Russian Chemical Reviews **80** (8) 751 – 770 (2011) © 2011 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2011v080n08ABEH004181

Graphene: chemical approaches to the synthesis and modification

E D Grayfer, V G Makotchenko, A S Nazarov, S-J Kim, V E Fedorov

Contents

I.	Introduction	751
II.	Preparation of graphene from various precursors	753
III.	Chemical modification of graphene	760
IV.	Conclusion	767

Abstract. Published data on the new carbon nanomaterial, graphene, are described systematically from the chemist's standpoint. The attention is focused on the chemical methods of the synthesis of graphene-like materials from various precursors: natural and expanded graphite, graphite oxide, graphite intercalation compounds, *etc*. Approaches to the chemical modification of the graphene plane by various reagents and routes for the preparation of colloidal dispersions of graphene are considered. The bibliography includes 220 references.

I. Introduction

Graphene is a single graphite plane in which the sp^2-hybridized carbon atoms form a hexagonal lattice. Graphene can be considered as a 'building block' for graphite, nanotubes and other carbon materials (Fig. 1). The term 'graphene' designating a separate graphite layer was introduced in 1994 according to the IUPAC recommendations for the nomenclature of graphite intercalation compounds (GIC; they are also called graphite inclusion compounds or graphite interstitial compounds).[1] The term was proposed by analogy with the names of polycyclic aromatic hydrocarbons (anthracene, coronene, *etc*.). Currently, the studies dealing with graphene are not limited to single-layer samples; the structures containing two or more (up to 10) graphene layers are also of interest.[2–5]

E D Grayfer, V G Makotchenko, A S Nazarov, V E Fedorov A V Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, prosp. Akad. Lavrentieva 3, 630090 Novosibirsk, Russian Federation. Fax (7-383) 330 94 89, tel. (7-383) 316 56 34, e-mail: catherine.graifer@gmail.com (E D Grayfer), mwg@niic.nsc.ru (V G Makotchenko), albert@niic.nsc.ru (A S Nazarov), tel. (7-383) 330 92 53, e-mail: fed@niic.nsc.ru (V E Fedorov)
S-J Kim Ewha Womans University, 120750 Seoul, Republic of Korea. Fax (82-2) 3277 – 3419, tel. (82-2) 3277 – 2350, e-mail: sjkim@ewha.ac.kr

Received 28 August 2010
Uspekhi Khimii **80** (8) 784 – 804 (2011); translated by Z P Svitanko

In recent years, the synthesis and properties of graphene have been among the most widely discussed and rapidly developing subject matters in chemistry and physics. This is indicated by the exponential growth of the number of scientific publications on this issue (Fig. 2). The enhanced interest in the new material is related to a number of its unique properties: electronic, optical, mechanical and other. The first experiments with graphene obtained by mechanical exfoliation showed its unusual electronic structure, very high mobility of charge carriers at room temperature and a number of quantum effects (quantum Hall effect, ballistic transport effect and so on). These observations defined the potential of graphene as a material for the design of new-generation field-effect transistors. Moreover, currently graphene is considered as a possible basis for the future nanoelectronics[6] and in the long view, it may serve as substitute for silicon in integrated microcircuits.[7–10] The current research concerns the electronic properties of not only mechanically exfoliated graphene but also more readily

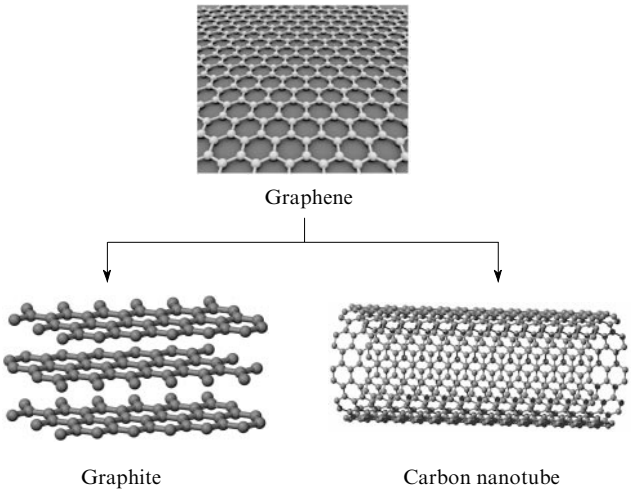


Figure 1. Graphene as a 'building block' of graphite and carbon nanotubes.

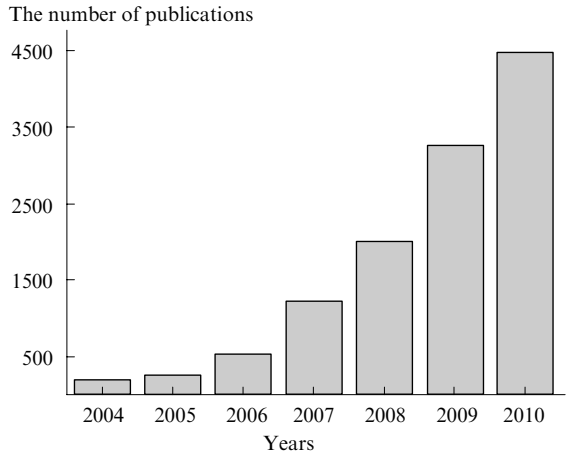


Figure 2. Dynamics of graphene investigations according to the American Chemical Society Chemical Abstract Service (ScholarFinder) database (the data of November 15, 2010).

accessible materials prepared by chemical methods.[9, 11–14] Unlike the massive analogue, *viz*., graphite, graphene is transparent and can be used in optical devices. Having high electrical conductivity and transparency, graphene may become an alternative to the expensive solid solution of tin dioxide in indium(III) oxide (ITO), which is used as a transparent electrode in liquid-crystalline displays, solar batteries and other devices.[15–19] In addition, graphene tends to have high mechanical rigidity, thermal conductivity and specific surface area (according to calculations, 2630 $m^2\ g^{-1}$), which makes it promising as a component of polymeric and inorganic composite materials.[20–23] Owing to the presence of the graphene filler, the matrix acquires enhanced strength, rigidity and electrical and thermal conductivity characteristics.[20–24] The graphene–polymer composites are considered in a recent review.[25] Graphene materials can find use in energy storage devices (as electrodes in battery cells, capacitors and so on).[26] For example, supercapacitors require high-conductivity and large surface area electrodes, and graphene exactly meets these demands.[27] In addition, the possibility of hydrogen storage on graphene structures is being elucidated.[28, 29] Graphene is also studied as regards bioelectronics[30, 31] and sensor[32–34] applications where the large accessible surface area plays an important role. However, currently, the large-scale manufacture of graphene materials is at its early stage, and the major part of the manufactured graphene is spent for the scientific studies.

The theoretical investigations of graphene date back in the 1930–1940s well before real samples were prepared. The calculations showed that an ideal free two-dimensional film (tens of atomic layers thick) should be thermodynamically unstable, like other low-dimensional systems.[2] For this reason, monolayers had long been prepared only on the surface of three-dimensional structures. The first steps towards the synthesis of single carbon layers were made in the 1960–1970s using colloidal solutions of graphite oxide[35, 36] and using chemical vapour deposition techniques based on decomposition of ethylene on transition metal[37] and metal carbide[38, 39] surfaces. High-temperature treatment of SiC with silicon vaporization gives rise to single-crystalline single-layer carbon film.[40] According to another approach, electrophoretic deposition and heat treatment of diamond nanoparticles on the highly oriented pyrolytic graphite surface were used.[41] Attempts were made to prepare graphene from GIC, for example, from KC_8, which were cleaved in reactions with unsaturated hydrocarbons[42] or alcohols.[43, 44] However, the metastable structures obtained in these processes were up to 30 graphene planes thick and rolled up to give nanoscrolls on sonication.[43] The technique of mechanical exfoliation of graphene layers from the highly oriented pyrolytic graphite began to develop in the 1990s, for example, by means of an atomic-force microscope tip.[45] A detailed review of early experiments on the synthesis of thin graphite layers was reported.[5]

A new stage of graphene investigations started in 2004 where Russian and British scientists isolated the first graphene by repeated mechanical exfoliation of graphene layers from highly oriented pyrolytic graphite.[46, 47] In these studies, single- and double-layer graphenes were transferred onto an oxidized silicon substrate to which they were bound only by weak van der Waals forces. Thus, dissolution of the substrate gave free graphenes, which were transferred onto a metallic scaffold, and devices for measuring the electronic properties of a single graphene layer were produced.[48] It was demonstrated for the first time that the new material has unique electronic and other properties. Simultaneously, investigation methods for graphene materials have been actively developed. Currently, the number of layers and defectiveness of graphene samples are usually determined by atomic force microscopy (AFM) and Raman spectroscopy. The state-of-the-art of these methods as applied to graphene is described in reviews.[7, 49–52]

The methods for graphene preparation can be subdivided into several groups

1) mechanical exfoliation of graphene layers from highly oriented pyrolytic graphite;[2, 6, 46–48]

2) growth on the substrate[8, 53] (chemical vapour deposition with hydrocarbon decomposition on a metal[37, 54, 55] or metal carbide[38, 39] surface, thermal decomposition of SiC,[40, 56] processes comprising electrical arc heating of graphite electrodes in hydrogen[57]);

3) organic synthesis;[58, 59]

4) chemical method using colloidal dispersions based on compounds containing graphene layers.[24, 60]

These methods have been considered in reviews.[2–8, 18, 19, 24, 53, 58, 60–66] Each of them has advantages and shortcomings. The mechanical exfoliation of graphene, so-called Scotch method, currently provides the highest-quality samples; however, it is labour-consuming and the yield of graphene is rather low. Apparently, this approach is inapplicable for a large-scale production of graphenes but it is still indispensable for the fundamental and applied research of graphene properties. In the growth of graphenes on the substrate, the key difficulty is to control the growth of a single graphene layer and to prevent building up of the subsequent layers. The synthesis of large polycyclic aromatic molecules, which can be considered as nano-sized graphene sheets, is hampered by the fact that the solubility of these compounds considerably decreases as the number of fused rings increases and by side reactions. The key advantages of chemical liquid-phase approaches to the graphene synthesis are good applicability to large-scale manufacture and relatively easy modification of the properties depending on the future application. In addition, transfer of graphene to colloidal dispersions is needed for a

variety of processing operations: mixing, deposition, impregnation, functionalization and so on.

A number of reviews are devoted to chemical methods for the preparation of graphenes;[24, 60–62, 64] detailed consideration of the preparation of highly monodisperse graphenes by solution techniques has been reported by Green and Hersam.[63] However, since this area is vigorously developing, it would be pertinent to describe the latest achievements in the chemical synthesis and chemical modification of graphene. In this review, we consider the key methods for the preparation of aqueous and organic solutions and dispersions of graphene from various starting materials (graphite oxide, natural and expanded graphite, graphite intercalation compounds and so on), in particular, the methods using surfactants, polymers and biomolecules and discuss the chemical reactions that can take place with the graphene surface.

II. Preparation of graphene from various precursors

Colloidal dispersions of graphene can be prepared from both natural or highly oriented pyrolytic graphite and other materials having graphene layers in the structure: thermally expanded graphite, GIC, graphite oxide, graphite fluoride and carbon nanotubes (Fig. 3). Before considering the details of preparation of graphene colloids from these compounds, it would be expedient to describe some general aspects of chemical preparation of graphene.

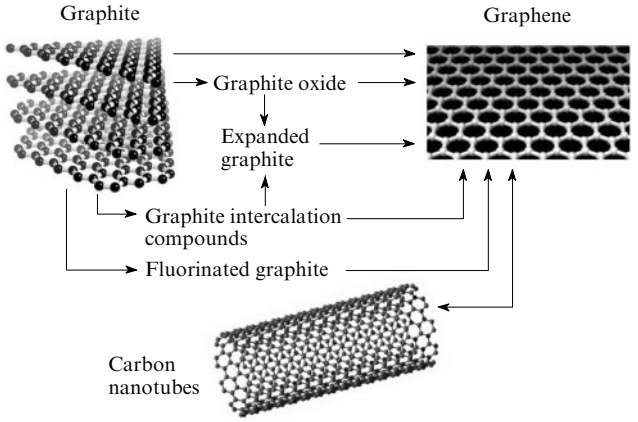


Figure 3. Routes to graphene preparation by cleavage of various precursors.

For splitting graphene stacks into separate sheets, it is necessary to overcome the attraction forces that exist between the layers in the precursor and to stabilize the single-layer graphenes. This can be achieved by either covalent modification of the surface of graphene sheets by various functional groups (see Section III)[24, 60] or non-covalent functionalization (adsorption) by organic solvents,[67–71] surfactants,[72–75] polymers,[76–78] biomolecules[31] and aromatic donor or acceptor molecules.[16, 79–84] The many-year experience in dispersing carbon nanotubes was the key to successful preparation of graphene colloids. It was shown that the most efficient organic solvents have a surface energy close to the surface energy of nanotubes.[85] Since the surface energies of nanotubes and graphene are apparently similar, it was expected that solvents that readily disperse nanotubes would also be promising for the preparation of graphene dispersions. Experiments confirmed this assumption; moreover, not only solvents but also surfactants and polymers used in the case of nanotubes[86] proved to be also efficient for graphenes.[72, 73] Many methods and approaches of covalent functionalization (chemical reactions of the graphene surface) used for carbon nanotubes[87] were also successfully extended to graphene materials.[24, 60]

The dispersion process usually includes the sonication stage of the starting compound in the chosen reaction medium. The ultrasonic waves help the liquid to penetrate between the layers of graphite, graphite oxide or another layered precursor of graphene and facilitate its cleavage. The role of sonication in the production of graphenes was considered in detail in a recent review.[62] The final stage is usually centrifugation of the mixture to separate large non-extoliated precursor particles.

1. Preparation of graphene from graphite

Direct preparation of graphene dispersions from natural or highly oriented pyrolytic graphite can be performed in the following reaction media: polar and non-polar organic solvents,[67–71, 88] acetic acid with a surfactant (cetyltrimethylammonium bromide),[89] aqueous solutions containing surfactants: sodium dodecylbenzenesulfonate[72] and sodium cholate,[73, 75] aqueous solutions in the presence of aromatic molecules.[84]

Hernandez *et al.*[67] prepared graphene colloids by sonication of graphite in *N*-methylpyrrolidone (NMP), dimethylacetamide, γ-butyrolactone and 1,3-dimethylimidazolidin-2-one followed by centrifugation. The yield of high-quality unoxidized graphene stacks not more than 5 sheets thick was ~1 mass %, and the concentration of the dispersions reached 0.01 mg ml^{-1} (Fig. 4). The optimal solvent surface tension (the Helmholtz surface energy) for graphite was found to be ~40–50 mJ m^{-2}, which exactly corresponds to the properties of carbon nanotubes and confirms the van der Waals nature of the solvent–graphite interaction.[69, 85] Based on the testing results of 40 solvents, it was found[69] that for successful dispersion of graphite (as

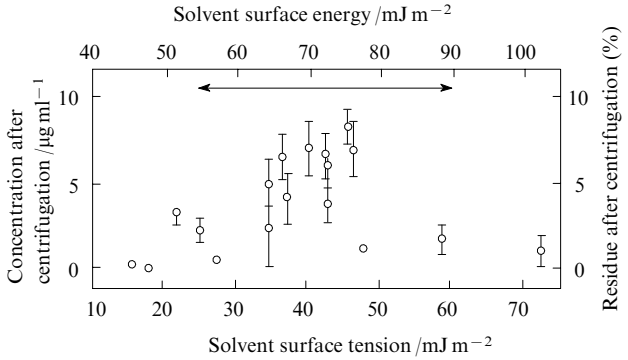


Figure 4. Concentrations of graphene dispersions obtained from graphite after centrifugation for a number of solvents with various surface tension values.[67]
The concentration before centrifugation is 0.1 mg ml^{-1}. The horizontal arrow shows the approximate range of graphite surface energies.

well as nanotubes), the Hildebrand solubility (δ_T) should be ~ 23 MPa$^{1/2}$ and the Hansen solubility parameters should be $\delta_d \approx 18$ MPa$^{1/2}$, $\delta_p \approx 9.3$ MPa$^{1/2}$ and $\delta_H \approx 7.7$ MPa$^{1/2}$.

In low-polarity *o*-dichlorobenzene (ODB), the concentration of the graphene dispersion was 0.03 mg ml^{-1}; cleavage was incomplete, and mainly 7–10-nm thick multilayer graphenes were produced.[68] The possibility of further covalent modification of graphene sheets dissolved in ODB by alkyl and aryl groups has been considered in the literature[68,90] (see Section III). However, in the preparation of graphene films from ODB dispersions, the main difficulty is to remove the residual high-boiling solvent, which markedly reduces the conductivity of the films.[68]

It was shown[71] that graphene dispersions can be formed from graphite on treatment with fluorinated aromatic compounds (hexafluorobenzene, octafluorotoluene, pentafluorobenzonitrile and pentafluoropyridine) or with other reagents including pyridine, benzylamine, ethyl acetate, vinyl acetate, methyl chloroacetate, 2-methoxyethyl ether and *N*,*N*,*N*′,*N*′-tetramethylmethylenediamine. The concentration of dispersions in fluorinated solvents varied in the range of 0.05–0.1 mg ml^{-1} and the yield of graphene was 1%–2%. The best results were obtained for C_6F_5CN. Note that analogous non-fluorinated compounds, except for pyridine, do not form graphene dispersions. In pyridine, dispersions with a graphene concentration of 0.3 mg ml^{-1} stable over 1 week were obtained in 6% yield, while in benzylamine the concentration reached 1 mg ml^{-1}. The dispersion mechanism includes apparently the charge transfer through $\pi-\pi$ stacking where graphite can be either electron donor or acceptor. In the case of organofluorine solvents, the charge is transferred from electron-saturated carbon layers to electron-deficient aromatic molecules, and in the case of pyridine, the charge is transferred in the opposite direction, from the donor pyridine molecules to graphite layers. In addition, dispersion is facilitated by the proximity of the surface energy values of the components.

Upon dispersion of natural graphite in an aqueous solution of sodium dodecylbenzenesulfonate, the colloidal solution phase contained up to 3% of single-layer defect-free graphene; stabilization of the dispersion was interpreted from the standpoint of the stability theory of colloidal systems and the Hamaker theory.[72] By using sodium cholate, a 90 μg ml^{-1} concentration was attained; moreover, with this surfactant, gradient ultracentrifugation was successfully employed to prepare monodisperse graphenes and thus to improve the conductivity and transparency parameters of graphene films obtained from dispersions.[73] Lotya *et al.*,[75] who also used sodium cholate, were able to attain a concentration of 0.3 mg ml^{-1} by using long-term (up to 400 h) exposure to low-power ultrasound. In the transmission electron microscopy (TEM) images, $\sim 20\%$ of graphenes were single-layered; the average size of the graphene structures (1 μm × 400 nm) proved to be fairly resistant to long-term sonication. The effect of centrifugation conditions was also studied. The films prepared from these dispersions had a Young's modulus of 4–10 GPa, an ultimate strength of 15–33 MPa, a conductivity before annealing of 7000 S m^{-1} and a conductivity after annealing of 17 500 S m^{-1}. The graphenes formed upon treatment of highly oriented pyrolytic graphite with cetyltrimethylammonium bromide in acetic acid could be re-dispersed in DMF.[89] Although the surface energies of acetic acid and graphite are not very similar, the result is comparable with the best organic solvents:[67] the yield of graphene reached 10%.

Another approach consists in dispersing graphite in water by ultrasound in the presence of an aromatic compound, tetrasodium pyrene-1,3,6,8-tetrasulfonate.[84] The Raman spectra of graphenes show a D-band splitting caused by violation of symmetry. The method provides high yields (up to 90%) of single-layer graphenes with modified electronic structure, resulting in the 'opening' of the band gap. It is noted that on using monoaromatic compounds (benzene, toluene) instead of this salt, no single-layer graphenes were detected; probably, the interaction between a separate aromatic ring and graphite is insufficient for cleavage.

2. Preparation of graphene from expanded graphite

Expanded graphite (EG), which is also called thermally expanded and thermally split graphite,[91–93] is formed upon fast heating of graphite intercalation compounds;[94] it is one of the most promising precursors for the production of graphene dispersions. On heating of GIC in the thermal shock mode, the intercalant pressure in the interlayer space sharply increases, which induces the separation of the graphite matrix into layers. This gives rise to a porous carbon defective structure composed of layered graphite domains. Expanded graphite of widely used brands manufactured in Russia and abroad is produced from graphite bisulfate or nitrate; usually this EG consists of 30–100 nm graphene stacks, which corresponds to hundreds of graphene planes. Even long-term sonication in alcohol does not induce considerable EG cleavage and the stack thickness exceeds 50 nm.[95] It was shown recently[96] that combining alcohol and acid treatments reduces the thickness of stacks to 6–7 nm. The preparation of graphene colloids by using both EG from industrial sources and new forms of EG consisting of only 10–15 graphene layers has been reported.[97–101]

Graphene nanoribbons, *i.e.*, narrow graphene bands with a width of about 10–100 nm, were prepared from commercial EG.[78] These objects differ from graphene samples having more extended basal planes as regards their physical properties: they possess semiconducting properties, the band gap width being dependent on the width of the ribbon and on the arrangement of atoms at the edges. As a result, such nanoribbons are considered as promising items for the design of a graphene-based transistor with high switching rate and high charge carrier mobility at room temperature. Upon sonication of EG in a solution of poly(*p*-phenylenevinylene-co-2,5-dioctyloxy-*m*-phenylenevinylene) in dichloroethane and the subsequent separation of large particles by centrifugation, the liquid phase contained non-covalently stabilized micrometre-sized graphene sheets and graphene nanoribbons of various shapes and sizes with smooth armchair or zigzag-type edges (Fig. 5).

The dissolution of commercial EG in aqueous (alkaline) and polar organic media using 7,7,8,8-tetracyanoquinodimethane (TCNQ) has been reported;[79] the anion of this compound in DMSO or DMF stabilized the graphene dispersion through $\pi-\pi$ stacking. The effect of sonication on the formation of the dispersion and on the adsorption of the TCNQ anion was also emphasized.[62] It is of interest that this reagent, unlike most surfactants, does not deteriorate the conducting properties of graphene, as it has a highly conjugated system of π-electrons.

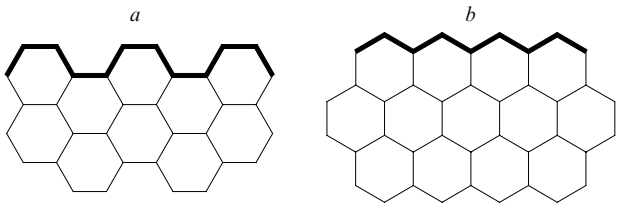


Figure 5. Various types of edges of graphene nanoribbon: armchair (*a*), zigzag (*b*).

Osváth *et al.*[102] obtained single-layer graphenes from EG by gradual thermal oxidation of the films deposited from EG dispersions in benzene on a silicon substrate. The thermal oxidation in air makes the graphene layers on the substrate thinner due to removal of the upper layers.

Apart from the ultrasonic method, there are hydrothermal[103] and microwave[104] methods for the preparation of colloidal solutions of graphene from EG. Using the hydrothermal method, increased yields (10% – 12%) of dispersions of single- and double-layer graphenes in acetonitrile were obtained from commercial EG without using surfactants.[103] Owing to the low boiling point of acetonitrile in an autoclave heated to 180 °C, high pressure (up to 1.1 MPa) was generated, and this facilitated effective penetration of the solvent molecules between the EG layers and cleavage of its particles. This is also promoted by the great dipole moment of acetonitrile.

By using microwave radiation and sonication, commercial EG was cleaved to give an aqueous ammonia dispersion containing graphenes consisting of several layers with large lateral (*i.e.*, in-plane) dimensions ranging from tens to hundreds micrometres.[104] The use of ammonia is needed to avoid the introduction of a large amount of oxygen, and, hence, defects into the samples. The size of graphenes depended on the concentration of ammonia. The hypothetical mechanism of cleavage includes the insertion of a solution of ammonia between the EG layers and the subsequent microwave-assisted formation of gaseous NH_3 and H_2O, which then cleave the EG.

The highly exfoliated graphite (HEG) with a bulk density of 1.3 – 1.8 kg m^{-3} with particles comprising only 10 – 15 graphene layers can be obtained upon fast thermal decomposition of intercalated dicarbon polyfluoride $C_2F \cdot x\,R$ (R is the intercalant). During the process, the volume of material sharply increases and the colour changes from yellow, orange, red, *etc.* to black (Fig. 6 *a*,*b*).[97 – 101] A specific feature of the preparation of a new type of HEG is that it is formed not only due to the fast increase in the pressure of intercalated molecules but also due to evolution of gaseous products upon thermal decomposition of the fluorographite matrix. This accounts for more intense separation into layers, and the new HEG has a greater interplanar spacing (up to 3.49 Å) than graphite or usual EG (3.35 Å), higher specific surface area (up to 380 $m^2\ g^{-1}$) and a small number of graphene planes down to single- and double-layer graphene structures (Fig. 6 *b*). Hence, this material can be considered as a multilayered graphene. The HEG obtained in this way can be easily dispersed in water using sodium dodecylbenzenesulfonate or in organic solvents such as NMP, DMF, dimethylacetamide, diethylene glycol and toluene.[100, 101] Graphene dispersions of this type are stable for more than 6 months. Deposition of the dispersion on a poly(ethylene terephthalate) substrate gave a high-quality pure graphene film with a specific surface resistance of ~3 kΩ per square and a ~80% transparency. In addition, HEG can be transferred to stable aqueous dispersions by chemical modification with a mixture of concentrated nitric and sulfuric acids.[99]

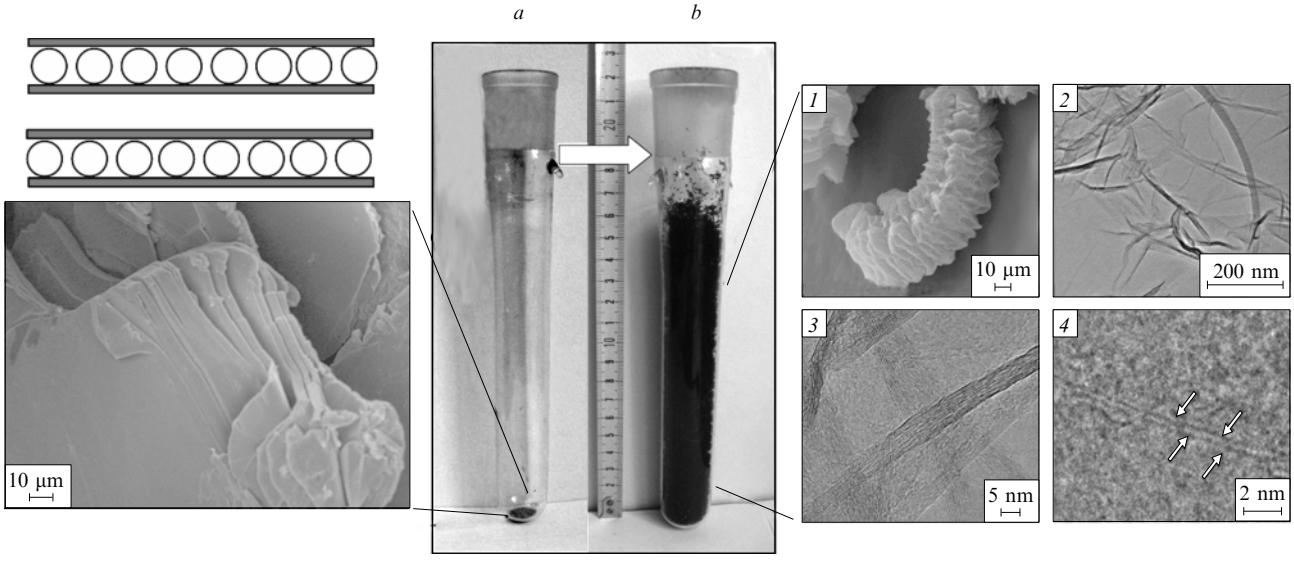


Figure 6. Preparation of highly exfoliated γραπħιτε φρωμ ιντερψαλατεδ διψαρβων πωλθφλυωριδε ψωμπωυνδ $\Psi\Phi \cdot x\,R$.[97 – 101]
(*a*) Initial compound $C_2F \cdot x\,ClF_3$; schematic view of the structure and scanning electron microscopy (SEM) image; (*b*) HEG formed upon thermal decomposition of $C_2F \cdot x\,ClF_3$; SEM (*1*) and TEM images of HEG (*2* – *4*). Figures (*2* – *4*) show various areas of the sample; the arrows in image (*4*) mark the thin section with a thickness of two graphene layers.

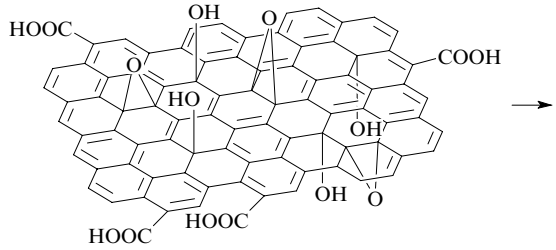
3. Preparation of graphene by reduction of graphite oxide

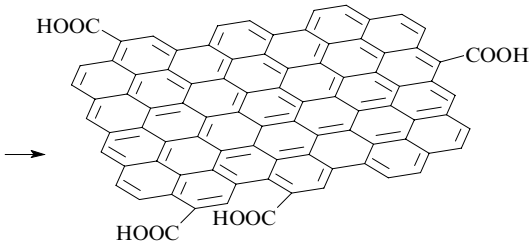
In the first studies devoted to liquid-phase graphene preparation from dispersions, graphene structures were obtained by reduction of graphite oxide;[20, 35, 76, 105] even now, graphite oxide is used as the starting material in a large part of investigations concerned with liquid-phase graphene synthesis.

Graphite oxide (GO) means products of variable composition formed upon graphite oxidation. The synthesis, structure and chemical properties of GO were recently summarized and described in detail in reviews.[106, 107] A compound of this type was obtained for the first time back in the 19th century by oxidation of graphite by potassium chlorate in fuming nitric acid (Brodie method [108]); later, this method was improved by Staudenmaier,[109] and in 1958, Hummers and Offeman [110] proposed a method for graphite oxidation with $KMnO_4$ in concentrated sulfuric acid, which was later modified by Kovtyukhova and co-workers.[111] The compounds obtained in this way consist of hydrophilic layers of graphene oxide (interplanar spacings of 6 to 12 Å) and intercalated water molecules.[60, 106, 107, 112–115] The structure of graphite oxide has not been reliably determined; a number of models have been proposed.[106] Presumably, the carbon atoms in GO may be connected to hydroxy groups or to epoxide bridges and plane edges may be modified by carboxyl and carbonyl groups. Owing to the hydrophilic properties, GO readily forms stable colloidal solutions in water with concentrations of up to 14 mg ml^{-1}, which was observed back in 1960s [35, 36] and was studied in detail more recently in relation to the enhanced interest in this material as a graphene precursor.[60, 76, 106, 116] In addition, upon sonication, GO is completely exfoliated in polar organic solvents such as DMF [106, 117, 118] or propylene carbonate [119] (although contradictory data on this issue were also reported [120]). Aqueous solutions of GO are miscible with DMF, DMSO, NMP, ethanol, methanol and acetonitrile [11, 120] but are precipitated by the addition of toluene or diethyl ether.[120] In acetone and THF, the dispersion is coagulated within 24 h. The graphene oxide sheets can be transferred from water to chloroform by means of quaternary ammonium salts.[74]

Unlike graphene, GO is a dielectric; therefore, numerous studies of its reduction are in progress. The resulting material is called chemically reduced graphene (CRG). The reducing agents used most often are aqueous solutions of hydrazine [16, 31, 76, 80, 82, 105, 121–123] or anhydrous hydrazine,[81, 124] but processes using dimethylhydrazine,[20] hydroquinone,[121, 125] sodium tetrahydroborate,[121, 126] $NaBH_4$–concentrated sulfuric acid system,[127] *p*-phenylenediamine,[128] sodium hydride [129] and aluminium powder [130] were also proposed.

Detailed discussion of the reduction of GO and the formation of CRG can be found in a review;[106] this reaction can be represented schematically as follows:





According to a publication,[122] hydrazine does not reduce the carboxyl groups at the graphene plane edges.

As the reduction progresses, the hydrophilicity of GO gradually decreases, and the reduced graphene sheets are deposited. The precipitate cannot be re-dispersed even by ultrasound or surfactants.[105] The irreversible aggregation is often prevented by adding polymers,[20, 76, 77, 131] surfactants,[123] biomolecules [31] or large aromatic donor or acceptor molecules that are able to stabilize graphenes through $\pi-\pi$ interactions.[16, 80–83] Other approaches to stabilization of reduced graphene colloids are based on the use of reagents that function simultaneously as reducing agents and as stabilizers or solvents,[124, 128, 129] on thorough control of the reduction conditions [120, 122, 132] and on the chemical covalent modification of graphenes (see Section III). Thin graphene-like layers can also be obtained by reducing substrate-deposited GO sheets with hydrazine vapour [11] or hydrogen.[15]

Stankovich *et al.*[76] studied the hydrazine reduction of a GO colloidal dispersion in the presence of anionic polymer, poly(sodium 4-styrenesulfonate) (PSS), and surfactants (sodium dodecyl sulfate or Triton X-100). It was found that only SPSS provided the formation of stable colloids in which every single graphene plane was coated by the polymer on both sides. In this case, the interaction between the polymer and graphene sheets is caused by hydrophobic attraction. An interesting case is the use of the conductive Nafion polymer, which has a fluorocarbon backbone and sulfonic acid side groups.[77] Stabilization is caused by the steric and electrostatic repulsion between the negatively charged graphene particles with the adsorbed polymer. Nafion has a beneficial effect on the conducting properties of the films prepared from the colloid: the specific surface resistance of such films is only 30 kΩ per square at a 80% transparency (for $\lambda = 550$ nm). When Nafion is washed away, the resistance increases threefold.

Patil *et al.*[31] reduced GO with hydrazine in the presence of single-stranded DNA. In the absence of a biomolecule, the material was agglomerated during reduction and was not dispersed upon the subsequent addition of DNA. An important role in the stabilization of colloids by single-stranded DNA is played by hydrophobic interactions and also by weak electrostatic contacts and hydrogen bonds between the primary amino groups of nitrogen bases and the residual carboxyl and hydroxyl groups of graphene sheets. The DNA molecules orient themselves in such a way that the charged sugar phosphate backbone is exposed to the solution. The concentration of the prepared aqueous dispersions of graphene reached 2.5 mg ml^{-1}. These materials are of interest for the possibilities of self-assembly of new nanobiocomposites based on graphene containing intercalated DNA molecules; DNA and cytochrome *c* co-intercalates may also be obtained. These composites tend to

have an ordered lamellar structure where the biomolecules are arranged between the graphene stacks and are accessible for small reducing molecules that diffuse from the solution.

A series of works have been devoted to the dispersions of graphene stabilized through $\pi-\pi$ interactions with polyaromatic molecules (most often, pyrene derivatives) by analogy with stabilization of carbon nanotubes. The use of these compounds not only helps to obtain stable graphene dispersions but also may modify the electronic properties of graphene as a result of charge transfer between the components. Xu *et al.*[16] reduced GO with hydrazine in the presence of 1-pyrenebutyrate. By filtering the dispersion stabilized in this way, graphene films with conductivity of up to 200 S m^{-1} were obtained. The effective energy or electrons transfer between the components is confirmed by changes in the luminescence spectra: the emission maximum shifted and was considerably quenched. According to powder X-ray diffraction data, the interplanar spacing was 0.355 nm. The 30 μm-thick film had a modulus and an ultimate strength of 4.2 GPa and 8.4 MPa, respectively, which is comparable with the data for graphite foil. In another work,[80] during the GO reduction, a pyrene derivative having donor properties (pyrene-1-sulfonic acid sodium salt) or a compound having acceptor properties (diasodium salt of 3,4,9,10-perylenetetracarboxylic diimide bisbenzenesulfonic acid) was introduced. This gave graphene sheets with non-covalent functionalization on both sides. The charge transfer is confirmed by X-ray photoelectron spectra (XPS) and Raman spectra. Upon annealing, the conductivity is improved to reach 1314 S cm^{-1}; this was attributed to the fact that pyrene derivatives serve as nanographene building blocks. Dong *et al.*[81] reduced GO with hydrazine in the presence of tetrasodium pyrene-1,3,6,8-tetrasulfonate (the same compound was used in another study[84] for ultrasonic dispersion of graphite). Graphene sheets had a large area (30×50 μm) and the yield of single-layer graphenes exceeded 80%. The resulting graphenes were investigated as regards their use in field-effect transistors.

In other works, CRG dispersions stabilized by aromatic dyes: Methylene Green[82] and Congo Red[83] were prepared from GO. Not only the formation of stable dispersions with Methylene Green was demonstrated[82] but also the electrochemical properties and electrocatalytic activity of the composites with respect to nicotinamide adenine dinucleotide (NADH) oxidation was studied. The SO_3Na groups serve as active binding sites for other species as shown using the example of gold nanoparticles stabilized by an ionic liquid.[83] High water solubility (7.5 mg ml^{-1}) of the resulting composite was noted. Furthermore, the composite was soluble in ethanol, methanol, DMF, DMSO and was partly soluble in other 10 solvents.

The use of alternative reducing agents such as sodium hydride and *p*-phenylenediamine is of interest as it enables simultaneous reduction and stabilization of the graphene colloid. In the case of *p*-phenylenediamine, the reduced graphene is electrostatically stabilized by adsorption of the product of oxidation of *p*-phenylenediamine and forms stable colloids of positively charged graphene sheets in ethanol.[128] Sodium hydride reduces rapidly (<1 min) the graphene oxide colloid in methanol; simultaneously, methanol is converted to methoxide ions, which stabilize the reduced graphene material.[129] Anhydrous hydrazine also provided a colloid of the chemically reduced graphene by functioning simultaneously as a reducing agent, a solvent and a stabilizer owing to the $N_2H_4^+$ ions.[124] The dimensions of the graphene planes thus obtained were up to 20×40 μm; this is one of the greatest lateral dimensions attained.

The conductivities of the films obtained by GO reduction with sodium tetrahydroborate and hydrazine were compared;[126] in the former case, the conductivity was higher, because in the latter case, C—N groups were formed, which can act as donors of electrons counterbalancing the hole conductivity of CRG.

Often, the presence of stabilizers in a graphene sample is undesirable; therefore, it was proposed to prepare colloidal dispersions of CRG stabilized by the electrostatic interaction of the edge carboxyl groups.[122] The reduction of graphite oxide washed from impurities was carried out by hydrazine under carefully controlled conditions, in alkaline medium (pH 10), which made it possible to retain negative charge on the carboxyl groups. Under these conditions, most of the oxygen-containing groups, except for the carboxyl groups, were removed, and a stable CRG colloid formed down to individual graphenes. The film conductivity was 7200 S m^{-1}. Park *et al.*[132] made the GO surface groups (carboxyl, hydroxyl, epoxide) to react with KOH prior to the hydrazine reduction; consequently, the GO surface acquired a negative charge and became surrounded by K^+ ions. The conductivity of films made of this material was 690 S m^{-1}.

Organic dispersions of CRG without stabilizers or surfactants have been obtained.[120] Hydrazine reduction was performed for the GO pre-dispersed in a water-organic mixture (water : DMF = 1 : 9). According to AFM, almost all graphenes were single-layered (0.7–0.8 nm thick). When DMF was replaced by other solvents (DMSO, NMP, ethanol, acetonitrile), the dispersion precipitated during the hydrazine reduction. The different dispersing abilities of the solvents were interpreted, as in the case of graphite and nanotube dispersions, using Hansen solubility parameters. The powder X-ray diffraction pattern of the dried 'paper' obtained by filtering a water-organic dispersion of CRG shows a peak corresponding to $d_{002}=0.386$ nm. The conductivity of this 'paper' dried at room temperature was 1690 S m^{-1} and after heating at 150 °C, it was 16400 S m^{-1}; this is one of the greatest values obtained for materials of this type. The C : O ratio was 11.

It was reported[133] that treatment of GO with concentrated alkali at moderate heating (50–90 °C) leads to removal of oxygen-containing groups without using other reducing agents. The dispersions thus formed are stable for several days, probably, due to the electrostatic repulsion of the remaining oxygen-containing groups, which is enhanced in alkaline medium. The reduction mechanism is obscure, although it has been suggested that this is a 'reverse' of graphite oxidation processes in strong acids. A dependence of the reaction rate on the pH was observed; the higher the pH, the faster the reduction.

Apart from the GO reduction to CRG by chemical reagents under ambient conditions, thermal[134–136] and microwave[137] reduction in the solid phase are also possible; this is similar to thermal decomposition processes of GIC in the preparation of expanded graphites.[97–101] The reduction of GO under specific conditions, *e.g.*, the reduction under supercritical conditions with a hydrazine solution[138] or directly with organic solvents or water,[26,139,140] are also

possible. Microwave,[26,141] electrochemical[142] and photocatalytic reduction processes of solutions of GO have been described (see Section III).[143]

The reduction of GO under solvothermal conditions gave a higher-quality product than the reduction at lower temperature.[138] Apparently, at higher temperature hydrazine removes oxygen-containing groups more efficiently. However, in any case, a considerable number of defects is retained and sp^2-conjugated areas have limited size.

Stable aqueous graphene dispersions were obtained from GO by hydrothermal method without using hydrazine.[139] The process was carried out under supercritical conditions where water itself is the reducing agent. The possible mechanisms of the removal of oxygen-containing groups and reduction of π-bonds in GO under supercritical water were considered. The conditions of hydrothermal treatment affect the optical and conducting properties of the obtained graphenes.

Murugan *et al.*[26] used both supercritical conditions and microwave radiation to prepare graphene colloids from GO without using hydrazine. The reduction of GO was carried out in high-boiling tetraethylene glycol (TEG) at 300 °C (or in DMF, ethanol, butan-1-ol) or in water at 180 °C on microwave irradiation. The selective energy transfer to a microwave-absorbing solvent ensured fast pressure growth and short reaction time (5–15 min). Under supercritical conditions, TEG, DMF and water acted as reducing agents. In addition, the reaction was carried out in alkaline medium (in an ammonia or sodium hydroxide solution). Powder X-ray diffraction analysis of the reduced products showed somewhat increased interplanar spacings as compared with graphite (0.355 nm for the product obtained in TEG, 0.362–0.387 nm for the products obtained in other solvents). This increase in the interplanar spacing was attributed to the presence of residual oxygen-containing groups, and the authors concluded that the most efficient reduction takes place in TEG or DMF and also at higher temperatures and pressures. According to XPS data, as regards the oxygen content (8.3%), the samples reduced under these conditions are similar to the samples reduced by hydrazine.

4. Preparation of graphene from graphite intercalation compounds

The layered inclusion compounds of graphite or graphite intercalation compounds are formed upon the insertion of atoms or small molecules (intercalants) between the layers of the graphite crystal lattice.[94] As this takes place, the interplanar spacings between the neighbouring layers of graphite in the inclusion compounds sharply increase: for example, for some GIC[7,94] they increase to 1 nm or more (in graphite, the distance is 0.335 nm). According to the density functional theory calculations, the insertion of a bromine molecule results in a decrease in the interaction energy of the graphite planes more than tenfold.[144] Therefore, GIC are promising precursors of graphene dispersions. However, the first experiments on the preparation of graphene from alkali metal-intercalated graphite showed that graphene layers rolled up to form nanoscrolls on sonication.[43] Treatment of graphite with supercritical CO_2 yielded the cleaved material; however, the level of single- or double-layer graphenes was not attained.[145] Only a few attempts to prepare graphene from GIC were successful.

The inclusion compound with molecular bromine can be cleaved under sonication to give a graphene dispersion in water.[144] The graphite intercalation compound $K(THF)_xC_{24}$ obtained from natural expanded or highly oriented pyrolytic graphite is readily cleaved to graphene layers upon the reaction with NMP; the graphene yield is 20%.[146] In solution (0.15 mg ml^{-1}), graphene sheets bear a negative charge and are sensitive to the atmosphere but on drying, they are oxidized to the neutral state. The driving force of the dissolution is the gain in entropy upon solvation of the counter-ions (as in polyelectrolytes), resulting in the formation of a real thermodynamic solution. Using this approach, it is possible to eliminate the sonication stage and retain the large lateral dimensions of the graphene sheets.

A repeated intercalation method has been reported; according to this method, commercial GIC with sulfuric or nitric acid was decomposed to give EG, and then the resulting EG was successively treated with oleum and Bu^n_4NOH (Fig. 7).[147] Under the action of ultrasound, the product gave a stable dispersion in DMF containing

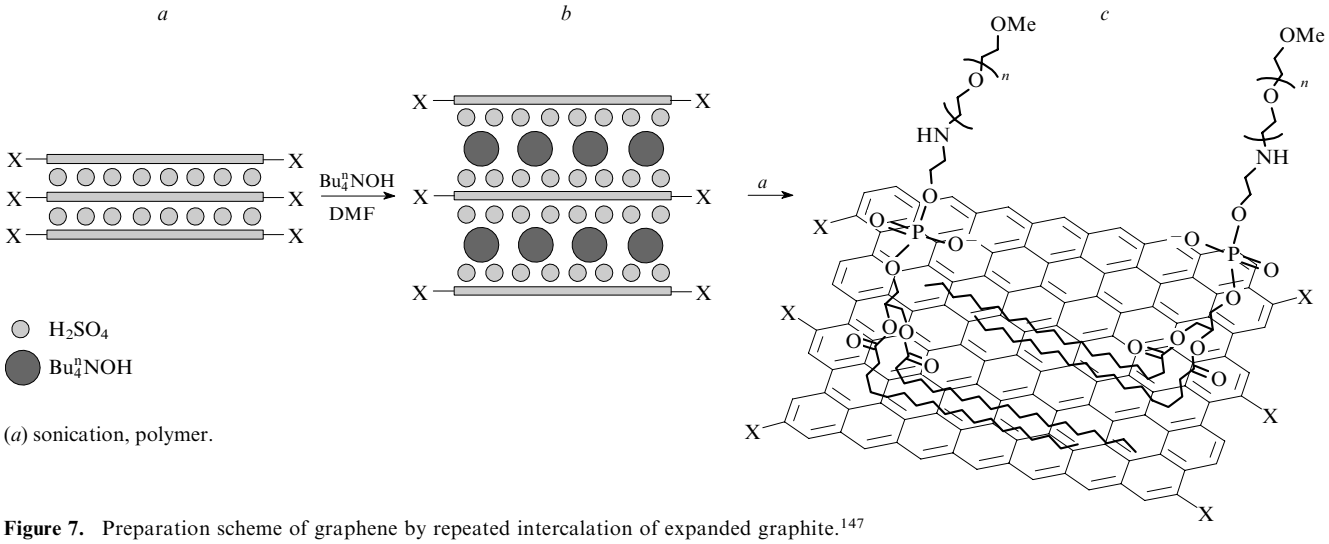


Figure 7. Preparation scheme of graphene by repeated intercalation of expanded graphite.[147]
(*a*) Schematic structure of the expanded graphite with re-intercalated sulfuric acid; (*b*) insertion of tetrabutylammonium hydroxide into intercalated EG; (*c*) graphene stabilized by polymer molecules.

1,2-distearoyl-*sn*-glycero-3-phosphoethanolamine-N-[methoxy(polyethyleneglycol)-5000] and could be successfully transferred to 1,2-dichloroethane. Thorough control of the oleum treatment conditions allowed the researchers to avoid noticeable chemical modification of graphene planes and to ensure low electric resistance of graphene films. It was noted that upon treatment with oleum at room temperature, the oxidative effect is much less pronounced than in the Hummers oxidation ($KMnO_4$ in concentrated H_2SO_4).[110] The introduced carboxyl and hydroxyl groups were located apparently at the edges of graphene planes, as follows from the close values of electrical conductivity of the initial and annealed (800 °C) graphene sheets. For 100 nm wide graphene sheets, the resistance at room temperature was 10–30 kΩ. The obtained stable organic suspensions were used to prepare transparent conducting Langmuir–Blodgett films on transparent substrates, including glass or quartz. For this purpose, a drop of the dispersion in 1,2-dichloroethane was placed onto water, the organic solvent was vaporized and the floating film was transferred onto the substrate. Single-, double- and triple-layer films demonstrated resistances of 150, 20 and 8 kΩ at room temperature and transparency of 93%, 88% and 83%, respectively. In the later works, the authors reported on the additional decrease in the number of defects and oxygen-containing groups in this product under hydrothermal conditions, which provided a substantial increase in the conductivity almost up to the defect-free graphene level.[138] These films are capable of self-assembly on the gold surface.[148]

Ang *et al.*[149] used intercalation of tetrabutylammonium hydroxide in DMF to prepare a colloidal solution of single-layer graphene from slightly oxidized GO. The latter was obtained by the modified Hummers method and then partly dissolved in water. Usually, this is followed by the reduction procedure, and the colloid is used; however, in this approach, water-insoluble precipitate was used for Bu^n_4NOH intercalation. The authors suggested that it consists of multilayer graphene stacks where only the outer layers are oxidized, while the inner layers remain intact. The method is distinguished by a high yield of single-layer graphenes (up to 90%) and retention of great linear dimensions of graphenes owing to the abnsence of the sonication stage.

5. Preparation of graphene by unrolling carbon nanotubes

Quite recently, in 2009, a number of new chemical methods for longitudinal cutting of carbon nanotubes to give graphene structures have been found. For example, narrow graphene nanoribbons (with a 10–20 nm width) were obtained[150] from plasma discharge-treated nanotube–polymeric matrix composites.

The following chemical approaches are used to cut carbon nanotubes.

1. Treatment of multilayer nanotubes by the oxidative mixture H_2SO_4–$KMnO_4$.[151,152]

2. Simultaneous intercalation of lithium and NH_3 followed by fast heating to 1000 °C.[153]

3. Catalytic cutting of single-, double- and multilayer nanotubes by palladium[154] or nickel and cobalt[155] metal nanoparticles.

4. Sonication, in an organic solvent, of nanotubes oxidized in the gas phase.[156]

Recently, a review devoted to this topic was published.[157]

According to the first method, multilayer carbon nanotubes obtained by chemical vapour deposition with a diameter of 40–80 nm containing 15 to 20 inner layers were dispersed in concentrated sulfuric acid and treated with $KMnO_4$, resulting in longitudinal unrolling and formation of oxidized graphene nanoribbons in an almost 100% yield (Fig. 8). The unrolling of nanotubes follows a

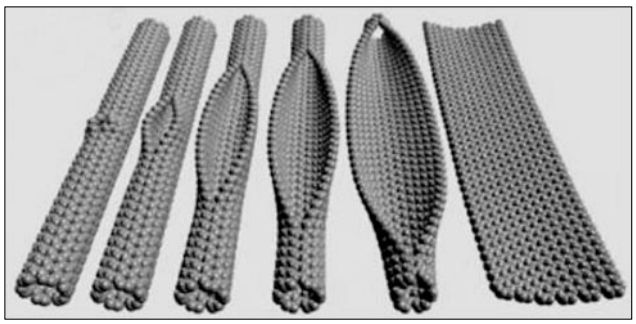
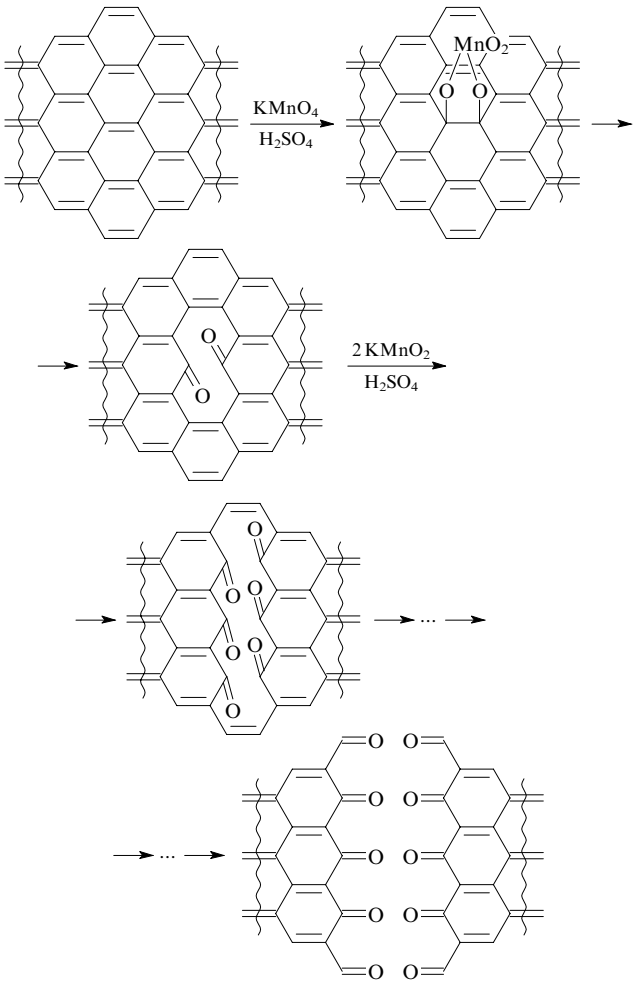


Figure 8. Formation of graphene nanoribbons from carbon nanotubes: gradual unrolling of one nanotube wall gives a nanoribbon.[151]

mechanism similar to the mechanism of alkene oxidation with potassium permanganate in acid where the formation of cyclic manganate ester is the rate-limiting step.



The reaction with potassium permanganate consecutively involves neighbouring atoms, unlike the reaction with concentrated nitric acid in which the nitronium ion attacks random sites. As a result, nanoribbons retain the length of up to 4 μm. The resulting oxidized graphene nanoribbons are distinguished by high solubility in water, ethanol and other polar solvents. For increasing the conductivity of these nanoribbons, they have to be reduced by hydrazine or hydrogen. The reaction with hydrazine hydrate in the presence of sodium dodecyl sulfate provides the reduction of nanoribbons and restores their electrical conductivity.[151] In the subsequent works, the authors demonstrated the use of the described procedure for the design of graphene devices from nanotube-based devices for field-effect transistors[152] and the possibilities of covalent modification of nanoribbons.[158, 159]

Another approach is based on simultaneous intercalation of Li and liquid NH_3 into multilayer nanotubes and subsequent cleavage induced first by HCl and then by heat treatment.[153] It is known that upon intercalation of lithium and ammonia into graphite, the interlayer spacings increase to 6.62 Å; therefore, it was suggested that for nanotubes, lattice expansion of this type would lead to wall destruction and unrolling. Before intercalation, cutting and opening of the nanotube ends in a $H_2SO_4-HNO_3$ mixture is performed. The authors proposed the mechanism of unrolling of nanotubes. The process starts at defects where insertion of the $Li(NH_3)_n$ complex and detachment of graphene layers proceed more easily. The newly formed graphene layers contain hydrogen atoms or amino groups at the edges. Then on treatment with HCl, exothermic reaction with lithium and neutralization of ammonia promote further unrolling of nanotubes. The process is completed by treatment of the material at 1000 °C, resulting in even more pronounced expansion, by analogy with the formation of EG from GIC. The final products include both graphene nanoribbons and graphene stacks, the yield being up to 60%.

According to the third, catalytic method,[154] the nanotubes containing 10% Pd were microwave treated in an aqueous medium. The products were composed of graphene stacks of 3–20 sheets with a width of 1–3 μm. This size is apparently a result of border fusion of relatively small sheets and nanoribbons with minimization of the surface energy of the system. A TEM study confirmed the absence of catalyst (Pd) particles in the graphene sheets; this suggests that palladium nanoparticles are anchored on the defecte sites of unreacted nanotubes. The importance of the oxygen-containing liquid medium was noted. The method is promising for the preparation of doped graphenes from doped nanotubes and indicates the possibility of preparing nanotube–graphene composites. Elias *et al.*[155] applied Co or Ni particles on the nanotube surface and then carried out catalytic hydrogenation in an argon and hydrogen flow (this gave methane) for the longitudinal unrolling of nanotubes. Nitrogen-doped nanoribbons were obtained from doped nanotubes in the same way. Nanoribbons were 15–40 nm wide and 100–500 nm long.

Finally, the fourth method implies two-stage unrolling of multilayer nanotubes:[156] first, the tubes are heated at 500 °C in air to oxidize wall defects and the nanotube ends, and then they are dispersed in 1,2-dichloroethane in the presence of poly(*m*-phenylenevinylene-co-2,5-dioctoxy-*p*-phenylenevinylene); during the dispersion the annealed nanotubes are efficiently unrolled starting with the defective sites to give nanoribbons (yield ~2%). Single-, double- and triple-layer nanoribbons were 10–30 nm wide. Graphene nanoribbons formed the basis for a field-effect transistor with excellent characteristics.

It is also of interest that the reverse transformation of oxidized graphene sheets into soluble nanotubes is also possible.[160] This was attained by sonication of graphene oxide in 70% nitric acid. First, GO decomposed to polyaromatic hydrocarbons, which were condensed to form rolled carbon structures under the action of cavitation.

6. Preparation of graphene by other chemical methods

Some other materials apart from those described above have been proposed for the preparation of graphenes. The reaction of graphite fluoride $(CF_x)_n$ with alkyllithium reagents gave graphenes with covalently attached alkyl chains.[161] Unlike the precursors $(CF_x)_n$, modified graphenes were soluble in THF, *o*-dichlorobenzene and dichloromethane. The highest solubility was found for the graphene with hexyl groups in THF (0.54 g litre^{-1}). The graphene plates retained fairly large lateral dimensions (1.6 μm) and were 0.95 nm thick. During annealing, dealkylation can be performed.

An original approach to the preparation of large amounts of graphene was proposed;[162] the products of the solvothermal reaction of sodium with ethanol, which were then pyrolyzed, served as the precursors of single-layer graphene. Note that the product of reaction of sodium with ethanol, sodium ethoxide, was not the major product in the system. In the closed reaction medium, the ethanol solution was saturated by the arising alkoxide and then a clathrate-like structure was formed in which the alcohol molecules were incorporated in the metal alkoxide structure.

III. Chemical modification of graphene

The development of the chemistry of graphene 'solutions' is necessary, first of all, for preparing composites,[20–23, 25] catalysts,[163] biologically active formulations,[30, 164] *etc.*, since in these cases, the graphene material should not only be soluble in water or organic media but it often should be able to form covalent bonds, *i.e.*, have reactive functional groups on the surface. In addition, covalent modification can play an important role for controlling the electronic properties and the type and concentration of charge carriers.[24, 165] If graphene is covalently bonded to electron-withdrawing oxygen-containing functional groups, this may give rise to p-type semiconductor properties. Conversely, if graphene is functionalized by electron-donating nitrogen-containing groups, the formation of n-type semiconductor is possible.

From the chemistry standpoint, the ideal single-layer graphene can be considered as a giant polyaromatic molecule with an extensive surface accessible from both sides, which can undergo numerous reactions by analogy with unsaturated systems in organic molecules; however, the following important differences should be taken into account:[24]

— graphene sheets are extensive conjugated systems with 100–1000 times larger dimensions as compared with usual organic molecules;

— graphene is not a polyaromatic hydrocarbon but an aromatic system containing only carbon atoms;

— graphene sheets can be functionalized on both sides.

Note that currently no exact data on the dependence of the reactivity of graphene sheets on the size and shape and on the possibility of controlling the stoichiometry have been obtained.

The formation of covalent bonds on the basal plane of a graphene sheet gives rise to sp^3-hybridized carbon atoms. The reactivity of the site adjoining the site that has formed the covalent bond increases, and this induces a 'chain reaction' starting at the site of the primary attack. The sites of geometric deformation (strain) also possess enhanced reactivity. The graphene edges (zigzag or armchair) also have different reactivities, as the zigzag-type structure is thermodynamically unstable and more reactive; however, the control of the structure of graphene edges is difficult.[24]

Among the reactions known for graphene planes, noteworthy are hydrogenation and fluorination and also the addition of organic molecules and inorganic species.

1. Hydrogenation and fluorination of graphene

The existence of hydrogenated graphene, graphane, was predicted by total energy calculations.[166] This material is a fully saturated hydrocarbon described by the formula CH. Graphane contains hydrogen atoms on both sides of the graphene plane, the sp^3-hybridized carbon atoms being displaced up and down from the plane (Fig. 9).

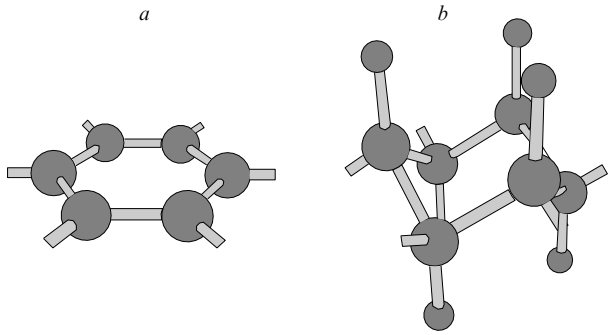


Figure 9. Schematic view of the fragments of the graphene crystal structure (*a*) and theoretically predicted graphane (*b*).[167]

The calculation showed that the formation of graphane is energetically favourable. The existence of two favourable conformations, chair and boat, is possible. Of these, the chair conformation in which the hydrogen atoms alternate on both sides of the graphene plane is preferred. According to calculations, graphane is the most stable structure characterized by C : H = 1 : 1, which is supported by the bond energy of graphane in the chair conformation (6.56 eV atom^{-1}) compared with other compounds characterized by C : H = 1 : 1, in particular, benzene (6.49 eV atom^{-1}) and acetylene (5.90 eV atom^{-1}). However, direct treatment of graphite with hydrogen results neither in graphane nor in intercalation of hydrogen. According to the experimentally confirmed knowledge about the existence of graphane obtained from mechanically exfoliated graphene,[167–169] the key issue in the graphane synthesis is the use of atomic hydrogen of cold hydrogen plasma. Yet another possible route to graphane might consist of hydrogen substitution for fluorine atoms in CF.[166] However, direct treatment of C_xF with hydrogen leads to removal of fluorine atoms to give HF and graphite but not graphane.[94, 166, 170] A different approach to hydrogenation of carbon nanotubes, fullerenes or graphite has been proposed by Pekker *et al.*[171] Hydrogenation was performed by the modified Birch reaction (reduction of aromatic compounds on treatment with alkali metal and ethanol in liquid ammonia) and yielded hydrogenated layered compounds described as C_5H for graphite and $C_{11}H$ for nanotubes. The compounds C_8H were obtained from intercalated graphite C_8K back in the 1970s.[172] Approaches of this type may prove promising also for the synthesis of graphane.

Fluorinated graphene derivatives were obtained by plasma-induced decomposition of CF_4 above graphene prepared by thermal reduction of graphite oxide.[173] The covalent addition of fluorine was proved by XPS and IR spectroscopy. Then fluorine atoms can be replaced by other functional groups, for example, upon reactions with amines.[173–175] Fluorination of mechanically exfoliated[176] or substrate-grown[177] graphene with xenon difluoride was carried out. This fluorographene had a hexagonal symmetry and good thermal stability (it was stable up to 200 °C). Fluorographene is a semiconductor with a large band gap (3 eV) having high specific resistance. The elastic modulus of fluorographene is only three times lower than that of graphene and is equal to 0.3 TPa. Nair *et al.*[176] also manufactured a fluorographene 'paper', *i.e.*, a large number of fluorographene crystals fused together. This 'paper' easily transmits visible light and actively absorbs violet radiation. The mechanical exfoliation of fluorinated graphene layers from massive graphite fluoride $(CF)_n$ has been reported.[178]

2. Reaction of graphene with organic reagents

Apart from atomic hydrogen or fluorine, graphene can also form covalent bonds with organic molecules. Organic functional groups can be covalently attached to graphene structures obtained from graphite or EG in a solvent or to dispersed graphene oxide by the reaction with its oxygen-containing functional groups.[106] In the reactions of GO with many reagents, intercalation can take place, irrespective of the reaction with functional groups.[113] There are examples of functionalization of either the graphene plane[179–181] or mainly the edges.[182, 183] The described reactions may be classified as follows:

— amidation by the reaction with compounds containing amino groups,[24, 181, 183–185] in particular, biomolecules[30, 186, 187] and fullerene derivatives;[187, 188]

— nucleophilic opening of the epoxide ring (Refs 23, 113, 121, 189 and 190) by the reaction with amines, in particular, biomolecules;[164]

— esterification (preparation of esters from acids and alcohols);[191, 192]

— reaction with isocyanates;[193–195]

— reaction with sodium azide and click reactions;[195]

— cycloaddition;[180, 196]

— radical reactions: radical addition of alkyl groups,[68, 90, 179] free radical polymerization[197] and electrochemical reactions with an ionic liquid that follow a radical mechanism;[198]

— reactions with diazonium salts (Refs 123, 158, 159, 165, 182, 199–201)

a. Amidation

Amidation was one of the first examples of covalent functionalization of graphene sheets by long organic molecules (Scheme 1, path *a*).[183] First, acid treatment of graphite generated carboxy groups at the edges of graphene planes, and these groups were subsequently activated with thionyl chloride.

$$\text{Graphene}-\text{COOH} + \text{SOCl}_2 \longrightarrow$$
$$\longrightarrow \text{graphene}-\text{C(O)Cl} + \text{SO}_2 + \text{HCl}.$$

In the next stage, octadecylamine was added to the reaction mixture:

$$\text{graphene}-\text{C(O)Cl} + \text{n-C}_{18}\text{H}_{37}\text{NH}_2 \longrightarrow$$
$$\longrightarrow \text{graphene}-\text{C(O)NHC}_{18}\text{H}_{37}\text{-n} + \text{HCl}.$$

Such octadecylamido graphite is obtained in 20% yield relative to the initial oxidized graphite and had a solubility in THF of 0.5 mg ml^{-1} and was also soluble in CCl_4 and 1,2-dichloroethane. The AFM images showed that dispersions contained 5.3 Å-thick graphite plates, which were classified by the authors as single-layer covalently modified graphenes, in view of functionalization and the possibility of the presence of the solvent between the substrate and graphene.

This approach was developed by Cao *et al.*,[184] who demonstrated that modification of graphene sheets by long alkyl chains improves the miscibility of the graphene material with polymers. The chemically reduced graphene containing edge carboxy groups reacted with octadecylamine in the presence of an activating reagent (*N*,*N*′-dicyclohexylcarbodiimide) in DMF to give a product similar to the product obtained by Niyogi *et al.*[183] The dispersion of the product in non-polar solvents, toluene and xylenes, often used to dissolve non-polar polymers, was noted. According to AFM data, the plate thickness was ~1.3 nm. Owing to the lipophilic properties, the modified graphene was readily dispersed in isotactic polypropylene, thus enhancing its thermal properties.

'Grafting' of the star-like polyethylene glycol to graphite oxide can be used to obtain biocompatible materials for cell visualization and targeted drug delivery.[181, 185] Before reacting with the polymer having terminal amino groups, graphene was treated with chloroacetic acid in a highly alkaline medium to reach the highest concentration of the carboxy groups, which react with polymer amino groups. The reaction was carried out in the presence of *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide. As a result, star-like polyethylene glycol can add to the graphene surface through several amide bonds. Unlike other graphene materials, this material was stably dispersed in the salt medium and in biological fluids. In addition, the hybrid exhibited fluorescence properties in the near-IR region. The possibility of *in vitro* targeted delivery to cancer cells of the antitumour drug Doxorubicin, which was adsorbed on the hybrid prefunctionalized by an antibody, was studied. Liu *et al.*[185] employed polyethylene glycol-modified graphene oxide for the targeted delivery of the compound SN38, an analogue of Camptothecin drug. The aromatic SN38 molecules insoluble in water formed complexes with graphene through van der Waals contacts. The complexes were readily soluble in water and simultaneously retained the antitumour activity comparable with the activity of the free agent in organic solvents.

Along with modification of graphene planes with long alkyl chains and polymers, amidation provides the route to covalent attachment of porphyrins to the graphene sheet. The resulting nanohybrid composites are of interest as components of catalysts, sensors, medications, organic semiconductors, liquid crystals and nonlinear optical materials (see Scheme 1, pathway *a*).[186, 187] For the synthesis of the graphene–porphyrin nanohybrid material, $SOCl_2$-activated graphene oxide was made to react with 5-(4-aminophenyl)-10,15,20-triphenylporphyrin in DMF in the presence of triethylamine.[186] The amide bond formation was confirmed by IR data. The hybrid material formed homogeneous dispersions in DMF. As in the case of porphyrin–nanotubes hybrid, luminescence quenching was observed, which is indicative of strong interaction of the excited states of the porphyrin and graphene moieties of the hybrid; a probable quenching mechanism is the electron transfer in the donor–acceptor hybrid. This hybrid, like another synthesized material comprising a graphene plane and covalently attached fullerene[187, 188] (see Scheme 1, pathway *a*), shows nonlinear optical properties.[187]

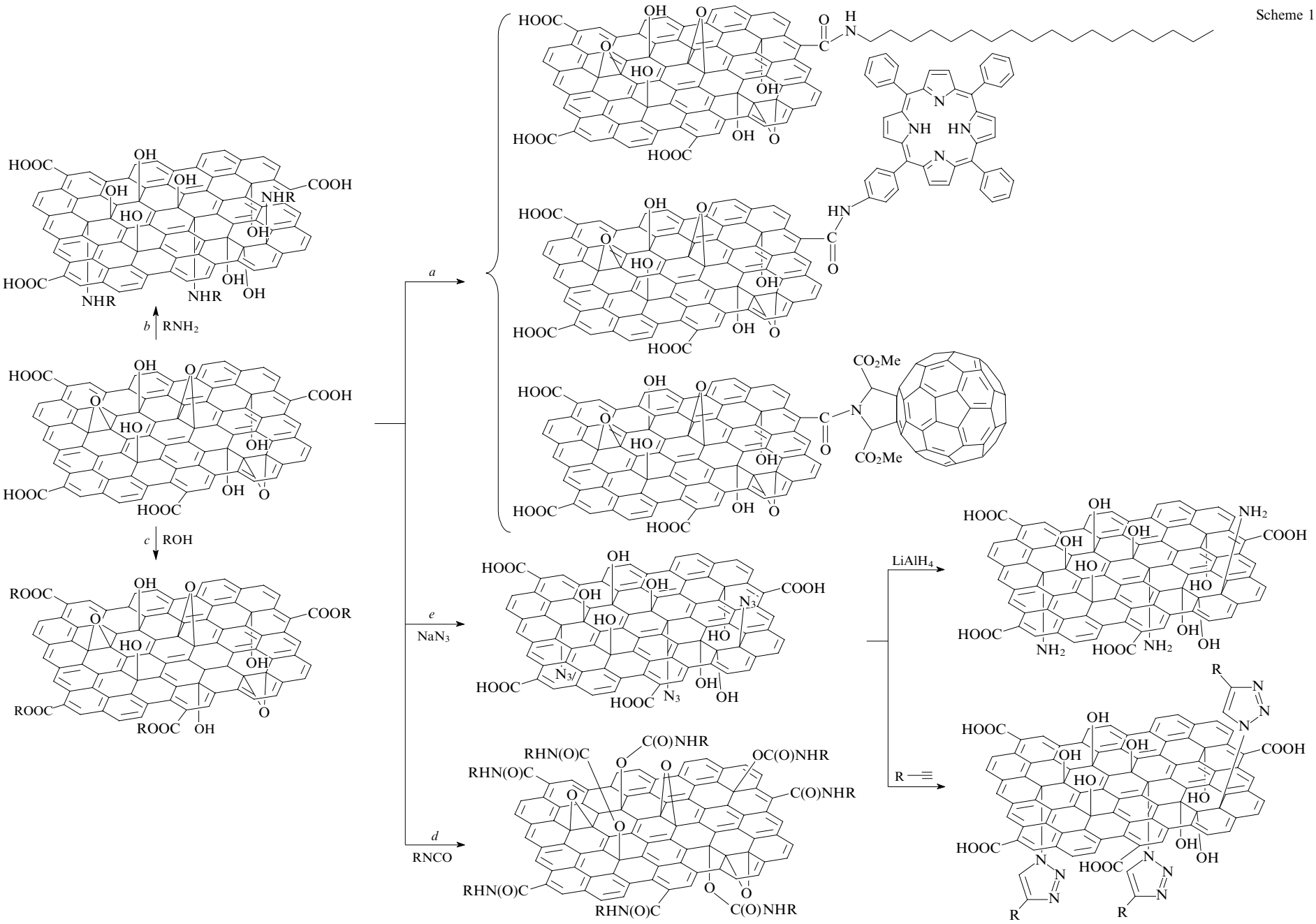
The results on the covalent functionalization of substrate-deposited graphene oxide by DNA molecules for the development of biomolecular devices were reported.[30] Oligodeoxynucleotide containing 20 bases (amine-AAC TGC CAG CCT AAG TCC AA) reacted with the carboxyl groups of graphite oxide in the presence of an activator. The confocal microscopy technique often applied to biological objects showed that DNA is predominantly bound in 'thicker' sites in particular, in the folds, as follows from the higher fluorescence intensity in these sites. Interestingly, no enhanced fluorescence is observed at the graphene plane edges where the carboxyl groups to which DNA is linked are supposed to be located. The authors concluded that the carboxyl groups are evenly distributed over the graphene oxide surface.

b. Nucleophilic opening of the epoxide ring

The reaction of GO with amines can also involve epoxide groups located in the plane of GO sheets (Scheme 1, pathway *b*).[106, 113, 121] The cross-linking of graphite oxide to polyallylamine has been reported.[23] The nucleophilic attack by the amino group on the epoxide groups induced opening of the epoxide ring to give new C–N bonds. The structure of the resulting product and the reaction mechanism have not been entirely elucidated; it was shown that the covalently bound graphene composites with polyallylamine have enhanced rigidity and strength as compared with the non-modified material and are promising for the use in polymeric composite materials and thin films.

Octadecylamine can also be linked to graphene oxide planes *via* opening of the epoxide rings in alkaline medium.[189] The authors noted that functionalization of only edge COOH groups is insufficient to make large graphene sheets soluble. As in the case of the product described by Niyogi *et al.*,[183] octadecylamine-modified graphene gave stable dispersions in THF, as well as in toluene, chlorobenzene and *o*-dichlorobenzene. According to AFM data, the graphene plates were 1.8 nm thick including the contribution of the basal plane and the C_{18} groups. The effect of heat treatment conditions on the change in the

Scheme 1


HOOC
COOH
NHR
HO
OH
O
NHR
NHR
b RNH2
c ROH
ROOC
COOR
a
e
NaN3
d
RNCO
N3
RHN(O)C
C(O)NHR
OC(O)NHR
LiAlH4
R
NH2
CO2Me
NH
HN
N

electrical conductivity of a modified graphene film (from insulator to conductor) and the electronic properties of these materials were studied.

A similar approach, *i.e.*, the reaction of epoxide groups of graphite oxide with amino groups, was used[164] to prepare the biocompatible graphene–poly(L-lysine) composite, which is of interest for a number of biological applications (hydrogen peroxide biosensor, targeted drug delivery, cell aggregation, *etc.*). The process of composite preparation also included the stage of sodium tetrahydroborate reduction of the obtained material. The covalent bonding of poly(L-lysine) to graphene sheet was confirmed by XPS, IR and electronic spectroscopy. The thickness of functionalized graphenes after reduction was 3.6 nm (according to AFM data), which was indicative of two-sided grafting of poly(L-lysine) to graphene. Promising results in the design of hydrogen peroxide biosensor based on horseradish peroxidase immobilized on the resulting nanomaterial were obtained.

One more example of using reactive epoxide groups of graphene oxide is the covalent addition of the ionic liquid aimed at preparing readily and stably soluble graphenes.[190] The cation of the ionic liquid, 1-(3-aminopropyl)-3-methylimidazolium bromide, containing terminal amino groups was bound to graphene oxide sheets *via* KOH-catalyzed nucleophilic opening of the epoxide groups; the 'grafted' cation stabilized the graphene dispersions in water, DMSO and DMF owing to electrostatic repulsion.

c. Esterification

Examples of esterification of the COOH groups of GO[192] and graphene sheets prepared from EG on alcohol or acid treatment[191] are known (see Scheme 1, pathway *c*). In both cases, the reactions were carried out in poly(vinyl alcohol). The functionalized product was dissolved in water[191,192] and in DMSO.[191] Salavagione *et al.*[192] studied the GO linked to poly(vinyl alcohol) and also the material obtained by the reduction of this composite. The CRG samples with covalently grafted alcohol fragments remain water-soluble. In the case of functionalization of modified EG,[191] the content of the COOH groups introduced upon pre-treatment was estimated as 1 per 50 carbon atoms. Polyvinyl alcohol was covalently attached (through the OH groups) to these groups *via* carbodiimide-activated esterification.[181,184] According to TEM images, the obtained samples consisted of 6–7 graphene layers. In both works, the reaction was noted to restrict the mobility of polymer chains and to change the thermal properties of the composite.

d. Reactions with isocyanates

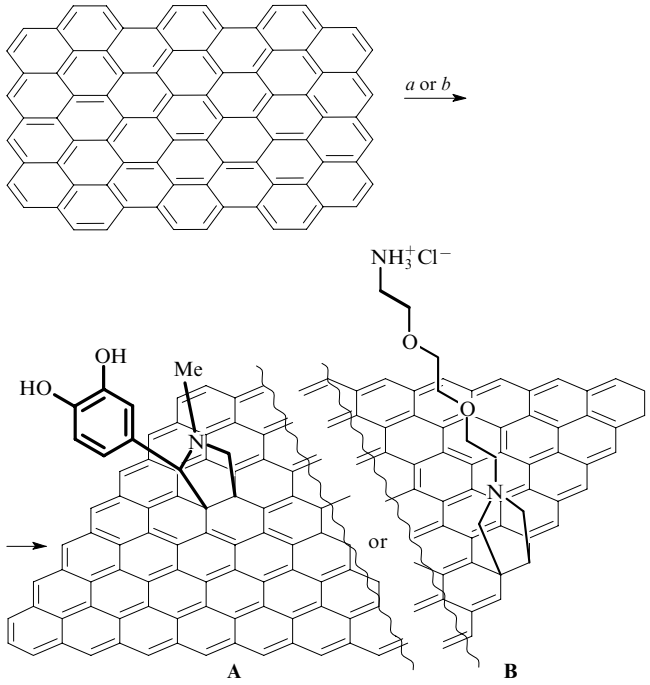
In 2006, graphene derivatives were prepared from GO and a number of isocyanates, in particular, those containing additional reactive groups.[193] The reaction may involve both edge carboxyl groups of GO and the hydroxyl groups located on the basal plane to give amides and urethanes, respectively (see Scheme 1, pathway *d*). The degree of functionalization was proportional to the reactivity of isocyanate: for Bu^tNCO, this was 1 group per 20 carbon atoms and for 4-AcC_6H_4NCO, this was 1 group per 7.6 carbon atoms. These derivatives lost the solubility in water but could be dispersed in polar aprotic solvents: DMF, DMSO, NMP, hexamethylphosphoramide (1 mg ml^{-1}). Less polar solvents (THF, acetone, toluene, *etc.*) were inefficient. The reaction of GO with toluene-2,4-diisocyanate and then with ampliphilic oligoester gave rise to GO possessing both hydrophilic and hydrophobic properties.[194]

e. Reaction with sodium azide and click reactions

Salvio *et al.*[195] successively carried out the reaction of GO with NaN_3 and the $LiAlH_4$ reduction (see Scheme 1, pathway *e*). The resulting material covalently modified by amino groups reacted with isocyanate groups pre-grafted on the silica substrate surface. Upon sonication, the material not attached to the substrate was removed, and only single-layer covalently bonded graphene remained. In addition, GO modified by NaN_3 underwent so-called click reactions: cycloaddition of azide to terminal alkyne to give 1,2,3-triazole. The reaction gave GO functionalized by long hydrocarbon chains connected to the graphene plane through the triazole ring.

f. Cycloaddition

Cycloaddition has been successfully used to modify various carbon nanomaterials: fullerenes, nanotubes, nano-onions and so on.[87,180,196] In the case of nanotubes and fullerenes, the reactivity depends on the degree of surface curvature, which is correlated with the contribution of sp^3-hybridized carbon atoms. The reactivities of nanotubes and graphene are different; nevertheless, 1,3-dipolar cycloaddition of azomethine ylides to defect-free graphenes obtained by dispersion of graphite in organic solvents was simultaneously carried out in two works.[180,196]



(*a*) 3,4-$(HO)_2C_6H_3CHO$, $MeNHCH_2CO_2H$, Py, DMF;
(*b*) 1) $(CH_2O)_n$, $BocNH(CH_2CH_2O)_2CH_2CH_2NHCH_2CO_2H$, NMP;
2) HCl;
Boc is *tert*-butoxycarbonyl.

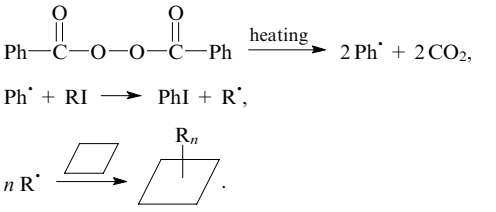
In one of these works,[196] the reaction was performed using a graphene dispersion in pyridine, while in the other study,[180] a graphene dispersion in NMP was used. In both cases, graphene was modified by aldehyde and amino acid condensation. According to thermogravimetric analysis

(TGA) data, product **A** contained one functional group per 40 carbon atoms,[196] while product **B** had one functional group per 128 carbon atoms.[180] The number of grafted amino-containing groups was determined using their selective binding to gold nanowires.[180] The homogeneous distribution of nanoparticles over the graphene sheet surface indicates that functionalization has occurred not only on the graphene edges but also at the basal C=C bonds. Successful dispersion of the product in DMF and in ethanol was noted (concentrations of up to 0.5 mg ml^{-1}) were achieved.

g. Radical reactions

Previously, covalent modification techniques using free radical reactions have been developed for carbon nanotubes,[87,202] and now these techniques are applied to graphene materials. For example, it was shown that thermal decomposition of benzoyl peroxide in the presence of alkyl iodides makes it possible to attach various functional groups to carbon nanotubes. On heating to 75–80 °C, benzoyl peroxide decomposes to give carbon dioxide and phenyl radicals, which react with alkyl iodides (RI) to give PhI and the radical R$^{\bullet}$ (Scheme 2). Hamilton *et al.*[90] performed the addition of perfluorinated alkyl radicals to graphene materials obtained by ultrasonic dispersion of microcrystalline or expanded graphite in *o*-dichlorobenzene by two methods: 1) thermal decomposition of benzoyl peroxide in the presence of perfluoroalkyl iodides and 2) UV-photolysis of perfluorodecyl iodide. According to XPS and TGA data, (perfluorododecyl)graphene contained approximately one functional group per 35 carbon atoms. In the case of perfluorodecylgraphene, one group per 29 carbon atoms was introduced. The degree of cleavage of perfluorodecylgraphene was higher (according to AFM, < 5 nm) than that of (perfluorododecyl)graphene (5–7 nm). However, since n-$C_{10}F_{21}CH_2CH_2I$ and n-$C_{10}F_{21}I$ reacted with graphene dispersions obtained from different precursors, namely, expanded graphite and microcrystalline graphite, respectively, it is impossible to say what is the reason for different degrees of cleavage. The products formed stable dispersions in chloroform.

Scheme 2



The polystyrene–polyacrylamide copolymer was covalently added to CRG obtained from GO by free radical polymerization in the presence of benzoyl peroxide.[197] According to TGA, the graphene to polymer ratio in the composite was 1 : 4. Good cleavage of graphene layers down to 1–3-layer structures (1.2 nm thick) was shown by AFM. The resulting material was readily dispersible in water due to hydrophilic polyacrylamide blocks and also in xylene, which readily dissolves polystyrene.

The phenyl radicals resulting from benzoyl peroxide decomposition can also themselves be grafted to the graphene planes by the photoexcitation mechanism.[179] This reaction was performed for graphene prepared by mechanical exfoliation and deposited onto a silicon substrate. The reaction was initiated by an argon laser (514.5 nm, 0.4 mW) and then studied *in situ* by Raman spectroscopy. It was shown that single-layer graphene is 14 times more reactive than double-layer graphene. The reaction mechanism probably includes 1) electron transfer from photoexcited graphene to adsorbed benzoyl peroxide molecules, 2) formation of intermediate benzoyl peroxide radical anion, 3) its irreversible decomposition to give a phenyl radical, 4) reaction of the phenyl radical with the graphene surface to give sp^3-defect sites on the graphene basal plane. It was noted that this reaction does not proceed without irradiation, although for nanotubes functionalization in a similar system was carried out without irradiation.[203] This may be due to low defectiveness of the mechanically prepared graphene.

h. Reactions with diazonium salts

Reactions with diazonium salts have been used earlier to attach aryl groups to the surface of carbon nanotubes[87] or other carbon materials and are used now for graphenes prepared by various methods: GO reduction,[123,201] EG dissolution or mechanical cleavage,[182,200] epitaxial growth,[165] mechanical exfoliation,[199] unrolling of carbon nanotubes.[158]

Si and Samulski[201] added one more stage in the GO reduction to CRG, namely, the reaction with a diazonium salt (Fig. 10 *a*). First preliminary reduction with sodium tetrahydroborate was carried out, this was followed by the reaction with the diazonium salt of sulfanilic acid, and at the final stage, the product was reduced with hydrazine. The covalent introduction of the $C_6H_4SO_3H$ groups prior to the reduction made it possible to avoid the aggregation of graphene sheets. The final product of hydrazine reduction contained a minor amount of SO_3H groups, which, on the one hand, ensured its good solubility in water (up to 2 mg ml^{-1}) and, on the other hand, did not decrease appreciably the conducting properties (1250 S m^{-1}). In another work,[123] GO functionalization with the diazonium salts 4-R–Ar–N_2^+ BF_4^- (R = NO_2, Cl, Br, OMe) was performed after and not before the reduction, in order to obtain graphene covalently bonded to aryl groups (see Fig. 10 *a*). The process was carried out in the presence of sodium dodecylbenzenesulfonate; hence, more concentrated GO dispersions could be used and the number of attached groups could be increased. The GO reduction is accompanied by partial restoration of aromaticity, which gives rise to the surface needed to attach aryl substituents. The products were single- and double-layer graphenes, probably, functionalized on both sides, and readily dispersible in DMF, NMP and dimethylacetamide (1 mg ml^{-1}).

Nitrophenyl groups were grafted to epitaxially grown graphene *via* the reaction with the diazonium salt.[165] The reaction mechanism includes spontaneous electron transfer from graphene to the diazonium salt. Electrochemical reduction of the NO_2 group to NH_2 was also performed. The strength of the C–C bonds between the aryl groups and the graphene surface was demonstrated.

One more application of the diazonium salts for the preparation of modified graphenes is to make them to react with bulk EG (see Fig. 10 *b*).[182] Bromophenyl groups were attached at the edges of graphite planes; the subsequent sonication of this material in DMF afforded stable dispersion of covalently modified graphene at concentration of

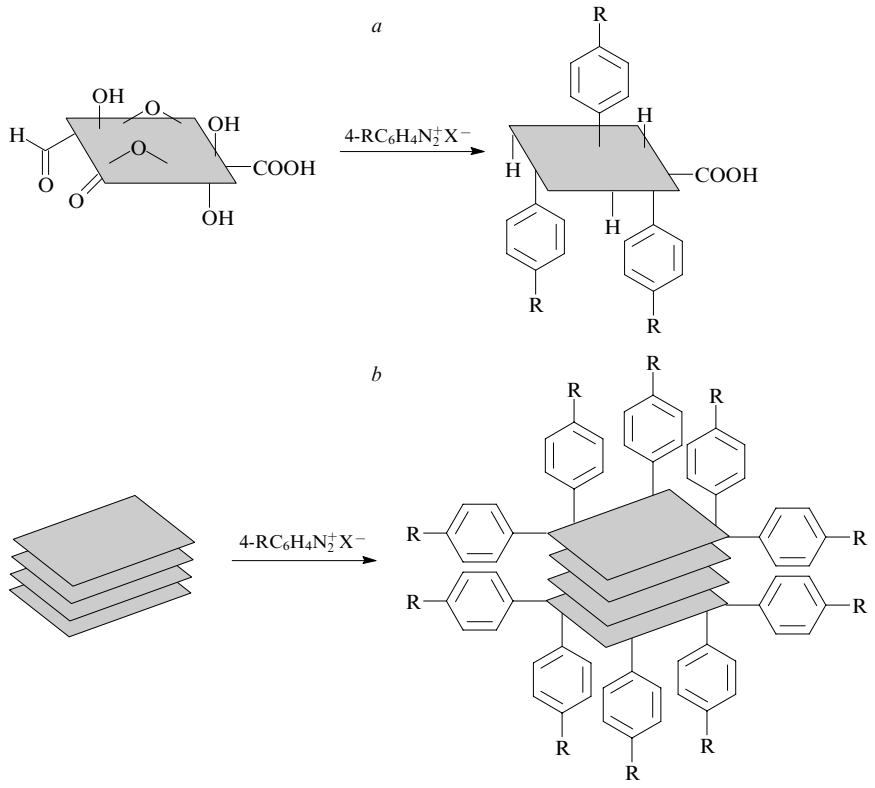


Figure 10. Reactions of graphene materials with diazonium salts.
(*a*) Reduction and functionalization of GO by aryl groups by the reaction with diazonium salts;[123] (*b*) cleavage of EG by selective edge functionalization[182] (R = NO_2,[123, 158, 159, 165, 199, 200] Br (Refs 123, 159, 182, 200), Cl,[123, 159, 200] I,[200] OMe,[123, 159] SO_3H,[201] CO_2H,[200] C≡CH,[200] C≡N.[200]

$0.01-0.02$ mg ml^{-1}. Another method is mechanical mixing of EG obtained by thermal reduction of GO with various diazonium salts in a mortar in the presence of an ionic liquid.[200] The graphene derivatives obtained in this way were also soluble in DMF. The solubility was higher for the products with aryl halide or arylnitro substituents ($0.25-0.45$ mg ml^{-1}) than for products with $Ar-CO_2H$, $Ar-C\equiv CH$, $Ar-C\equiv N$ type groups ($0.02-0.04$ mg ml^{-1}).

The diazonium salt modification is also possible for substrate-deposited mechanically exfoliated graphene[199] and for graphene nanoribbons obtained by chemical unrolling of nanotubes.[158] The single-layer graphenes were found to be 10 times more reactive than multilayer ones; and the edge carbon atoms are twice more reactive than the plane atoms.[199] In the case of graphene nanoribbons modified by aryl groups, the effect of covalent modification on the electronic properties of nanoribbons was noted and a kinetic model for describing the process was proposed.[158]

3. Supported nanoparticles of inorganic compounds

Currently the deposition of catalytic metal (platinum,[204–207] gold,[205, 208–213] palladium[205, 214]) and metal oxide [TiO_2,[143, 215] ZnO,[216] SnO_2,[217, 218] NiO,[218] MnO_2,[218] Mn_3O_4 (Ref. 219)] particles on the graphene surface (decoration) is under vigorous research as these composites are promising for catalytic, fuel cell and other applications. This is the subject of the recent review;[163] here we consider only briefly the key approaches to the preparation of nanocomposites.

Titanium and zinc oxides are large band gap semiconductors having photocatalytic activity upon UV irradiation: the electrons pass from the valence to the conduction band, thus leaving positively charged 'holes'. Owing to these electronic properties, the TiO_2 and ZnO particles can be used to reduce GO upon mere mixing of suspensions of both substances on exposure to UV light, for example:[143, 163, 216]

$$TiO_2 + h\nu \longrightarrow TiO_2(h^+ + e^-) \xrightarrow{C_2H_5OH} \longrightarrow TiO_2(e^-) + {}^{\bullet}C_2H_4OH + H^+,$$

$$TiO_2(e^-) + GO \longrightarrow TiO_2 + \text{reduced GO},$$

H^+ is hole.

The reaction affords partially reduced GO with TiO_2 or ZnO particles on the surface. The oxide particles are apparently bonded to the GO surface through the interaction with carboxy groups that are not affected during the reduction.[143]

The method provides single-layer graphenes with supported titanium dioxide particles of $2-7$ nm size. During the preparation of composites with ZnO, it is convenient to monitor the interaction between the components by observing the degree of ZnO luminescence quenching following the addition of GO dispersion.[163]

The metal particles are dispersed on the graphene surface by mixing a metal precursor (salt or acid, for example, Na_2PdCl_4, $HAuCl_4$, H_2PtCl_6), a graphene or GO dispersion and a reducing agent, and the resulting metal nanoparticles are stabilized on the CRG surface.[163, 208, 209] The reduction of GO and the precursor of metal particles can occur both simultaneously and successively. It was shown that the functional groups of GO act as nucleation sites for metal nanoparticles.[163, 209] The obtained nanocomposites can be deposited as a film on platinum or carbon electrodes for electrocatalytic applications. The studies aimed at simultaneous deposition of semiconductor and metal particles on the graphene surface for water decomposition processes are in progress (Fig. 11).[163] In these systems, the semiconductor is supposed to absorb light and initiate the oxidation and

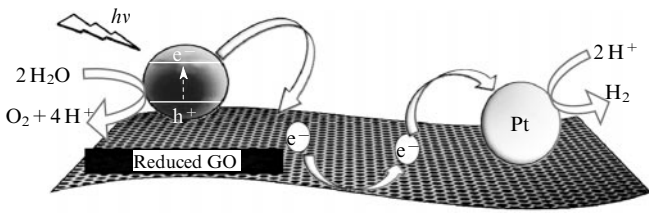


Figure 11. Scheme of the selective decomposition of water on two different catalytic sites supported on the same graphene sheet.[163]

the CRG plane should deliver the electrons along the two-dimensional carbon lattice to platinum nanoparticles, thus facilitating the reduction. The ability of CRG sheets to transfer electrons is also of interest for nanostructured solar cell applications.

IV. Conclusion

The most topical issue in the graphene chemistry is the possibility of control and fine tuning of the properties of synthesized graphenes — defectiveness, dimensions, content of functional groups (which represent a drawback for some applications and a necessary prerequisite for other applications). For performing stoichiometric reactions with the graphene surface, it would be of interest to create periodic deformations (defects) with enhanced reactivity in the lattice. There exists the problem of separation of graphene materials according to their polydispersity, and the research along this line has already been started.[63, 73, 220] As regards graphene nanoribbons, the goal is to develop reliable methods for targeted synthesis of nanoribbons with armchair and zigzag type edges, the nature of which affects the electronic properties of these materials. Of interest is the targeted change in the optical properties of graphene materials by controlled reduction of GO or its specific functionalization. The precise control of the border between p-doped and n-doped graphene regions can bring success in the design of the electron–hole p–n transition in graphene.

Graphene materials are very promising for the whole series of applications starting with electronics and ending with medicine. Therefore, at present, one of the primary tasks is the development of new and improving of the existing methods for the synthesis of graphenes and their colloidal dispersions that would allow preparing graphene materials in large amounts.

This work was supported by Grant from Korean Defense Acquisition Programme Administration and Agency for Defense Development. E D Grayfer wishes to thank Russian Science Support Foundation for their Grant 'The best postgraduates of RAS' and Novosibirsk Region Administration and Haldor Topsoe for their PhD scholarships.

References

1. H P Boehm, R Setton, E Stumpp *Pure Appl. Chem.* **66** 1893 (1994)
2. A K Geim, K S Novoselov *Nat. Mater.* **6** 183 (2007)
3. C N R Rao, A K Sood, K S Subrahmanyam, A Govindaraj *Angew. Chem., Int. Ed.* **48** 7752 (2009)
4. C N R Rao, A K Sood, R Voggu, K S Subrahmanyam *J. Phys. Chem. Lett.* **1** 572 (2010)
5. B Jang, A Zhamu *J. Mater. Sci.* **43** 5092 (2008)
6. A K Geim *Science* **324** 1530 (2009)
7. M J Allen, V C Tung, R B Kaner *Chem. Rev.* **110** 132 (2010)
8. C Soldano, A Mahmood, E Dujardin *Carbon* **48** 2127 (2010)
9. S Wang, P K Ang, Z Wang, A L L Tang, J T L Thong, K P Loh *Nano Lett.* **10** 92 (2010)
10. A H Castro Neto *Mater. Today* **13** (3) 12 (2010)
11. S Gilje, S Han, M Wang, K L Wang, R B Kaner *Nano Lett.* **7** 3394 (2007)
12. I Jung, D A Dikin, R D Piner, R S Ruoff *Nano Lett.* **8** 4283 (2008)
13. G Eda, G Fanchini, M Chhowalla *Nat. Nanotechnol.* **3** 270 (2008)
14. G Eda, M Chhowalla *Nano Lett.* **9** 814 (2009)
15. X Wang, L Zhi, K Müllen *Nano Lett.* **8** 323 (2008)
16. Y Xu, H Bai, G Lu, C Li, G Shi *J. Am. Chem. Soc.* **130** 5856 (2008)
17. G Eda, Y-Y Lin, S Miller, C-W Chen, W-F Su, M Chhowalla *Appl. Phys. Lett.* **92** 233305 (2008)
18. S Unarunotai, Y Murata, C E Chialvo, N Mason, I Petrov, R G Nuzzo, J S Moore, J A Rogers *Adv. Mater.* **22** 1072 (2010)
19. J K Wassei, R B Kaner *Mater. Today* **13** (3) 52 (2010)
20. S Stankovich, D A Dikin, G H B Dommett, K M Kohlhaas, E J Zimney, E A Stach, R D Piner, S T Nguyen, R S Ruoff *Nature (London)* **442** 282 (2006)
21. T Ramanathan, A A Abdala, S Stankovich, D A Dikin, M Herrera-Alonso, R D Piner, D H Adamson, H C Schniepp, X Chen, R S Ruoff, S T Nguyen, I A Aksay, R K Prud'homme, L C Brinson *Nat. Nanotechnol.* **3** 327 (2008)
22. A Yu, P Ramesh, M E Itkis, E Bekyarova, R C Haddon *J. Phys. Chem. C* **111** 7565 (2007)
23. S Park, D A Dikin, S T Nguyen, R S Ruoff *J. Phys. Chem. C* **113** 15801 (2009)
24. K P Loh, Q Bao, P K Ang, J Yang *J. Mater. Chem.* **20** 2277 (2010)
25. H Kim, A A Abdala, C W Macosko *Macromolecules* **43** 6515 (2010)
26. A V Murugan, T Muraliganth, A Manthiram *Chem. Mater.* **21** 5004 (2009)
27. M D Stoller, S Park, Y Zhu, J An, R S Ruoff *Nano Lett.* **8** 3498 (2008)
28. G Srinivas, Y Zhu, R Piner, N Skipper, M Ellerby, R Ruoff *Carbon* **48** 630 (2010)
29. K S Subrahmanyam, S R C Vivekchand, A Govindaraj, C N R Rao *J. Mater. Chem.* **18** 1517 (2008)
30. N Mohanty, V Berry *Nano Lett.* **8** 4469 (2008)
31. A J Patil, J L Vickery, T B Scott, S Mann *Adv. Mater.* **21** 3159 (2009)
32. J T Robinson, F K Perkins, E S Snow, Z Wei, P E Sheehan *Nano Lett.* **8** 3137 (2008)
33. C-H Lu, H-H Yang, C-L Zhu, X Chen, G-N Chen *Angew. Chem., Int. Ed.* **48** 4785 (2009)
34. H Jang, Y-K Kim, H-M Kwon, W-S Yeo, D-E Kim, D-H Min *Angew. Chem., Int. Ed.* **49** 5703 (2010)
35. H P Boehm, A Clauss, G O Fischer, U Hofmann, in *Proceedings of the 5th Conference on Carbon* (Oxford: Pergamon Press, 1962) p. 73
36. H P Boehm, A Clauss, G O Fischer, U Hofmann *Z. Naturforsch. B* **17** 150 (1962)
37. M Eizenberg, J M Blakely *Surf. Sci.* **82** 228 (1979)
38. T Aizawa, R Souda, S Otani, Y Ishizawa, C Oshima *Phys. Rev. Lett.* **64** 768 (1990)
39. C Oshima, A Nagashima *J. Phys.: Condens. Matter* **9** 1 (1997)
40. A J Van Bommel, J E Crombeen, A Van Tooren *Surf. Sci.* **48** 463 (1975)

41. A M Affoune, B L V Prasad, H Sato, T Enoki, Y Kaburagi, Y Hishiyama *Chem. Phys. Lett.* **348** 17 (2001)
42. H Shioyama *J. Mater. Sci. Lett.* **20** 499 (2001)
43. L M Viculis, J J Mack, R B Kaner *Science* **299** 1361 (2003)
44. L M Viculis, J J Mack, O M Mayer, H T Hahn, R B Kaner *J. Mater. Chem.* **15** 974 (2005)
45. X Lu, M Yu, H Huang, R S Ruoff *Nanotechnology* **10** 269 (1999)
46. K S Novoselov, A K Geim, S V Morozov, D Jiang, Y Zhang, S V Dubonos, I V Grigorieva, A A Firsov *Science* **306** 666 (2004)
47. K S Novoselov, D Jiang, F Schedin, T J Booth, V V Khotkevich, S V Morozov, A K Geim *Proc. Natl. Acad. Sci. USA* **102** 10451 (2005)
48. J C Meyer, A K Geim, M I Katsnelson, K S Novoselov, T J Booth, S Roth *Nature (London)* **446** 60 (2007)
49. M A Pimenta, G Dresselhaus, M S Dresselhaus, L G Cançado, A Jorio, R Saito *Phys. Chem. Chem. Phys.* **9** 1276 (2007)
50. Z Ni, Y Wang, T Yu, Z Shen *Nano Res.* **1** 273 (2008)
51. M S Dresselhaus, A Jorio, M Hofmann, G Dresselhaus, R Saito *Nano Lett.* **10** 751 (2010)
52. J Kim, F Kim, J Huang *Mater. Today* **13** (3) 28 (2010)
53. J Hass, W A de Heer, E H Conrad *J. Phys.: Condens. Matter* **20** 323202 (2008)
54. K S Kim, Y Zhao, H Jang, S Y Lee, J M Kim, K S Kim, J-H Ahn, P Kim, J-Y Choi, B H Hong *Nature (London)* **457** 706 (2009)
55. A Reina, X Jia, J Ho, D Nezich, H Son, V Bulovic, M S Dresselhaus, J Kong *Nano Lett.* **9** 30 (2009)
56. C Berger, Z Song, X Li, X Wu, N Brown, C Naud, D Mayou, T Li, J Hass, A N Marchenkov, E H Conrad, P N First, W A de Heer *Science* **312** 1191 (2006)
57. K S Subrahmanyam, L S Panchakarla, A Govindaraj, C N R Rao *J. Phys. Chem. C* **113** 4257 (2009)
58. L Zhi, K Müllen *J. Mater. Chem.* **18** 1472 (2008)
59. X Yang, X Dou, A Rouhanipour, L Zhi, H J Rider, K Müllen *J. Am. Chem. Soc.* **130** 4216 (2008)
60. S Park, R S Ruoff *Nat. Nanotechnol.* **4** 217 (2009)
61. J Zhu *Nat. Nanotechnol.* **3** 528 (2008)
62. G Cravotto, P Cintas *Chem. – Eur. J.* **16** 5246 (2010)
63. A A Green, M C Hersam *J. Phys. Chem. Lett.* **1** 544 (2010)
64. Y Zhu, S Murali, W Cai, X Li, J W Suk, J R Potts, R S Ruoff *Adv. Mater.* **22** 3906 (2010)
65. C N R Rao, K Biswas, K S Subrahmanyam, A Govindaraj *J. Mater. Chem.* **19** 2457 (2009)
66. C N R Rao, K S Subrahmanyam, H S S Ramakrishna Matte, B Abdulhakeem, A Govindaraj, B Das, P Kumar, A Ghosh, D J Late *Sci. Technol. Adv. Mater.* **11** 054502 (2010)
67. Y Hernandez, V Nicolosi, M Lotya, F M Blighe, Z Sun, S De, I T McGovern, B Holland, M Byrne, Y K Gun'ko, J J Boland, P Niraj, G Duesberg, S Krishnamurthy, R Goodhue, J Hutchison, V Scardaci, A C Ferrari, J N Coleman *Nat. Nanotechnol.* **3** 563 (2008)
68. C E Hamilton, J R Lomeda, Z Sun, J M Tour, A R Barron *Nano Lett.* **9** 3460 (2009)
69. Y Hernandez, M Lotya, D Rickard, S D Bergin, J N Coleman *Langmuir* **26** 3208 (2010)
70. J Wang, Y Hernandez, M Lotya, J N Coleman, W J Blau *Adv. Mater.* **21** 2430 (2009)
71. A B Bourlinos, V Georgakilas, R Zboril, T A Steriotis, A K Stubos *Small* **5** 1841 (2009)
72. M Lotya, Y Hernandez, P J King, R J Smith, V Nicolosi, L S Karlsson, F M Blighe, S De, Z Wang, I T McGovern, G S Duesberg, J N Coleman *J. Am. Chem. Soc.* **131** 3611 (2009)
73. A A Green, M C Hersam *Nano Lett.* **9** 4031 (2009)
74. Y Liang, D Wu, X Feng, K Müllen *Adv. Mater.* **21** 1679 (2009)
75. M Lotya, P J King, U Khan, S De, J N Coleman *ACS Nano* **4** 3155 (2010)
76. S Stankovich, R D Piner, X Chen, N Wu, S T Nguyen, R S Ruoff *J. Mater. Chem.* **16** 155 (2006)
77. Y Liu, L Gao, J Sun, Y Wang, J Zhang *Nanotechnology* **20** 465605 (2009)
78. X Li, X Wang, L Zhang, S Lee, H Dai *Science* **319** 1229 (2008)
79. R Hao, W Qian, L Zhang, Y Hou *Chem. Commun.* 6576 (2008)
80. Q Su, S Pang, V Alijani, C Li, X Feng, K Müllen *Adv. Mater.* **21** 3191 (2009)
81. X Dong, C Y Su, W Zhang, J Zhao, Q Ling, W Huang, P Chen, L-J Li *Phys. Chem. Chem. Phys.* **12** 2164 (2010)
82. H Liu, J Gao, M Xue, N Zhu, M Zhang, T Cao *Langmuir* **25** 12006 (2009)
83. F Li, Y Bao, J Chai, Q Zhang, D Han, L Niu *Langmuir* **26** 12314 (2010)
84. X Dong, Y Shi, Y Zhao, D Chen, J Ye, Y Yao, F Gao, Z Ni, T Yu, Z Shen, Y Huang, P Chen, L-J Li *Phys. Rev. Lett.* **102** 135501 (2009)
85. J N Coleman *Adv. Funct. Mater.* **19** 3680 (2009)
86. L Vaisman, H D Wagner, G Marom *Adv. Colloid Interface Sci.* **128 – 130** 37 (2006)
87. D Tasis, N Tagmatarchis, A Bianco, M Prato *Chem. Rev.* **106** 1105 (2006)
88. P Blake, P D Brimicombe, R R Nair, T J Booth, D Jiang, F Schedin, L A Ponomarenko, S V Morozov, H F Gleeson, E W Hill, A K Geim, K S Novoselov *Nano Lett.* **8** 1704 (2008)
89. S Vadukumpully, J Paul, S Valiyaveettil *Carbon* **47** 3288 (2009)
90. C E Hamilton, J R Lomeda, Z Sun, J M Tour, A R Barron *Nano Res.* **3** 138 (2010)
91. A Celzard, J F Marêché, G Furdin *Prog. Mater. Sci.* **50** 93 (2005)
92. G Furdin *Fuel* **77** 479 (1998)
93. D D L Chung *J. Mater. Sci.* **22** 4190 (1987)
94. M S Dresselhaus, G Dresselhaus *Adv. Phys.* **51** 1 (2002)
95. G Chen, W Weng, D Wu, C Wu, J Lu, P Wang, X Chen *Carbon* **42** 753 (2004)
96. L M Veca, M J Meziani, W Wang, X Wang, F Lu, P Zhang, Y Lin, R Fee, J W Connell, Y-P Sun *Adv. Mater.* **21** 2088 (2009)
97. A E Teplykh, S G Bogdanov, Y A Dorofeev, A N Pirogov, Y N Skryabin, V G Makotchenko, A S Nazarov, V E Fedorov *Cryst. Rep.* **51** (Suppl. 1) 62 (2006)
98. S G Bogdanov, E Z Valiev, Y A Dorofeev, A N Pirogov, Y N Skryabin, V G Makotchenko, A S Nazarov, V E Fedorov *Cryst. Rep.* **51** (Suppl. 1) 12 (2006)
99. E D Grayfer, A S Nazarov, V G Makotchenko, S-J Kim, V E Fedorov *J. Mater. Chem.* **21** 3410 (2011)
100. J H Lee, D W Shin, V G Makotchenko, A S Nazarov, V E Fedorov, Y H Kim, J-Y Choi, J M Kim, J-B Yoo *Adv. Mater.* **21** 4383 (2009)
101. J H Lee, D W Shin, V G Makotchenko, A S Nazarov, V E Fedorov, J H Yoo, S M Yu, J-Y Choi, J M Kim, J-B Yoo *Small* **6** 58 (2010)
102. Z Osváth, Al Darabont, P Nemes-Incze, E Horváth, Z E Horváth, L P Biró *Carbon* **45** 3022 (2007)
103. W Qian, R Hao, Y Hou, Y Tian, C Shen, H Gao, X Liang *Nano Res.* **2** 706 (2009)
104. I Janowska, K Chizari, O Ersen, S Zafeiratos, D Soubane, V Da Costa, V Speisser, C Boeglin, M Houllé, D Bégin, D Plee, M-J Ledoux, C Pham-Huu *Nano Res.* **3** 126 (2010)
105. S Stankovich, D A Dikin, R D Piner, K A Kohlhaas, A Kleinhammes, Y Jia, Y Wu, S T Nguyen, R S Ruoff *Carbon* **45** 1558 (2007)
106. D R Dreyer, S Park, W Bielawski, R S Ruoff *Chem. Soc. Rev.* **39** 228 (2010)
107. G Eda, M Chhowalla *Adv. Mater.* **22** 2392 (2010)

108. B C Brodie *Philos. Trans. R. Soc. London* **149** 249 (1859)
109. L Staudenmaier *Ber. Dtsch. Chem. Ges.* **31** 1481 (1898)
110. W S Hummers, R E Offeman *J. Am. Chem. Soc.* **80** 1339 (1958)
111. N I Kovtyukhova, P J Ollivier, B R Martin, T E Mallouk, S A Chizhik, E V Buzaneva, A D Gorchinskiy *Chem. Mater.* **11** 771 (1999)
112. A Buchsteiner, A Lerf, J Pieper *J. Phys. Chem. B* **110** 22328 (2006)
113. A Lerf, H He, M Forster, J Klinowski *J. Phys. Chem. B* **102** 4477 (1998)
114. H-K Jeong, Y P Lee, R J W E Lahaye, M-H Park, K H An, I J Kim, C-W Yang, C Y Park, R S Ruoff, Y H Lee *J. Am. Chem. Soc.* **130** 1362 (2008)
115. T Szabó, O Berkesi, P Forgó, K Josepovits, Y Sanakis, D Petridis, I Dékány *Chem. Mater.* **18** 2740 (2006)
116. G I Titelman, V Gelman, S Bron, R L Khalfin, Y Cohen, H Bianco-Peled *Carbon* **43** 641 (2005)
117. D Cai, M Song *J. Mater. Chem.* **17** 3678 (2007)
118. J I Paredes, S Villar-Rodil, A Martínez-Alonso, J M D Tascón *Langmuir* **24** 10560 (2008)
119. Y Zhu, M D Stoller, W Cai, A Velamakanni, R D Piner, D Chen, R S Ruoff *ACS Nano* **4** 1227 (2010)
120. S Park, J An, I Jung, R D Piner, S J An, X Li, A Velamakanni, R S Ruoff *Nano Lett.* **9** 1593 (2009)
121. A B Bourlinos, D Gournis, D Petridis, T Szabó, A Szeri, I Dékány *Langmuir* **19** 6050 (2003)
122. D Li, M B Müller, S Gilje, R B Kaner, G G Wallace *Nat. Nanotechnol.* **3** 101 (2008)
123. J R Lomeda, C D Doyle, D V Kosynkin, W-F Hwang, J M Tour *J. Am. Chem. Soc.* **130** 16201 (2008)
124. V C Tung, M J Allen, Y Yang, R B Kaner *Nat. Nanotechnol.* **4** 25 (2009)
125. G Wang, J Yang, J Park, X Gou, B Wang, H Liu, J Yao *J. Phys. Chem. C* **112** 8192 (2008)
126. H-J Shin, K K Kim, A Benayad, S-M Yoon, H K Park, I-S Jung, M H Jin, H-K Jeong, J M Kim, J-Y Choi, Y H Lee *Adv. Funct. Mater.* **19** 1987 (2009)
127. W Gao, L B Alemany, L Ci, P M Ajayan *Nat. Chem.* **1** 403 (2009)
128. Y Chen, X Zhang, P Yu, Y Ma *Chem. Commun.* 4527 (2009)
129. N Mohanty, A Nagaraja, J Armesto, V Berry *Small* **6** 226 (2010)
130. Z Fan, K Wang, T Wei, J Yan, L Song, B Shao *Carbon* **48** 1686 (2010)
131. Q Yang, X Pan, F Huang, K Li *J. Phys. Chem. C* **114** 3811 (2010)
132. S Park, J An, R D Piner, I Jung, D Yang, A Velamakanni, S T Nguyen, R S Ruoff *Chem. Mater.* **20** 6592 (2008)
133. X Fan, W Peng, Y Li, X Li, S Wang, G Zhang, F Zhang *Adv. Mater.* **20** 4490 (2008)
134. M J McAllister, J-L Li, D H Adamson, H C Schniepp, A A Abdala, J Liu, M Herrera-Alonso, D L Milius, R Car, R K Prud'homme, I A Aksay *Chem. Mater.* **19** 4396 (2007)
135. H C Schniepp, J-L Li, M J McAllister, H Sai, M Herrera-Alonso, D H Adamson, R K Prud'homme, R Car, D A Saville, I A Aksay *J. Phys. Chem. B* **110** 8535 (2006)
136. O Akhavan *Carbon* **48** 509 (2010)
137. Y Zhu, S Murali, M D Stoller, A Velamakanni, R D Piner, R S Ruoff *Carbon* **48** 2118 (2010)
138. H Wang, J T Robinson, X Li, H Dai *J. Am. Chem. Soc.* **131** 9910 (2009)
139. Y Zhou, Q Bao, L A L Tang, Y Zhong, K P Loh *Chem. Mater.* **21** 2950 (2009)
140. C Nethravathi, M Rajamathi *Carbon* **46** 1994 (2008)
141. W Chen, L Yan, P R Bangal *Carbon* **48** 1146 (2010)
142. H-L Guo, X-F Wang, Q-Y Qian, F-B Wang, X-H Xia *ACS Nano* **3** 2653 (2009)
143. G Williams, B Seger, P V Kamat *ACS Nano* **2** 1487 (2008)
144. E Widenkvist, D W Boukhvalov, S Rubino, S Akhtar, J Lu, R A Quinlan, M I Katsnelson, K Leifer, H Grennberg, U Jansson *J. Phys. D: Appl. Phys.* **42** 112003 (2009)
145. N-W Pu, C-A Wang, Y Sung, Y-M Liu, M-D Ger *Mater. Lett.* **63** 1987 (2009)
146. C Vallés, C Drummond, H Saadaoui, C A Furtado, M He, O Roubeau, L Ortolani, M Monthioux, A Pgnicaud *J. Am. Chem. Soc.* **130** 15802 (2008)
147. X Li, G Zhang, X Bai, X Sun, X Wang, E Wang, H Dai *Nat. Nanotechnol.* **3** 538 (2008)
148. H Wang, X Wang, X Li, H Dai *Nano Res.* **2** 336 (2009)
149. P K Ang, S Wang, Q Bao, J T L Thong, K P Loh *ACS Nano* **3** 3587 (2009)
150. L Jiao, L Zhang, X Wang, G Diankov, H Dai *Nature (London)* **458** 877 (2009)
151. D V Kosynkin, A L Higginbotham, A Sinitskii, J R Lomeda, A Dimiev, B K Price, J M Tour *Nature (London)* **458** 872 (2009)
152. Z Zhang, Z Sun, J Yao, D V Kosynkin, J M Tour *J. Am. Chem. Soc.* **131** 13460 (2009)
153. A G Cano-Márquez, F J Rodríguez-Macías, J Campos-Delgado, C G Espinosa-González, F Tristán-López, D Ramírez-González, D A Cullen, D J Smith, M Terrones, Y I Vega-Cantú *Nano Lett.* **9** 1527 (2009)
154. I Janowska, O Ersen, T Jacob, P Vennégues, D Bégin, M-J Ledoux, C Pham-Huu *Appl. Catal., A* **371** 22 (2009)
155. A L Elías, A R Botello-Méndez, D Meneses-Rodriguez, V J González, D Ramírez-González, L Ci, E Muñoz-Sandoval, P M Ajayan, H Terrones, M Terrones *Nano Lett.* **10** 366 (2010)
156. L Jiao, X Wang, G Diankov, H Wang, H Dai *Nat. Nanotechnol.* **5** 321 (2010)
157. M Terrones *ACS Nano* **4** 1775 (2010)
158. A Sinitskii, A Dimiev, D A Corley, A A Fursina, D V Kosynkin, J M Tour *ACS Nano* **4** 1949 (2010)
159. Y Zhu, A L Higginbotham, J M Tour *Chem. Mater.* **21** 5284 (2009)
160. S Wang, L A I Tang, Q Bao, M Lin, S Deng, B M Goh, K P Loh *J. Am. Chem. Soc.* **131** 16832 (2009)
161. K A Worsley, P Ramesh, S K Mandal, S Niyogi, M E Itkis, R C Haddon *Chem. Phys. Lett.* **445** 51 (2007)
162. M Choucair, P Thordarson, J A Stride *Nat. Nanotechnol.* **4** 30 (2009)
163. P V Kamat *J. Phys. Chem. Lett.* **1** 520 (2010)
164. C Shan, H Yang, D Han, Q Zhang, A Ivaska, L Niu *Langmuir* **25** 12030 (2009)
165. E Bekyarova, M E Itkis, P Ramesh, C Berger, M Sprinkle, W A de Heer, R C Haddon *J. Am. Chem. Soc.* **131** 1336 (2009)
166. J O Sofo, A S Chaudhari, G D Barber *Phys. Rev. B* **75** 153401 (2007)
167. D C Elias, R R Nair, T M G Mohiuddin, S V Morozov, P Blake, M P Halsall, A C Ferrari, D W Boukhvalov, M I Katsnelson, A K Geim, K S Novoselov *Science* **323** 610 (2009)
168. Z Luo, T Yu, K-j Kim, Z Ni, Y You, S Lim, Z Shen, S Wang, J Lin *ACS Nano* **3** 1781 (2009)
169. S Ryu, M Y Han, J Maultzsch, T F Heinz, P Kim, M L Steigerwald, L E Brus *Nano Lett.* **8** 4597 (2008)
170. Y Sato, H Watano, R Hagiwara, Y Ito *Carbon* **44** 664 (2006)
171. S Pekker, J-P Salvetat, E Jakab, J-M Bonard, L Forró *J. Phys. Chem. B* **105** 7938 (2001)
172. D E Bergbreiter, J M Killough *J. Am. Chem. Soc.* **100** 2126 (1978)
173. S Bittolo Bon, L Valentini, R Verdejo, J L Garcia Fierro, L Peponi, M A Lopez-Manchado, J M Kenny *Chem. Mater.* **21** 3433 (2009)

174. S Bittolo Bon, L Valentini, R M Moustafa, F M Jradi, B R Kaafarani, R Verdejo, M A Lopez-Manchado, J M Kenny *J. Phys. Chem. C* **114** 11252 (2010)
175. L Valentini, M Cardinali, S Bittolo Bon, D Bagnis, R Verdejo, M A Lopez-Manchado, J M Kenny *J. Mater. Chem.* **20** 995 (2010)
176. R R Nair, W Ren, R Jalil, I Riaz, V G Kravets, L Britnell, P Blake, F Schedin, A S Mayorov, S Yuan, M I Katsnelson, H -M Cheng, W Strupinski, L G Bulusheva, A V Okotrub, I V Grigorieva, A N Grigorenko, K S Novoselov, A K Geim *Small* **6** 2877 (2010)
177. J T Robinson, J S Burgess, C E Junkermeier, S C Badescu, T L Reinecke, F K Perkins, M K Zalalutdinov, J W Baldwin, J C Culbertson, P E Sheehan, E S Snow *Nano Lett.* **10** 3001 (2010)
178. F Withers, M Dubois, A K Savchenko *Phys. Rev. B* **82** 073403 (2010)
179. H Liu, S Ryu, Z Chen, M L Steigerwald, C Nuckolls, L E Brus *J. Am. Chem. Soc.* **131** 17099 (2009)
180. M Quintana, K Spyrou, M Grzelczak, W R Browne, P Rudolf, M Prato *ACS Nano* **4** 3527 (2010)
181. X Sun, Z Liu, K Welsher, J T Robinson, A Goodwin, S Zaric, H Dai *Nano Res.* **1** 203 (2008)
182. Z Sun, S-i Kohama, Z Zhang, J R Lomeda, J M Tour *Nano Res.* **3** 117 (2010)
183. S Niyogi, E Bekyarova, M E Itkis, J L McWilliams, M A Hamon, R C Haddon *J. Am. Chem. Soc.* **128** 7720 (2006)
184. Y Cao, J Feng, P Wu *Carbon* **48** 1683 (2010)
185. Z Liu, J T Robinson, X Sun, H Dai *J. Am. Chem. Soc.* **130** 10876 (2008)
186. Y Xu, Z Liu, Xid Zhang, Y Wang, J Tian, Y Huang, Y Ma, Xia Zhang, Y Chen *Adv. Mater.* **21** 1275 (2009)
187. Z-B Liu, Y-F Xu, X-Y Zhang, X-L Zhang, Y-S Chen, J-G Tian *J. Phys. Chem. B* **113** 9681 (2009)
188. X Zhang, Y Huang, Y Wang, Y Ma, Z Liu, Y Chen *Carbon* **47** 334 (2009)
189. S Wang, P-J Chia, L-L Chua, L-H Zhao, R-Q Png, S Sivaramakrishnan, M Zhou, R G-S Goh, R H Friend, A T-S Wee, P K-H Ho *Adv. Mater.* **20** 3440 (2008)
190. H Yang, C Shan, F Li, D Han, Q Zhang, L Niu *Chem. Commun.* 3880 (2009)
191. L M Veca, F Lu, M J Meziani, L Cao, P Zhang, G Qi, L Qu, M Shrestha, Y-P Sun *Chem. Commun.* 2565 (2009)
192. H J Salavagione, M A Gómez, G Martínez *Macromolecules* **42** 6331 (2009)
193. S Stankovich, R D Piner, S B T Nguyen, R S Ruoff *Carbon* **44** 3342 (2006)
194. C Xu, X Wu, J Zhu, X Wang *Carbon* **46** 386 (2008)
195. R Salvio, S Krabbenborg, W J M Naber, A H Velders, D N Reinhoudt, W G van der Wiel *Chem. – Eur. J.* **15** 8235 (2009)
196. V Georgakilas, A B Bourlinos, R Zboril, T A Steriotis, P Dallas, A K Stubos, C Trapalis *Chem. Commun.* **46** 1766 (2010)
197. J Shen, Y Hu, C Li, C Qin, M Ye *Small* **5** 82 (2009)
198. N Liu, F Luo, H Wu, Y Liu, C Zhang, J Chen *Adv. Funct. Mater.* **18** 1518 (2008)
199. R Sharma, J H Baik, C J Perera, M S Strano *Nano Lett.* **10** 398 (2010)
200. Z Jin, J R Lomeda, B K Price, W Lu, Y Zhu, J M Tour *Chem. Mater.* **21** 3045 (2009)
201. Y Si, E T Samulski *Nano Lett.* **8** 1679 (2008)
202. Y Ying, R K Saini, F Liang, A K Sadana, W E Billups *Org. Lett.* **5** 1471 (2003)
203. F Liang, J M Beach, P K Rai, W Guo, R H Hauge, M Pasquali, R E Smalley, W E Billups *Chem. Mater.* **18** 1520 (2006)
204. B Seger, P V Kamat *J. Phys. Chem. C* **113** 7990 (2009)
205. C Xu, X Wang, J Zhu *J. Phys. Chem. C* **112** 19841 (2008)
206. E Yoo, T Okata, T Akita, M Kohyama, J Nakamura, I Honma *Nano Lett.* **9** 2255 (2009)
207. Y Si, E T Samulski *Chem. Mater.* **20** 6792 (2008)
208. R Muszynski, B Seger, P V Kamat *J. Phys. Chem. C* **112** 5263 (2008)
209. G Goncalves, P A A P Marques, C M Granadeiro, H I S Nogueira, M K Singh, J Grácio *Chem. Mater.* **21** 4796 (2009)
210. K Jasuja, V Berry *ACS Nano* **3** 2358 (2009)
211. Y-K Kim, H-K Na, Y W Lee, H Jang, S W Han, D-H Min *Chem. Commun.* **46** 3185 (2010)
212. B-S Kong, J Geng, H-T Jung *Chem. Commun.* 2174 (2009)
213. Y-K Kim, H-K Na, D-H Min *Langmuir* **26** 13065 (2010)
214. R S Sundaram, C Gómez-Navarro, K Balasubramanian, M Burghard, K Kern *Adv. Mater.* **20** 3050 (2008)
215. D Wang, D Choi, J Li, Z Yang, Z Nie, R Kou, D Hu, C Wang, L V Saraf, J Zhang, I A Aksay, J Liu *ACS Nano* **3** 907 (2009)
216. G Williams, P V Kamat *Langmuir* **25** 13869 (2009)
217. S-M Paek, E Yoo, I Honma *Nano Lett.* **9** 72 (2009)
218. D Wang, R Kou, D Choi, Z Yang, Z Nie, J Li, L V Saraf, D Hu, J Zhang, G L Graff, J Liu, M A Pope, I A Aksay *ACS Nano* **4** 1587 (2010)
219. H Wang, L-F Cui, Y Yang, H Sanchez Casalongue, J T Robinson, Y Liang, Y Cui, H Dai *J. Am. Chem. Soc.* **132** 13978 (2010)
220. Z-S Wu, W Ren, L Gao, B Liu, C Jiang, H-M Cheng *Carbon* **47** 493 (2009)