastable state was reported by Kwon et al.[162] A ND annealed at a relatively lower temperature suffers morphological transition into a ND-graphite core-shell structure. It was established that the ND was not completely transformed into graphite by simple annealing at relatively lower process temperature and pressure and the highest graphitization probability decreased with increasing annealing temperature. However, according to Leyssale's data[163], the annealing of a small ND cluster at 1500 K, as studied by molecular dynamics, led to an almost fully graphitized carbon onion. The remaining 17% of sp^3 atoms were delocalized on the whole particle, both under the form of isolated point defects and of small diamond-like clusters separating large graphite-like domains. This is in accordance with the results of similar investigations, where it was found that the diamond nanoparticles begin to graphitize in the range of 1100–1200°C and all the particles transform into onion-like carbons at 1400°C.[164] Other aspects of graphitization have also been discussed,[165–167] in particular ND graphitization in conditions of laser ablation[168] or stimulated by electron-hole recombination.[169]

NANODIAMOND FILMS AND COMPOSITE MATERIALS

ND films, methods and mechanisms of their formation have been extensively covered. Thus, ND films deposited by energetic species using the direct-current glow-discharge (DC-GD) deposition technique were reviewed by Hoffman et al.[170,171] ND film and growth was explained as a sub-surface process in terms of a four step cyclic process. ND films with a large area, low stress and smooth surface were deposited on mirror-polished Si wafers under continuous ion bombardment by a hot-filament CVD (HFCVD) chamber equipped with a substrate bias system.[172] The size of diamond clusters in the film can be controlled by a suitable selection of deposition parameters such as the ratio of CH_4 to H_2. To verify a statement, that ion bombardment is the main mechanism in the bias-enhanced-nucleation process during the initial stage of diamond film growth by CVD, mass-separated ion-beam deposition experiments were carried out, in which a pure C ion beam, with precisely defined low energy, was selected for investigating the ion-bombardment effect on a Si substrate.[173] The obtained results supported the ion-bombardment-enhanced-nucleation mechanism. NCD films were found to be good support for adhesion, growth and differentiation of osteogenic cells and could be used for surface modification of bone implants to improve their integration with the surrounding bone tissue.[174]

Such substrates as carbides or silicon were used as supports for ND depositation by MPCVD techniques. Thus, the diamond coating containing elemental Si was deposited on a cemented carbide substrate with use of H_2, CH_4 and octamethyl cyclotetrasiloxane (D4) as precursors by MWCVD.[175] The results revealed that when the flow of D4 was larger than that of CH_4, the cellular structure was obtained, and the diamond-coating with good quality and good adhesion was deposited with a little Si only when the flow of D4 was equivalent to that of CH_4. NCD thin films (grain size 10–20 nm) were grown on silicon substrates at 480°C using methanol and hydrogen mixtures in MPCVD conditions.[176] The high quality NCD film could be deposited on a 50 mm diameter Si substrate by increasing the methanol concentration and reducing the deposition temperature. NCD films are highly strained materials, in general.[177] Unstrained failure-resistant NCD films were obtained by performing bias-enhanced nucleation in a MWCVD system followed by NCD deposition in a hot-filament CVD system. Simple method for synthesizing diamond nanofilm with MW plasma at low temperature, patented by Zhou et al.,[178] included the steps of a) introducing argon and hydrogen to a microwave plasma synthesis chamber, b) ionizing at 600–750 W and 900–1,100 Pa to obtain plasma, and c) standing till the plasma is stable, and introducing methane to precipitate diamond nanofilm.

A grand variety of composite materials has been manufactured on the ND basis and *polymers* in order to improve properties of polymer matrixes. Thus, an efficient method was developed to achieve improved dispersion of detonation ND particles in amorphous thermoplastic matrices. It was found that the reinforcing and toughening effects of uniformly-dispersed nanoparticles on polymer matrixes was pronounced at lower loading compared with traditional mixing procedure.[179] Transparent heat-resistant polymer-ND composites were obtained by Sawaguchi et al.[180] by dispersing ND in a polymerization solvent at the stage of polymerization reaction. Binary combinations of ND, few-layer graphene, and single-walled nanotubes were used to reinforce polyvinyl alcohol.[181] The mechanical properties of the resulting composites showed extraordinary synergy, improving the stiffness and hardness by as much as 400% compared to those obtained with single nanocarbon reinforcements. The effects of modifying additives of nanodispersed substances on rheological and relaxation properties of polymer-ND composite materials based on polydimethylsiloxane,[182] polyurethanes, nitrile rubber, and polycarbonates[183] were established. Effective method for introduction of dispersed filler particles of detonation ND into a polymeric matrix, based on disaggregation and uniform deposition of the filler onto the surface of polymeric particles in an inert liquid medium under the action of ultrasound, was developed.[184] Among other similar composites, preparation and application of fluoroalkyl-containing oligomer-ND composites was reported.[185]

Inorganic-based diamond and ND composites, generally leading to hard carbide- or nitride-containing coatings, are also known. Thus, ultrahard multilayer coating was composed of two chemically different layered nanocrystalline materials, ND and nano-cubic boron nitride (nano-cBN).[186] Nano-cBN layers were directly grown on ND crystallites using ion-assisted physical vapor deposition and ion-assisted plasma enhanced CVD (PECVD), again followed by ND deposition using CVD methods in cycles until the intended number of layers of the final composite was obtained. The obtained multilayer structure possessed extreme hardness (82 GPa), high surface smoothness, significantly reduced film stress compared with a single cBN layer of equivalent thickness, and great chemical stability.[187] A study of MPCVD diamond deposition on Si_3N_4-TiN composites with different TiN amounts (0–30 vol.% TiN) was performed[188] in order to obtain a suitable material to be cut by electrodischarge machining, aiming their use as substrates for cutting tools and tribological components. Composite thin films of ND and silica nanotubes were synthesized by means of MPCVD on silica nanotube matrix that was seeded with ND particles.[189] ND grew around silica nanotubes and filled the space left between silica nanotubes to form a continuous film. In a related work, fabrication of high density NCD-coated silica nanofibers with diameters of 1–5 μm was reported by a template technique,[190] consisting of the preparation of templates (SiO_2 nanofibers) by conventional vapor-liquid-solid method and the conformal coating of the nanofibers with ND by MWCVD technique in hydrogen-deficient conditions. A composite with hardness over 55 GPa is obtained by cobalt infiltration (min. 6 vol. %) into a ND at a pressure of 8 GPa.[191] In the presence of cobalt, graphite-like carbon was inversely transformed into diamond with a slight time delay. The hybrid diamond-graphite nanowires, consisting of a single crystalline diamond core of 5–6 nm in diameter oriented along the [110] principal axis and graphite shells of different thickness covering the core, with lengths up to a few hundred nanometers were identified as structural units in UNCD films synthesized by CVD with nitrogen gas added.[192]

Water-soluble (2-1 g/L) magnetic NDs (Figure 8) were prepared *via* solid-state microwave arcing of a ND-ferrocene mixed powder in a focused microwave oven.[193] It was shown that a magnetic nanodiamond (MND) was composed of iron nanoparticles encapsulated by graphene layers on the surface of NDs, had a saturation magnetization of ∼10 emu/g and a coercivity field 155 G, and via covalent surface grafting of organic fluorescent molecules can be converted to fluorescent MNDs (FMNDs), whose color of fluorescence was readily tunable depending on the polymerizable fluorescent monomer used in the surface grafting process. The FMNDs had an aqueous solubility of ∼2.1 g/L and were collectible with an external magnet, which is important in many biomedical applications. The authors stated that these NDs could serve as biocompatible cargos to transport various biologically active species, such as proteins, DNA, signal-transduction molecules, and drugs, into cells for various biomedical investigation or treatment of diseases. Also, ND composites were produced, in particular, in low-pressure microwave gas-discharge plasma,[194] laser-induced phase transition (ND on cast alloy A319),[195] or by the incorporation of ND into plated films,[196] among other techniques.[197–199]

APPLICATIONS

NDs have got a series of distinct applications in various areas, in particular medicine, electrochemistry and creation of novel materials. Thus, the sensing film for the gas sensor on the ND basis was prepared by coating semiconductor particles mixtures on a substrate and making semiconductor particles adsorb onto a metal film.[200] Nitrogen-incorporated ND electrodes were fabricated using MWCVD by N_2 incorporation achieved by the introduction of N_2 along with H_2 and CH_4 in the plasma[201] and used to study the detection of dopamine showing excellent electrochemical response. The electrochemical response of an electrode-immobilized layer of undoped, insulating diamond

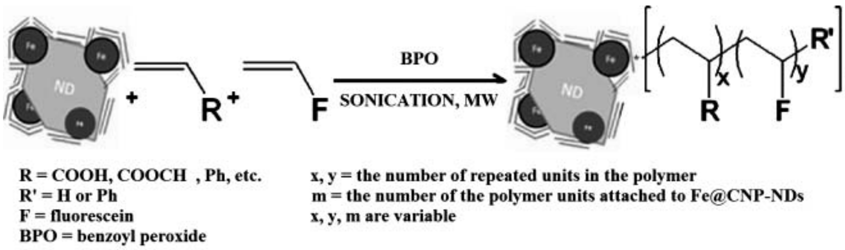


FIG. 8. Schematic process for surface functionalization of magnetic NDs.

nanoparticles was attributed to the oxidation and reduction of surface states.[202] It was established that the potentials of these surface states were pH-dependent and able to interact with solution redox species. Another electrochemistry-related achievement was the method for galvanic deposition of NDs-based coating compound by introduction of aqueous suspension of NDs into solution of electrolyte to initiate coating sedimentation by electrolysis was offered to improve wear resistance of metal surfaces.[203] ND applications in the production of composite electrolytic coatings on the basis of Cr, Ni, Au, and Ag, exhibited good service properties, and save on the use of noble metals and electrical power were exemplified,[204] as well as ND applications for the modification of plastics, antifriction lubricants, and oxide coatings grown by microarc oxidation of aluminum alloys.

The normal-temperature glass was prepared by acid- or alkali-hydrolyzing and dehydrocondensing an aqueous and/or alcohol solution of ND-dispersed metal alkoxide, applying on a substrate, and drying at ≤200°C.[205] This glass gave a film with good deodorization and antibacterial effect owing to ND and can be applied on the substrate with any surface. The method of obtaining polyfunctional ND sorbent for sorption and chromatographical separation, in particular of protein molecules, was offered including processing of polysaccharide matrix, which was first cleaned from preservatives with distillate water, and than processed with 0.5–10.0 wt % ND hydrosol.[206] The possibilities of applying of DND in untraditional areas were emphasized,[207] in particular their prospective use as polyfunctional adsorbents for purification of the proteins and enterosorbent and compound carrier applied for medical purposes. Protection of documents, valuable papers and products with diamond nanocrystals with active nitrogen-vacancy center by application or insertion of a special fluorescent mark on the protected document was offered by Zibrov et al.[208] ND was offered as a new type of lubricating additive due to its double performances of both diamond and nano-material.[209] The key problem was the surface modification of ND aggregates to achieve the deaggregation and stable dispersion of ND in the oil. As an example of composition for such a lubricant, the friction material was manufactured from nanometer diamond 1.2–14%, bronze powder 2–25%, rare earth oxides or fluorides, among others, 1–50%, and polytetrafluoroethylene to 100%.[210] Among other non-medical ND applications, we note its use as an additive for photocurable composite resin matrix, whose main filler was barium glass,[211] and as a reducing agent in energetic chlorate-based compounds.[212]

Biomedical applications of NDs are well-developed and related with the recently established fact that carbon NDs are much more biocompatible than most other carbon nanomaterials, including carbon blacks, fullerenes and carbon nanotubes.[213] Their tiny size, large surface area and ease functionalization with biomolecules, makes NDs attractive for various biomedical applications both *in vitro* and *in vivo*, for instance for single particle imaging in cells, drug delivery, protein separation and biosensing. Some radiation-damaged NDs can emit strong and stable photoluminescence (red or green) from nitrogen-vacancy defect centers embedded in the crystal lattice.[214] Specific use of NDs in both non-conjugated and conjugated forms as enterosorbents or solid phase carriers for small molecules including lysozyme, vaccines, and drugs was reviewed.[215]

Among a series of biomedical applications of NDs, we note direct observation of growth hormone receptor in one single cancer cell using ND-growth hormone complex as a specific probe, reported by Cheng et al.[216] The growing hormone molecules were covalently conjugated to 100 nm diameter carboxylated NDs, which can be recognized specifically by the growth hormone receptors of A549 cell. Bovine insulin was non-covalently bound to detonated NDs via physycal adsorption in an aqueous solution and demonstrated pH-dependent desorption of sodium hydroxide.[217] NDs combined with insulin at a 4:1 ratio showed 79.8±4.3% adsorption and 31.3±1.6% desorption in pH-neutral and alkaline solutions, respectively. The location and distribution of 100 nm carboxylated ND particles in cell division and differentiation was investigated by Liu et al.[218] ND's clusters were carried inside of cell but without inducing damages after long-term cell culture. Endocytic ND particles were found to be non-cytotoxic in cell division and differentiation, which can be applied for the labeling and tracking of cancer and stem cells. A platform approach of water-dispersible, ND cluster-mediated interactions with several therapeutics (Purvalanol A and 4-hydroxytamoxifen) to enhance their suspension in water with preserved functionality was demonstrated by Chen et al.[219] This approach served as a facile, broadly impacting and significant route to translate water-insoluble compounds toward treatment-relevant scenarios. For diamond nanoparticles used as fluorescent labels in cells,[220] the photoluminescence of a single color center embedded in a 30 nm diameter ND was compared to that to a single dye molecule and demonstrated the perfect photostability of the color centers. Optimal parameters to achieve a high fluorescence yield were determined.

CONCLUSIONS

Despite the fact that the diamond in its nanoforms is known during several decades, it continues being of an interest for researchers working in materials chemistry, biology, and medicine. As one of numerous carbon allotropic forms, which is much more biocompatible with human organism in comparison with others, the NDs, functionalized with biomolecules, have got a series of useful applications for drug delivery and as fluorescent labels in cells. Additionally, use of NDs for reinforcing polymers and creation of ultrahard composites are attractive for industrial applications. The functionalization capacity of NDs, as well as that of such other carbon forms as graphene,[221] fullerenes[222,223] or carbon nanotubes,[224] is very rich and, undoubtedly, subject to rapid progress in near future.

REFERENCES

1. Danilenko, V.V. On the history of the discovery of nanodiamond synthesis. *Physics of the Solid State* **2004**, 46(4), 595–599.
2. Shenderova, O.A., Zhirnov, V.V., and Brenner, D. W. Carbon nanostructures. *Critical Reviews in Solid State and Materials Sciences* **2002**, 27(3–4), 227–356.
3. Williams, O.A., Nesladek, M., Daenen, M., Michaelson, S., Hoffman, A., Osawa, E., Haenen, K., and Jackman, R.B. Growth, electronic properties and applications of nanodiamond. *Diamond and Related Materials* **2008**, 17(7–10), 1080–1088.
4. *IUPAC Gold Book*. Diamond-like carbon films. http://www.iupac.org/goldbook/D01673.pdf. Accessed December 4, 2009.
5. Huss, G.R. Meteoritic nanodiamonds: messengers from the stars. *Elements* **2005**, 1(2), 97–100.
6. Jones, A.P., and d'Hendecourt, L.B. Interstellar nanodiamonds. *Astronomical Society of the Pacific Conference Series* **2004**, 309, 589–601.
7. Khan, Z.H., and Husain, M. Nanodiamond: synthesis, transport property, field emission and applications. *Material Science Research India* **2006**, 3(1a), 1–22.
8. Tanaka, A. Tribology of carbon composites. *Toraiborojisuto* **2009**, 54(1), 16–21.
9. Hu, X.,Li, M., Sun, Z., Wang, Q.,Fan, D., and Chen, L. Research status and prospection of synthetic nanodiamonds. *Guanli Gongchengban* **2009**, 31(2), 301–304, 317.
10. Osawa, E. Nano carbon materials. Fullerenes and diamond. *Seramikkusu* **2004**, 39(11), 892–909.
11. Quiroz Alfaro, M.A., Martinez Huitle, U.A., and Martinez Huitle, C.A. Nanodiamantes. *Ingenierias* **2006**, IX(33), 37–43.
12. Freitas Jr., R.A. A Simple Tool for Positional Diamond Mechanosynthesis, and its Method of Manufacture. http://www.MolecularAssembler.com/Papers/DMSToolbuildProvPat.htm. **2003–2004**.
13. Freitas Jr., R.A. How To Make a Nanodiamond. http://www.kurzweilai.net/articles/art0632.html?printable = 1. **2006**.
14. Doan, H. *Nanodiamonds: Applications in Biology and Nanoscale Medicine*. Springer **2009**, 380 pp.
15. Shenderova, O.A., and Dieter M. Haber. *Ultrananocrystalline Diamond: Synthesis, Properties, and Applications*. William Andrew **2007**, 620 pp.
16. Tjong, S.C. Properties of chemical vapor deposited nanocrystalline diamond and nanodiamond/amorphous carbon composite films. *Nanocomposite Thin Films and Coatings* **2007**, 167–206.
17. Yang, N., Uetsuka, H., Williams, O.A., Osawa, E., Tokuda, N., and Nebel, C.E. Vertically aligned diamond nanowires: Fabrication, characterization, and application for DNA sensing. *Physica Status Solidi A: Applications and Materials Science* **2009**, 206(9), 2048–2056.
18. Kong, X.-L. Nanodiamonds used as a platform for studying noncovalent interaction by MALDI-MS. *Chinese J. Chem.* **2008**, 26(10), 1811–1815.
19. Tang, C.J., Neves, A.J., Gracio, J., Fernandes, A.J.S., and Carmo, M.C. A new chemical path for fabrication of nanocrystalline diamond films. *J. Cryst. Growth* **2008**, 310(2), 261–265.
20. Watanabe, M., and Yusa, H. Introduction of advanced materials laboratory and some topics - from repletion of basic research to development of practical materials. *Materials Integration* **2002**, 15(9), 8–13.
21. Yang, Q., Yang, S., Xiao, C., and Hirose, A. Transformation of carbon nanotubes to diamond in microwave hydrogen plasma. *Mater. Lett.* **2007**, 61(11–12), 2208–2211.
22. Kimura, Y., Kaito, C. Production of nanodiamond from carbon film containing silicon. *J. Cryst. Growth* **2003**, 255(3–4), 282–285.
23. West, J.A., and Kennett, J. Nanodiamonds and diamond-like particles from carbonaceous material. PCT Int. Appl., **2009**, 25 pp. WO 2009094481 A2 20090730 Application: WO 2009-US31731 20090122. Priority: US 2008-62350 20080125. CAN 151:227622 AN 2009:917817.
24. Dolmatov, V.Yu., Veretennikova, M.V., Marchukov, V.A., and Sushchev, V.G. Currently available methods of industrial nanodiamond synthesis. *Physics of the Solid State* **2004**, 46(4), 611–615.
25. Gruen, D.M. Ultrananocrystalline diamond films from fullerene precursors. *Perspectives of Fullerene Nanotechnology* **2002**, 217–222.
26. Korablov, S., Yokosawa, K., Korablov, D., Tohji, K., Yamasaki, N. Hydrothermal formation of diamond from chlorinated organic compounds. *Mater. Lett*. **2006**, 60(25–26), 3041–3044.
27. Chen, Q., Lou, Z., Wang, Q., Chen, C. Recent progress in diamond synthesis. *Wuli* **2005**, 34(3), 199–204.
28. Nickel, K.G., Kraft, T., Gogotsi, Y.G. Hydrothermal synthesis of diamond. *Handbook of Ceramic Hard Materials* **2000**, 1, 374–389.
29. Basavalingu, B., Byrappa, K., and Madhusudan, P. Hydrothermal synthesis of nano-sized crystals of diamond under sub-natural conditions. *J. Geological Society of India* **2007**, 69(3), 665–670.
30. Basavalingu, B., Byrappa, K., Yoshimura, M., Madhusudan, P., and Dayananda, A.S. Hydrothermal synthesis and characterization of micro to nano sized carbon particles. *J. Mater. Sci*. **2006**, 41(5), 1465–1469.
31. Yamasaki, N., Yokosawa, K., Korablov, S., and Tohjt, K. Synthesis of diamond particles under alkaline hydrothermal conditions. *Diffusion and Defect Data–Solid State Data, Pt. B: Solid State Phenomena* **2006**, 114 (High Pressure Technology of Nanomaterials), 271–276.
32. Korablov, S., Yokosawa, K., Korablov, D., Tohji, K., and Yamasaki, N. Hydrothermal formation of diamond from chlorinated organic compounds. *Mater. Lett*. **2006**, 60(25–26), 3041–3044.
33. Wang, Z.-X., Pan, Q.-Y., Hu, J.-G.,Yong, Z.-Z., Hu, Y.-Q., and Zhu, Z.-Y. Synthesis of diamond nanocrystals by double ions (40Ar+,C2H6+) bombardment. *Wuli Xuebao* **2007**, 56(8), 4829–4833.
34. Gouzman, I., Fuchs, O., Lifshitz, Y., Michaelson, Sh., and Hoffman, A. Nanodiamond growth on diamond by energetic plasma bombardment. *Diamond and Related Materials* **2007**, 16(4–7), 762–766.
35. Yao, Y., Liao, M.Y., Wang, Z.G., Lifshitz, Y., and Lee, S.T. Nucleation of diamond by pure carbon ion bombardment - A transmission electron microscopy study. *Appl. Phys. Lett*. **2005**, 87(6), 063103/1–063103/3
36. Yao, Y., Liao, M.Y., Kohler, Th., Frauenheim, Th., Zhang, R.Q., Wang, Z.G., Lifshitz, Y., and Lee, S.T. Diamond nucleation by energetic pure carbon bombardment. *Physical Review B: Condensed Matter and Materials Physics* **2005**, 72(3), 035402/1–035402/5.

37. Yang, G.W., Wang, J.B., Liu, Q.X. Preparation of nano-crystalline diamonds using pulsed laser induced reactive quenching. *J. Phys.-Condens. Mat*. **1998**, 10(35), 7923–7927.
38. Amans, D., Chenus, A.-C., Ledoux, G., Dujardin, C., Reynaud, C., Sublemontier, O., Masenelli-Varlot, K., and Guillois, O. Nanodiamond synthesis by pulsed laser ablation in liquids. *Diamond and Related Materials* **2009**, 18(2–3), 177–180.
39. Yang, G.W. Laser ablation in liquids: applications in synthesis of nanocrystals. *Prog. Mater. Sci.* **2007**, 52, 648–698.
40. Wang, J.B., Zhang, C.Y., Zhong X.L., and Yang G.W. Cubic and hexagonal structures of diamond nanocrystals formed upon pulsed laser induced liquid-solid interfacial reaction. *Chem. Phys. Lett*. **2002**, 361(1–2), 86–90.
41. Wang, J.B., Yang, G.W. Phase transformation between diamond and graphite in preparation of diamonds by pulsed-laser induced liquid-solid interface reaction. *J. Phys.-Condens. Mat*. **1999**, 11(37), 7089–7094.
42. Sun, J., Zhai, Q., Yang, X., Lei, Y., Du, X., and Yang, J. Synthesis of diamond nanopowders from carbon powders by laser bombarding. **2005**, 6 pp. CN 1663909 A 20050907 Patent written in Chinese. Application: CN 2004-10093973 20041220. Priority: CAN 144:152787 AN 2005:1332207.
43. Sun, J., Zhai, Q., Du, H., Jiang, L., Lei, Y., Yang, X., and Du, X. Effects of carbon material structures on the nanodiamond synthesis by laser irradiation. *Nami Jishu Yu Jingmi Gongcheng* **2006**, 4(3), 217–220.
44. Wang, C.X., Liu, P., Cui, H., and Yang, G.W. Nucleation and growth kinetics of nanocrystals formed upon pulsed-laser ablation in liquid. *Appl. Phys. Lett*. **2005**, 87(20), 201913/1-201913/3.
45. Liu, P., Wang, C.,Chen, J.,Xu, N.,Yang, G., Ke, N., and Xu, J. Localized Nanodiamond Crystallization and Field Emission Performance Improvement of Amorphous Carbon upon Laser Irradiation in Liquid. *J. Phys. Chem. C* **2009**, 113(28), 12154–12161.
46. Lu, Y.F., Huang, S.M., Sun, Z. Raman spectroscopy of phenylcarbyne polymer films under pulsed green laser irradiation. *J. Appl. Phys*. **2000**, 87(2), 945–951.
47. Goncharov, V.K., Ismailov, D.R., Lyudchik, O.R., Petrov, S.A., and Puzyrev, M.V. Determination of the optical bandgap for diamond-like carbon films obtained by laser plasma deposition. *J. Appl. Spectroscopy* **2007**, 74(5), 704–709.
48. Varyukhin, V.N., Shalaev, R.V., and Prudnikov, A.M. Properties of diamond films obtained in a glow discharge under laser irradiation. *Functional Materials* **2002**, 9(1), 111–114.
49. Kharissova, O.V., Osorio, M., Garza, M., and Kharisov, B. I. Study of Bismuth nanoparticles and nanotubes obtained by microwave heating. *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry* **2008**, 38(7), 567–572.
50. Kharissova, O.V., Castanon, M. Garza, Hernandez Pinero, J.L., Mendez, U. Ortiz, and Kharisov, B.I. Fast production method of fe-filled carbon nanotubes. *Mechanics of Advanced Materials and Structures* **2009**, 16(1), 63–68.
51. Rodriguez, M.G., Kharissova, O.V., Ortiz-Mendez, U. Formation of boron carbide nanofibers and nanobelts from heated by microwave. *Rev. Adv. Mat. Sci.* **2004**, 7(1), 55–60.
52. Lewis, D.,III, Imam, M.A., Fliflet, A.W., Bruce, R.W., Kurihara, L.K., Kinkead, A.K., Lombardi, M., and Gold, S.H. Recent advances in microwave and millimeter-wave processing of materials. *Materials Science Forum* **2007**, 539–543(Pt. 4, THERMEC 2006), 3249–3254.
53. Xiu-Tian Yan, and Yongdong Xu. *Chemical Vapour Deposition: An Integrated Engineering Design for Advanced Materials (Engineering Materials and Processes)*. Springer, **2009**, 327 pp.
54. Pierson, H.O. *Handbook of Chemical Vapor Deposition*, 2nd Edition, Second Edition: Principles, Technology and Applications (Materials Science and Process Technology Series). William Andrew, 2 edition, 2000, 506 pp.
55. Pradeep George. *Chemical Vapor Deposition*. VDM Verlag Dr. Mueller e.K. **2008**, 112 pp.
56. Gordillo-Vazquez, F.J., Gomez-Aleixandre, C., and Albella, J.M. Plasma chemistry in the CVD synthesis of nanodiamond films. *Proceedings - Electrochemical Society* **2005**, 2005-09(EUROCVD-15), 415–426.
57. Purohit, V.S., Jain, D., Sathe, V.G., Ganesan, V., and Bhoraskar, S.V. Synthesis of nanocrystalline diamonds by microwave plasma. *J. Phys. D: Applied Physics* **2007**, 40(6), 1794–1800.
58. Miyake, M., Ogino, A., and Nagatsu, M. Characteristics of nanocrystalline diamond films prepared in Ar/H2/CH4 microwave plasma. *Thin Solid Films* **2007**, 515(9), 4258–4261.
59. Chowdhury, S., Borham, J., Catledge, S.A., Eberhardt, A.W., Johnson, P.S., and Vohra, Y.K. Synthesis and mechanical wear studies of ultra smooth nanostructured diamond (USND) coatings deposited by microwave plasma chemical vapor deposition with He/H2/CH4/N2 mixtures. *Diamond and Related Materials* **2008**, 17(4–5), 419–427.
60. Butler, J.E., Sumant, A.V. The CVD of nanodiamond materials. *Chemical Vapor Deposition* **2008**, 14(7–8), 145–160.
61. Chen, W., Lu, X., Yang, Q., Xiao, C., Sammynaiken, R., Maley, J., and Hirose, A. Effects of gas flow rate on diamond deposition in a microwave plasma reactor. *Thin Solid Films* **2006**, 515(4), 1970–1975.
62. Nanba, A., Imai, T., Nishibayashi, Y., Yamamoto, Y., and Meguro, K. Microwave plasma CVD apparatus. JP 2005-218732 20050728. Priority: CAN 146:194557 AN **2007**:143909
63. Ariyada, O., Sato, S., and Suzuki, H. Microwave chemical vapor deposition apparatus for preparation of diamond, **2006**, 12 pp. JP 2006083405 A 20060330 Patent written in Japanese. Application: JP 2004-266462 20040914. Priority: CAN 144:321896 AN 2006:292991
64. Pichot, V., Comet, M., Fousson, E., and Spitzer, D. Detonation synthesis of nanodiamonds: their synthesis and use in pyrotechnics. *Actualite Chimique* **2009**, 329, 8–13.
65. Dolmatov, V.Yu. The structure of a cluster of a detonation-produced nanodiamond. *Sverkhtverdye Materialy* **2005**, (1), 28–32.
66. Dolmatov, V.Yu. Detonation-synthesis nanodiamonds: synthesis, structure, properties and applications. *Russ. Chem. Rev*. **2007**, 76(4), 339–360.
67. Dolmatov, V.Yu. Modern commercial technology for production of detonation nano-diamonds and the area of their application Report 1. *Sverkhtverdye Materialy* **2006**, (3), 10–21.
68. Dolmatov, V.Yu. Modern industrial methods for manufacture of detonation derived nanodiamonds and main areas of their use. Part 1. *Sverkhtverdye Materialy* **2006**, (2), 18–29.
69. Dolmatov, V.Yu., and Fujimura, T. Physical and chemical problems of modification of detonation nanodiamond surface properties. *NATO Science Series, II: Mathematics, Physics and Chemistry* **2005**, 192 (Synthesis, Properties and Applications of Ultrananocrystalline Diamond), 217–230.
70. Donnet, J.B., Fousson, E., Wang, T.K., Samirant, M., Baras, C., and Pontier Johnson, M. Dynamic synthesis of diamonds. *Diamond and Related Materials* **2000**, 9(3–6), 887–892
71. Osawa, E. Recent progress and perspectives in single-digit nanodiamond. *Diamond and Related Materials* **2007**, 16(12), 2018–2022.
72. Osawa, E. Disintegration and purification of crude aggregates of detonation nanodiamond. A few remarks on nano methodology. *NATO Science Series, II: Mathematics, Physics and Chemistry* **2005** 192 (Synthesis, Properties and Applications of Ultrananocrystalline Diamond), 231–240
73. Titov, V.M., Tolochko, B.P., Ten, K.A., Lukyanchikov, L.A., and Zubkov, P.I. The formation kinetics of detonation nanodiamonds. *NATO Science Series, II: Mathematics, Physics and Chemistry* **2005**, 192(Synthesis, Properties and Applications of Ultrananocrystalline Diamond), 169–180.
74. Puzyr, A.P., and Bondar, V.S. Production of nanodiamonds with an increased colloidal stability by using an explosion synthesis. 2005, RU 2252192 C2 20050520 Patent written in Russian. Application: RU 2003-119416 20030626. Priority: CAN 142:448964 AN 2005:428972
75. Nakanishi, E., Matsui, K., Yamaguchi, C., Nishino, H., and Kurusu, C. Manufacture of functional carbon materials, **2000**, 5 pp. JP 2000109310 A 20000418 Patent written in Japanese. Application: JP 99-218782

19990802. Priority: JP 98-219197 19980803. CAN 132:253156 AN 2000:247376

76. Khachatryan, A.Kh., Aloyan, S.G., May, P.W., Sargsyan, R., Khachatryan, V.A., and Baghdasaryan, V.S. Graphite-to-diamond transformation induced by ultrasound cavitation. *Diamond and Related Materials* **2008**, 17(6), 931–936.
77. Gordeev, S.K., and Korchagina, S.B. Method for preparation of nanodiamond powders for producing stable suspensions. **2007**, 3 pp. RU 2302994 C2 20070720 Patent written in Russian. Application: RU 2004-121069 20040701. Priority: CAN 147:191800 AN 2007:789603
78. Chen, L.-J., Tai, N.-H., Lee, C.-Y., and Lin, I.-N. Effects of pretreatment processes on improving the formation of ultrananocrystalline diamond. *J. Appl. Phys.* **2007**, 101(6), 064308/1-064308/6.
79. Hanada, K., Matsuzaki, K., and Sano, T. Nanocrystalline diamond films fabricated by sol-gel technique. *Surface Science* **2007**, 601(18), 4502–4505.
80. Iijima, S. Process and apparatus for manufacture of diamond powder in nanometer range by size reduction. 1992, 4 pp. JP 04132606 A 19920506 Heisei. Patent written in Japanese. Application: JP 90-254415 19900925. Priority: CAN 117:153818 AN 1992:553818
81. Namba, Y. Attempt to grow diamond phase carbon films from an organic solution. *J. Vac. Sci. Technol. A* **1992**, 10(5), 3368–3370.
82. Lim, P.K., Shen, M., and Cao, W. Temperature-Dependence of carbon film growth by electrolysis of a methanol solution. *Carbon* **2003**, 41, 594–598.
83. Roy, R.K., Deb, B., Bhattacharjee, B., and Pal, A.K. Synthesis of diamond-like carbon film by novel electrodeposition route. *Thin Solid Films* **2002**, 422, 92–97.
84. Sirk, A.H.C., and Sadoway D.R. Electrochemical Synthesis of Diamond-like Carbon Films. *J. Electrochem. Soc.* **2008**, 155(5), E49-E55.
85. Adler, J., Gershon, Y., Mutat, T., Sorkin, A., Warszawski, E., Kalish, R., and Yaish, Y. Visualizing nanodiamond and nanotubes with AViz. *Springer Proceedings in Physics*, **2009**, 123 (Computer Simulation Studies in Condensed-Matter Physics XIX), 56–60.
86. Adler, J., and Pine, P. Visualization techniques for modelling carbon allotropes. *Computer Physics Communications* **2009**, 180(4), 580–582.
87. El Bojaddaini, M., Chatei, H., El Hammouti, M., Robert, H., and Bougdira, J. Modeling of a pulsed microwave plasma discharge in view of diamond film synthesis. *Los Alamos National Laboratory, Preprint Archive, Physics* **2007**, 156, arXiv:0711.0845v1 [physics.soc-ph].
88. Fokin, A.A., and Schreiner, P.R. Band gap tuning in nanodiamonds: first principle computational studies. *Molecular Physics* **2009**, 107(8–12), 823–830.
89. Barnard, A.S., Russo, S.P., and Snook, I.K. Editor(s): Rieth, M., and Schommers, W. Modeling of stability and phase transformations in zero- and one-dimensional nanocarbon systems. *Handbook of Theoretical and Computational Nanotechnology* **2006**, 9, 573–622.
90. Barnard, A.S., Russo, S.P., and Snook, I.K. Simulation and bonding of dopants in nanocrystalline diamond. *J. Nanosci. Nanotechn.* **2005**, 5(9), 1395–1407.
91. Wang, C.X., Yang, Y.H., Xu, N.S., and Yang, G.W. Thermodynamics of diamond nucleation on the nanoscale. *J. Am. Chem. Soc.* **2004**, 126(36), 11303–11306.
92. Barnard, A.S., Russo, S.P., and Snook, I.K. Modeling of stability and phase transformations in quasi-zero dimensional nanocarbon systems. *J. Computational and Theoretical Nanosci.* **2005**, 2(2), 180–201.
93. La Torre Riveros, L., Tryk, D.A., and Cabrera, C.R. Chemical purification and characterization of diamond nanoparticles for electrophoretically coated electrodes. *Reviews on Advanced Materials Science* **2005**, 10(3), 256–260.
94. Novikov, N.V., Bogatyreva, G.P., Nevstruev, G.F., Il'nitskaya, G.D., and Voloshin, M.N. Magnetic methods of purification control of nanodiamond powders. *Physics of the Solid State (Translation of Fizika Tverdogo Tela (Sankt-Peterburg))* **2004**, 46(4), 672–674.
95. Lin, K., Hou, S., and Ma, B. Effect of ultrasonic-dispersion for diamond powder purification. *Jingangshi Yu Moliao Moju Gongcheng* **2007**, (6), 9–12.
96. Liu, S., Liu, J., Li, P., Li, Y., and Shen, Y. Process for purification of diamond by electrolysis. **2007**, 7 pp. CN 101049929 A 20071010 Patent written in Chinese. Application: CN 2007-10054424 20070518.
97. Ovcharenko, A.G., Ignatchenko, A.V., Sataev, R.R., and Brylyakov, P.M. Purification of ultradispersed diamond by removal of soluble and adsorbed impurities using electric field. **1996**, SU 1815933 A1 19960620 Patent written in Russian. Application: SU 90-4855039 19900727. Priority: CAN 125:333282 AN 1996:729518
98. Dolgaev, S.I., Kirichenko, N.A., Kulevskii, L.A., Lubnin, E.N., Simakin, A.V., and Shafeev, G.A. Laser purification of ultradispersed diamond in aqueous solution. *Quantum Electronics* **2004**, 34(9), 860–864.
99. Doynikov, Yu.A., Makhrachev, A.F., Kurbatov, K.K., Makarskii, I.V., Adodin, E.I., Yagupov, S.A., Tarasova, L.G., and Kovalenko, E.G. Method for purification of diamonds. **2009**, 7 pp. RU 2367601 C1 20090920 Patent written in Russian. Application: RU 2007-147784 20071225. Priority: CAN 151:384616 AN 2009:1153611
100. Zeng, H., An, X. Method for purifying diamond nanoparticle with Ce salt. **2004,** 11 pp. CN 1480252 A 20040310 Patent written in Chinese. Application: CN 2003-139849 20030718. Priority: CAN 142:357372 AN 2005:20996
101. Petrov, I.L., Skryabin, Yu.A., and Shenderova, O.A. Nanodiamond material, method and device for purifying and modifying a nanodiamond. **2008**, 21 pp. Patent written in Russian. Application: WO 2008-RU313 20080520. Priority: RU 2007-118553 20070521.
102. Lin, K., Pan, Y., Hou, S., Xiao, H., Ma, B. Discussion on purification techniques of synthetic diamond. *Jingangshi Yu Moliao Moju Gongcheng* **2005**, (5), 77–78, 80.
103. Dubois, M., Guerin, K., Petit, E., Batisse, N., Hamwi, A., Komatsu, N., Giraudet, J., Pirotte, P., and Masin, F. Solid-State NMR Study of Nanodiamonds Produced by the Detonation Technique. *J. Phys. Chem. C* **2009**, 113(24), 10371–10378.
104. Shames, A.I., Panich, A.M., Kempinski, W., Baidakova, M.V., Osipov, V.Yu., Enoki, T., and Vul, A.Ya. Magnetic resonance study of nanodiamonds. *NATO Science Series, II: Mathematics, Physics and Chemistry* **2005**, 192 (Synthesis, Properties and Applications of Ultrananocrystalline Diamond), 271–282.
105. Ferrari, A.C., and Robertson, J. Raman spectroscopy of amorphous, nanostructured, diamond-like carbon, and nanodiamond. *Philosophical Transactions of the Royal Society of London, Series A: Mathematical, Physical and Engineering Sciences* **2004**, 362(1824), 2477–2512.
106. Ballutaud, D., Jomard, F., Pinault, M.-A., Frangieh, G., Simon, N. sp2 carbon phases in nanocrystalline diamond. *ECS Transactions* **2008**, 13 (2, Dielectrics for Nanosystems 3: Materials Science, Processing, Reliability, and Manufacturing), 377–383.
107. Shushkanova, A.V., Dubrovinsky, L., Dubrovinskaya, N., Litvin, Yu.A., and Urusov, V.S. Synthesis and in-situ Raman spectroscopy of nanodiamonds. *Doklady Physics* **2008**, 53(1), 1–4.
108. Hamilton, T., Wilks, R.G., Yablonskikh, M.V., Yang, Q., Foursa, M.N., Hirose, A., Vasilets, V. N., and Moewes, A. Determining the sp2/sp3 bonding concentrations of carbon films using X-ray absorption spectroscopy. *Can. J. Phys.* **2008**, 86(12), 1401–1407.
109. Xiao, X., Sheldon, B.W., Qi, Y., and Kothari, A.K. Intrinsic stress evolution in nanocrystalline diamond thin films with deposition temperature. *Appl. Phys. Lett.* **2008**, 92(13), 131908/1–131908/3.
110. Tang, C.J., Neto, M.A., Soares, M.J., Fernandes, A.J.S., Neves, A.J., and Gracio, J. A comparison study of hydrogen incorporation among nanocrystalline, microcrystalline and polycrystalline diamond films grown by chemical vapor deposition. *Thin Solid Films* **2007**, 515(7–8), 3539–3546.
111. Koroleva, M.Yu., Berdnikova, D.V., Spitsyn, B.V., and Yurtov, E.V. Sedimentation stability of aqueous dispersions of nanodiamond agglomerates.

Theoretical Foundations of Chemical Engineering **2009**, 43(4), 478–481.

112. Osawa, E., Ho, D., Huang, H., Korobov, M.V., and Rozhkova, N.N. Consequences of strong and diverse electrostatic potential fields on the surface of detonation nanodiamond particles. *Diamond and Related Materials* **2009**, 18(5–8), 904–909.
113. Houska, J., Panyala, N.R., Pena-Mendez, E.M., and Havel, J. Mass spectrometry of nanodiamonds. *Rapid Communications in Mass Spectrometry* **2009**, 23(8), 1125–1131.
114. Raty, J.-Y., Galli, G. Structural and electronic properties of isolated nanodiamonds: A theoretical perspective. *NATO Science Series, II: Mathematics, Physics and Chemistry*, 2005, 192 (Synthesis, Properties and Applications of Ultrananocrystalline Diamond), 15–24.
115. Preclikova, J., Trojanek, F., Kromka, A., Rezek, B., Dzurnak, B., and Maly, P. Ultrafast photoluminescence of nanocrystalline diamond films. *Physica Status Solidi A: Applications and Materials Science* **2008**, 205(9), 2154–2157.
116. Kulakova, I.I. Surface chemistry of nanodiamonds. *Physics of the Solid State (Translation of Fizika Tverdogo Tela (Sankt-Peterburg))* **2004**, 46(4), 636–643.
117. Madaleno, J.C., Singh, M.K., Titus, E., Cabral, G., Gracio, J., and Pereira, L. Electron field emission from patterned nanocrystalline diamond coated a-SiO2 micrometer-tip arrays. *Appl. Phys. Lett.* **2008**, 92(2), 023113/1–023113/3.
118. Aggadi, N., Arnas, C., Benedic, F., Dominique, C., Duten, X., Silva, F., Hassouni, K., and Gruen, D.M. Structural and chemical characterization of soot particles formed in Ar/H2/CH4 microwave discharges during nanocrystalline diamond film synthesis. *Diamond and Related Materials* **2006**, 15(4–8), 908–912.
119. Popov, C., Novotny, M., Jelinek, M., Boycheva, S., Vorlicek, V., Trchova, M., and Kulisch, W. Chemical bonding study of nanocrystalline diamond films prepared by plasma techniques. *Thin Solid Films* **2006**, 506–507, 297–302.
120. Barnard, A.S. Stability of nanodiamond. *Ultrananocrystalline Diamond* **2006**, 117–154.
121. S. K. Gordeev, and S. B. Korchagina. On the Stability of Small Sized Nanodiamonds. *J. Superhard Mat.* **2007**, Vol. 29, No. 2, pp. 124–125.
122. Butenko, Yu.V., Coxon, P.R., Yeganeh, M., Brieva, A.C., Liddell, K., Dhanak, V.R., Siller, L. Stability of hydrogenated nanodiamonds under extreme ultraviolet irradiation. *Diamond and Related Materials* **2008**, 17(6), 962–966.
123. Wang, G.-z. Review on correlation of diamond performance and nitrogen. *Chaoying Cailiao Gongcheng* **2006**, 18(2), 33–36.
124. Turner, S., Lebedev, O.I., Shenderova, O., Vlasov, I.I., Verbeeck, J., and Van Tendeloo, G. Determination of size, morphology, and nitrogen impurity location in treated detonation nanodiamond by transmission electron microscopy. *Advanced Functional Materials* **2009**, 19(13), 2116–2124.
125. Kulakova, I.I. Chemical properties of nanodiamond. *NATO Science Series, II: Mathematics, Physics and Chemistry* **2005**, 200 (Innovative Superhard Materials and Sustainable Coatings for Advanced Manufacturing), 365–379.
126. Jiang, W., Lu, W.-y., Yang, B.-w., Yao, Y., Zhang, S.-x., and Kou, Z.-l. Method for analyzing impurity elements in diamond by detecting combustion residues of diamond with EDS and SEM. *Chaoying Cailiao Gongcheng* **2006**, 18(3), 6–11.
127. Bogatyreva, G.P., Maevskii, V.M., Il'nitskaya, G.D., Nevstruev, G.F., Tkach, V.N., and Zaitseva, I.N. Impurities and inclusions in synthetic diamond powders of the AC4 and AC6 grades. *Sverkhtverdye Materialy* **2006**, (4), 62–69.
128. Assali, L.V.C., Machado, W.V.M., Larico, R., and Justo, J.F. Cobalt in diamond: An ab initio investigation. *Diamond and Related Materials* **2007**, 16(4–7), 819–822.
129. Cheng, H.-F., Lee, Y.-C., Lin, S.-J., Chou, Y.-P., Chen, T.T., and Lin, I-N. Current image tunneling spectroscopy of boron-doped nanodiamonds. *J. Appl. Phys.* **2005**, 97(4), 044312/1–044312/5.
130. Yan, C.X., Dai, Y., Huang, B.B., Long, R., and Guo, M. Shallow donors in diamond: Be and Mg. *Computational Materials Sci.* **2009**, 44(4), 1286–1290.
131. Sakai, H., Kudou, H., Takahashi, M., and Arifuku, M. Method for producing dispersion of nanodiamond in organic solvent. WO **2008**-JP3215 20081106. Priority: JP 2007-290340 20071108. CAN 150:518067 AN 2009:587231.
132. Maitra, U., Gomathi, A., and Rao, C.N.R. Covalent and noncovalent functionalization and solubilisation of nanodiamond. *J. Experimental Nanosci.* **2008**, 3(4), 271–278.
133. Chen, L.-J., Tai, N.-H., Lee, C.-Y., and Lin, I.-N. Effects of pretreatment processes on improving the formation of ultrananocrystalline diamond. *J. Appl. Phys.* **2007**, 101(6), 064308/1–064308/6.
134. Das, D., and Singh, R.N. A review of nucleation, growth and low temperature synthesis of diamond thin films. *Int. Materials Reviews* **2007**, 52(1), 29–64.
135. Chernomordik, B., Dumpala, S., Chen, Z.Q., Sunkara, M.K. Nanodiamond tipped and coated conical carbon tubular structures. *Chemical Vapor Deposition* **2008**, 14(7–8), 256–262.
136. Askari, S.J., Chen, G.C., Akhtar, F., and Lu, F.X. Adherent and low friction nano-crystalline diamond film grown on titanium using microwave CVD plasma. *Diamond and Related Materials* **2008**, 17(3), 294–299.
137. Askari, S.J., Chen, G.C., Lu, F.X. Growth of polycrystalline and nanocrystalline diamond films on pure titanium by microwave plasma assisted CVD process. *Mat. Res. Bull.* **2008**, 43(5), 1086–1092.
138. Kulisch, W., Popov, C., Vorlicek, V., Gibson, P.N., and Favaro, G. Nanocrystalline diamond growth on different substrates. *Thin Solid Films* **2006**, 515(3), 1005–1010.
139. Teii, K., Ikeda, T. Effect of enhanced C2 growth chemistry on nanodiamond film deposition. *Appl. Phys. Lett.* **2007**, 90(11), 111504/1–111504/3.
140. Gordillo-Vazquez, F.J., and Albella, J.M. Distinct nonequilibrium plasma chemistry of C2 affecting the synthesis of nanodiamond thin films from C2H2 (1%)/H2/Ar-rich plasmas. *J. Appl. Phys.* **2003**, 94(9), 6085–6090.
141. Li, X.-H., Guo, W.-T., Chen, X.-K., Gan, W., Yang, J.-P., Wang, R., Cao, S.-Z., and Rong, Yu. Effect of pressure on growth rate and quality of diamond films prepared by microwave plasma chemical vapor deposition. *Wuli Xuebao* 2007, 56(12), 7183–7187.
142. Wang, L., Lu, J., Su, Q., Wu, N., Liu, J., Shi, W., and Xia, Y. [100]-textured growth of polycrystalline diamond films on alumina substrates by microwave plasma chemical vapor deposition. *Mater. Lett.* **2006**, 60(19), 2390–2394.
143. Abreu, C.S., Amaral, M.S., Oliveira, F.J., Tallaire, A., Benedic, F., Syll, O., Cicala, G., Gomes, J.R., and Silva, R. F. Tribological testing of self-mated nanocrystalline diamond coatings on Si3N4 ceramics. *Surface and Coatings Technology* **2006**, 200(22–23), 6235–6239.
144. Enoki, T., Takai, K., Osipov, V., Baidakova, M., and Vul, A. Nanographene and nanodiamond, new members in the nanocarbon family. *Chemistry–An Asian Journal* **2009**, 4(6), 796–804.
145. Grichko, V.P., Shenderova, O.A. Editor: Shenderova, O.A., and Gruen, D.M. Nanodiamond: designing the bio-platform. *Ultrananocrystalline Diamond* **2006**, 529–557.
146. Purtov, K.V., Burakova, L.P., Puzyr, A.P., and Bondar, V.S. The interaction of linear and ring forms of DNA molecules with nanodiamonds synthesized by detonation. *Nanotechnology* **2008**, 19(32), 325101/1–325101/3.
147. Komatsu, N. Size separation and surface functionalization of nanodiamond particles aiming at their biomedical applications. *Hyomen Kagaku* **2009**, 30(5), 273–278.
148. Ke, G., Huan, S., and Huang, F.-l. Synthesis and dispersibility of derivative of 1,3-propanediamine with nanodiamond. *Gongneng Cailiao* **2009**, 40(5), 863–866.
149. Remes, Z., Choukourov, A., Stuchlik, J., Potmesil, J., and Vanecek, M. Nanocrystalline diamond surface functionalization in radio frequency plasma. *Diamond and Related Materials* **2006**, 15(4–8), 745–748.

150. Mochalin, V.N., and Gogotsi, Y. Wet Chemistry Route to Hydrophobic Blue Fluorescent Nanodiamond. *J. Am. Chem. Soc*. **2009**, 131(13), 4594–4595.

151. Liang, Y., Ozawa, M., and Krueger, A. A General Procedure to Functionalize Agglomerating Nanoparticles Demonstrated on Nanodiamond. *ACS Nano* **2009**, 3(8), 2288–2296.

152. Yeap, W.S., Chen, S., and Loh, K.P. Detonation nanodiamond: an organic platform for the suzuki coupling of organic molecules. *Langmuir* **2009**, 25(1), 185–191

153. Baidakova, M., and Vul, A. New prospects and frontiers of nanodiamond clusters. *J. Physics D: Applied Physics* **2007**, 40(20), 6300–6311.

154. Puzyr, A.P., Bondar, V.S., Bukayemsky, A.A., Selyutin, G.E., and Kargin, V.F. Physical and chemical properties of modified nanodiamonds. *NATO Science Series, II: Mathematics, Physics and Chemistry* **2005**,192 (Synthesis, Properties and Applications of Ultrananocrystalline Diamond), 261–270.

155. Spitsyn, B.V., Gradoboev, M.N., Galushko, T.B., Karpukhina, T. A., Serebryakova, N.V., Kulakova, I.I., and Melnik, N.N. Purification and functionalization of nanodiamond. *NATO Science Series, II: Mathematics, Physics and Chemistry* **2005**, 192 (Synthesis, Properties and Applications of Ultrananocrystalline Diamond), 241–252.

156. Khabashesku, V.N., Margrave, J.L., and Barrera, E.V. Functionalized carbon nanotubes and nanodiamonds for engineering and biomedical applications. *Diamond and Related Materials* **2005**, 14(3–7), 859–866.

157. Khabashesku, V.N., Liu, Y., Margrave, J.L., and Margrave, M.L. Functionalization of nanodiamond powder through fluorination and subsequent derivatization reactions. U.S. Pat. Appl. Publ. **2005**, 18 pp. US 2005158549 A1 20050721 Patent written in English. Application: US 2004-996869 20041124. Priority: US 2003-525588 20031126.

158. Liu, Y., Khabashesku, V.N., and Halas, N.J. Functionalization of nanodiamond powder and applications for glass surface diamond coatings. Abstracts of Papers, 229th ACS National Meeting, San Diego, CA, United States, March 13–17, 2005, **2005**, COLL-581.

159. Liu, Y., Gu, Z., Margrave, J.L., and Khabashesku, V.N. Functionalization of nanoscale diamond powder: Fluoro-, alkyl-, amino-, and amino acid-nanodiamond derivatives. *Chem. Mater*. **2004**, 16(20), 3924–3930.

160. Liu, Y., Khabashesku, V.N., and Halas, N.J. Fluorinated Nanodiamond as a Wet Chemistry Precursor for Diamond Coatings Covalently Bonded to Glass Surface. *J. Am. Chem. Soc.* **2005**, 127(11), 3712–3713

161. Kuznetsov, V.L., and Butenko, Yu.V. Nanodiamond graphitization and properties of onion-like carbon. *NATO Science Series, II: Mathematics, Physics and Chemistry* **2005**, 192 (Synthesis, Properties and Applications of Ultrananocrystalline Diamond), 199–216.

162. Kwon, S.J., and Park, J.G. Theoretical analysis of the graphitization of a nanodiamond. *J. Phys.: Condensed Matter* **2007**, 19, 386215.

163. Leyssale, J.-M., and Vignoles, G.L. Molecular dynamics evidences of the full graphitization of a nanodiamond annealed at 1500K. *Chem. Phys. Lett*. **2008**, 454(4–6), 299–304.

164. Qiao, Z., Li, J., Zhao, N., Shi, C., Nash, P. Graphitization and microstructure transformation of nanodiamond to onion-like carbon. *Scripta Materialia* **2005**, Volume Date **2006**, 54(2), 225–229.

165. Narulkar, R., Bukkapatnam, S., Raff, L. M., and Komanduri, R. Graphitization as a precursor to wear of diamond in machining pure iron: A molecular dynamics investigation. *Computational Materials Science* **2009**, 45(2), 358–366

166. Brodka, A., Hawelek, L., Burian, A., Tomita, S., and Honkimaeki, V. Molecular dynamics study of structure and graphitization process of nanodiamonds. *J. Mol. Structure* **2008**, 887(1–3), 34–40.

167. Azevedo, A.F., Ramos, S.C., Baldan, M.R., and Ferreira, N.G. Graphitization effects of CH4 addition on NCD growth by first and second Raman spectra and by X-ray diffraction measurements. *Diamond and Related Materials* **2008**, 17(7–10), 1137–1142.

168. Kononenko, V.V., Kononenko, T.V., Pimenov, S.M., Sinyavskii, M.N., Konov, V. I., and Dausinger, F. Effect of the pulse duration on graphitisation of diamond during laser ablation. *Quantum Electronics* **2005**, 35(3), 252–256.

169. Strekalov, V.N. Graphitization of diamond stimulated by electron-hole recombination. *Applied Physics A: Materials Science & Processing* **2005**, 80(5), 1061–1066.

170. Gouzman, I., Michaelson, S., and Hoffman, A. Editors: Shenderova, O.A., and Gruen, D.M. Nanodiamond films deposited from energetic species: material characterization and mechanism of formation. *Ultrananocrystalline Diamond* **2006**, 229–272.

171. Hoffman, A. Mechanism and properties of nanodiamond films deposited by the DC-GD-CVD process. *NATO Science Series, II: Mathematics, Physics and Chemistry* **2005**, 192 (Synthesis, Properties and Applications of Ultrananocrystalline Diamond), 125–144.

172. Liu, W., and Gu, C. The preparation and properties of nanostructured diamond films deposited by a hot-filament chemical vapor deposition method via continuous ion bombardment. *Thin Solid Films* **2004**, 467(1–2), 4–9.

173. Liao, M., Qin, F., Zhang, J., Liu, Z., Yang, S., Wang, Z., and Lee, S.-T. Ion bombardment as the initial stage of diamond film growth. *J. Appl. Phys.* **2001**, 89(3), 1983–1985.

174. Grausova, L., Bacakova, L., Kromka, A., Potocky, S., Vanecek, M., Nesladek, M., and Lisa, V. Nanodiamond as promising material for bone tissue engineering. *J. Nanosci. Nanotechn*. **2009**, 9(6), 3524–3534.

175. Liu, S., Liu, W., Hei, L., Tang, W., and Lv, F. Research on preparation of diamond coatings containing Si by microwave plasma chemical vapor deposition. *Beijing Keji Daxue Xuebao* **2007**, 29(4), 408–412, 446.

176. Man, W., Wang, J., Wang, C., Ma, Z., Wang, S., and Xiong, L. Low temperature synthesis of nanocrystalline diamond films deposited by microwave CVD. *Wuhan Huagong Xueyuan Xuebao* **2006**, 28(4), 57–61.

177. Mujica, E.A., Piazza, F., De Jesus, J., Weiner, B.R., Wolter, S.D., and Morell, G. Synthesis of unstrained failure-resistant nanocrystalline diamond films. *Thin Solid Films* **2007**, 515(20–21), 7906–7910.

178. Zhou, J., Wang, L., Liu, G., and Ouyang, S. Method for synthesizing diamond nanofilm with microwave plasma at low temperature. 2007, 3 pp. CN 101024893 A 20070829 Patent written in Chinese. Application: CN 2007-10051244 20070111. Priority: CAN 147:353777 AN 2007:967265

179. Karbushev, V.V., Konstantinov, I.I., Parsamyan, I.L., Kulichikhin, V.G., Popov, V.A., and George, T.F. Preparation of polymer-nanodiamond composites with improved properties. *Advanced Materials Research* **2009**, 59 (1st International Conference on New Materials for Extreme Environments, 2008), 275–278.

180. Sawaguchi, T., Yano, S., Hagiwara, T., and Ito, H. Transparent heat-resistant polymer-nanodiamond composites. PCT Int. Appl. **2005**, 20 pp. WO 2005085359 A1 20050915 Patent written in Japanese. Application: WO 2005-JP3887 20050307. Priority: JP 2004-64281 20040308.

181. Eswar Prasad, K., Das, B., Maitra, U., Ramamurty, U., and Rao, C.N.R. Extraordinary synergy in the mechanical properties of polymer matrix composites reinforced with 2 nanocarbons. *Proceedings of the National Academy of Sciences of the United States of America, Early Edition* **2009**, 1–4, 4 pp.

182. Gavrilov, A.S., and Voznyakovskii, A.P. Rheological characteristics and relaxation properties of polymer-nanodiamond composites. *Russ. J. Appl. Chem*. **2009**, 82(6), 1041–1045.

183. Dolmatov, V.Yu. Polymer-diamond composites based on detonation nanodiamonds. Report 3. *Sverkhtverdye Materialy* **2007**, (4), 3–12.

184. Konstantinov, I.I., Karbushev, V.V., Semakov, A.V., and Kulichikhin, V.G. Combining carbon and polymeric particles in an inert fluid as a promising approach to synthesis of nanocomposites. *Russ. J. Appl. Chem*. **2009**, 82(3), 483–487.

185. Yoshioka, H., Furukuwa, R., and Sawada, H. Preparation and applications of fluoroalkylated oligomeric nanoparticles. *Hyomen* **2006**, 44(5), 167–182.

186. Zhang, W., Lee, S.-T., Bello, I., Leung, K.M., Li, H.-Q., Zou, Y.-S., Chong, Y.M., and Ma, K.L. Ultrahard multilayer coatings based on alternating layers of nanocrystalline diamond and nanocrystalline cubic boron nitride. U.S. Pat. Appl. Publ., **2009**, 14 pp. US 2009022969 A1 20090122 Patent written in English. Application: US 2007-880115 20070719. Priority: CAN 150:150364 AN 2009:93515

187. Li, H.Q., Leung, K.M., Ma, K.L., Ye, Q., Chong, Y.M., Zou, Y.S., Zhang, W.J., Lee, S.T., and Bello, I. Nanocubic boron nitride/nanodiamond multilayer structures. *Appl. Phys. Lett*. **2007**, 91(20), 201918/1–201918/3.
188. Almeida, F.A., Belmonte, M., Fernandes, A.J.S., Oliveira, F.J., Sand ilva, R.F. MPCVD diamond coating of Si3N4-TiN electroconductive composite substrates. *Diamond and Related Materials* **2007**, 16(4–7), 978–982.
189. Tzeng, Y., Chen, Y.-C., Cheng, A.-J., Hung, Y.-T., Yeh, C.-S., Park, M., and Wilamowski, B.M. Chemically vapor deposited diamond-tipped one-dimensional nanostructures and nanodiamond-silica-nanotube composites. *Diamond and Related Materials* **2009**, 18(2–3), 173–176.
190. Singh, M.K., Titus, E., Madaleno, J.C., Pereira, L., Cabral, G., Neto, V.F., and Gracio, J. Nanocrystalline diamond on SiO2 fiber: A new class of hybrid material. *Diamond and Related Materials* **2008**, 17(7–10), 1106–1109.
191. Ekimov, E.A., Zoteev, A., and Borovikov, N.F. Sintering of a nanodiamond in the presence of cobalt. *Inorg. Mater*. **2009**, 45(5), 491–494.
192. Vlasov, I.I., Lebedev, O.I., Ralchenko, V.G., Goovaerts, E., Bertoni, G., Van Tendeloo, G., and Konov, V.I. Hybrid diamond-graphite nanowires produced by microwave plasma chemical vapor deposition. *Adv. Mater*. **2007**, 19(22), 4058–4062.
193. Chang, I.P., Hwang, K.C., and Chiang, C.-S. Preparation of Fluorescent Magnetic Nanodiamonds and Cellular Imaging. *J. Amer. Chem. Soc.* **2008**, 130(46), 15476–15481.
194. Yafarov, R.K. Production of nanodiamond composites in a low-pressure microwave gas-discharge plasma. *Technical Physics* **2006**, 51(1), 40–46.
195. Blum, R., and Molian, P. Liquid-phase sintering of nanodiamond composite coatings on aluminum A319 using a focused laser beam. *Surface and Coatings Technology* **2009**, 204(1–2), 1–14.
196. Matsubara, H. Fabrication of novel materials by the incorporation of nanodiamond into plated films. *Hyomen Kagaku* **2009**, 30(5), 279–286.
197. Matsubara, H. Co-deposition behavior of nanodiamond with electrolessly plated nickel films. *Hyomen Gijutsu* **2006**, 57(7), 484–488
198. Detkov, P.Y., Popov, V.A., Kulichikhin, V.G., and Chukhaeva, S.I. Development of composite materials based on improved nanodiamonds. *Topics in Applied Physics* **2007**, 109 (Molecular Building Blocks for Nanotechnology), 29–43.
199. Uetsuka, H., Nakamura, T., Nebel, C.E. Nanodiamond-containing microstructure composites and method for transporting biological molecules into bodies by using them. **2009**, 7 pp. JP 2009119561 A 20090604 Patent written in Japanese. Application: JP 2007-296378 20071115.
200. Lee, S.H. Gas sensor using nanodiamond and gas detection method. **2009**, 6 pp. KR 2009066740 A 20090624 Patent written in Korean. Application: KR 2007-134421 20071220. Priority: CAN 151:92754 AN 2009:780521
201. Raina, S., Kang, W.P., and Davidson, J.L. Optimizing nitrogen incorporation in nanodiamond film for bio-analyte sensing. *Diamond and Related Materials* **2009**, 18(5–8), 718–721.
202. Holt, K.B., Caruana, D.J., and Millan-Barrios, E.J. Electrochemistry of Undoped Diamond Nanoparticles: Accessing Surface Redox States. *J. Am. Chem. Soc.* **2009**, 131(32), 11272–11273.
203. Larionova, I.S., Belyaev, V.N., Il'inykh, K.F., Frolov, A.V., Bychin, N.V., and Mitrofanov, V.M. Method for preparation and galvanic deposition of wear-resistant nanodiamonds based coating composition on metal surfaces. **2009**, 5 pp. RU 2357017 C1 20090527 Patent written in Russian. Application: RU 2007-128703 20070725. Priority: CAN 150:565842 AN 2009:646846
204. Vityaz, P.A. The State of the Art and Prospects of Detonation-Synthesis Nanodiamond Applications in Belarus. *Physics of the Solid State* **2004**, 46(4), 606–610.
205. Shiozaki, S. Normal-temperature glass, its formation, and normal temperature glass coating material. 2009, 18 pp. JP 2009102188 A 20090514 Patent written in Japanese. Application: JP 2007-274359 20071022. Priority: CAN 150:499296 AN 2009:583008
206. Purtov, K.V., Bondar, V.S., and Puzyr, A.P. Nanodiamond sorbent and method of its obtaining. **2009**, 7 pp. RU 2352387 C1 20090420 Patent written in Russian. Application: RU 2007-127892 20070719. Priority: CAN 150:450910 AN 2009:474289
207. Bondar, V.S., and Puzyr, A.P. Possibilities and prospects for creation of new nanoprocesses based on detonation nanodiamond particles: medico-biological and technical aspects. *Konstruktsii iz Kompozitsionnykh Materialov* **2005**, (4), 80–94.
208. Zibrov, S.A., Vasil'ev, V.V., Velichanskii, V.L., Pevgov, V.G., and Rudoi, V.M. Method for protection of documents, valuable papers or products with nanodiamonds with active NV centers. **2009**, 4 pp. RU 2357866 C1 20090610 Patent written in Russian. Application: RU 2008-136466 20080910. Priority: CAN 151:7812 AN 2009:703362
209. Zhang, D., Hu, X.-g., Tong, Y., and Huang, F.-l. The research development of nanodiamond as a lubricating additive. *Runhuayou* **2006**, 21(1), 50–54.
210. Qu, J., Li, X., and Song, B. Polytetrafluoroethylene friction material for ultrasonic motor, **2004**, 4 pp. CN 1473865 A 20040211 Patent written in Chinese. Application: CN 2003-132555 20030807. Priority: CAN 142:393210 AN 2004:1024000
211. Luo, J., Liu, X., and Wang, X. Effect of proportion of nano-diamond and zirconia on color of core resin. *Xiandai Kouqiang Yixue Zazhi* **2008**, 22(3), 251–254.
212. Comet, M., Pichot, V., Siegert, B., Spitzer, D., Moeglin, J.-P., and Boehrer, Y. Use of nanodiamonds as a reducing agent in a chlorate-based energetic composition. *Propellants, Explosives, Pyrotechnics* **2009**, 34(2), 166–173.
213. Xing, Y., and Dai, L. Nanodiamonds for nanomedicine. *Nanomedicine* **2009**, 4(2), 207–218.
214. Vaijayanthimala, V., and Chang, H.-C. Functionalized fluorescent nanodiamonds for biomedical applications. *Nanomedicine* **2009**, 4(1), 47–55
215. Schrand, A.M., Hens, S.A.C., and Shenderova, O.A. Nanodiamond Particles: Properties and Perspectives for Bioapplications. *Critical Reviews in Solid State and Materials Sciences* **2009**, 34(1–2), 18–74.
216. Cheng, C.-Y., Perevedentseva, E., Tu, J.-S., Chung, P.-H., Cheng, C.-L., Liu, K.-K., Chao, J.-I., Chen, P.-H., and Chang, C.-C. Direct and in vitro observation of growth hormone receptor molecules in A549 human lung epithelial cells by nanodiamond labeling. *Appl. Phys. Lett*. **2007**, 90(16), 163903/1-163903/3.
217. Shimkunas, R.A., Robinson, E., Lam, R., Lu, S., Xu, X., Zhang, X.-Q., Huang, H., Osawa, E., and Ho, D. Nanodiamond-insulin complexes as pH-dependent protein delivery vehicles. *Biomaterials* **2009**, 30(29), 5720–5728.
218. Liu, K.-K., Wang, C.-C., Cheng, C.-L., Chao, J.-I. Endocytic carboxylated nanodiamond for the labeling and tracking of cell division and differentiation in cancer and stem cells. *Biomaterials* **2009**, 30(26), 4249–4259.
219. Chen, M., Pierstorff, E.D., Lam, R., Li, S.-Y., Huang, H., Osawa, E., Ho, D. Nanodiamond-Mediated Delivery of Water-Insoluble Therapeutics. *ACS Nano* **2009**, 3(7), 2016–2022.
220. Faklaris, O., Joshi, V., Irinopoulou, T., Tauc, P., Girard, H., Gesset, C., Senour, M., Thorel, A., Arnault, J.-C., Boudou, J.-P., Curmi, P.A., and Treussart, F. Determination of the internalization pathway of photoluminescent nanodiamonds in mammalian cells for biological labeling and optimization of the fluorescent yield. arXiv.org, e-Print Archive, Physics **2009**, 1–24, arXiv:0907.1148v1 [physics.optics].
221. Kharissova, O.V., and Kharisov, B.I. Graphenes, one of the hottest areas in the nanotechnology: Attention of chemists is needed. *The Open Inorg. Chem. J*. **2008**, 2, 39–49.
222. Kharisov, B.I., Kharissova, O.V., Jimenez Gomez, M., and Ortiz Mendez, U. Recent advances in the synthesis, characterization, and applications of fulleropyrrolidines. *Ind. Eng. Chem. Res.* **2009**, 48(2), 545–571.
223. Jiménez Gómez, M.A., Garza Castañón, M., Kharissova, O.V., Kharisov, B.I., Ortiz Méndez, U. Synthesis by Prato reaction and in situ UV-characterization of several fulleropyrrolidine derivatives. *Int. J. Green Nanotechn*. **2009**, 1, M43-M51.
224. Kharisov, B.I., Kharissova, O.V., Leija Gutierrez, H., and Ortiz Méndez, U. Recent advances on the soluble carbon nanotubes. *Ind. Eng. Chem. Res.* **2009**, 48(2), 572–590.