

## Photochemical chlorination of nanodiamond and interaction of its modified surface with C-nucleophiles

G. V. Lisichkin, V. V. Korol'kov,\* B. N. Tarasevich, I. I. Kulakova, and A. V. Karpukhin

Department of Chemistry, M. V. Lomonosov Moscow State University,  
1 Leninskie Gory, 119992 Moscow, Russian Federation.  
Fax: +7 (495) 932 8846. E-mail: korolkov@list.ru

A procedure for the photochemical chlorination of nanodiamond by molecular chlorine in the liquid phase was proposed. This process was studied quantitatively for the first time. Hydrolytic stability of the chlorinated nanodiamond surface in air and in a 0.05 M solution of NaOH was determined. A possibility of disintegration of the initial aggregates (<60  $\mu\text{m}$ ) to finer aggregates (<200 nm) was shown. The reactions of a series of C-nucleophiles (organolithium reagents,  $\text{CN}^-$  ion) with the chlorinated surface were carried out.

**Key words:** nanodiamond, surface chemistry, grafted surface compounds, organolithium compounds, IR spectroscopy.

Natural and synthetic diamonds possess several unique physicochemical properties that attract significant interest in these systems as industrially important materials.

Diversity of diamond materials should be mentioned. These are single crystals and powders of natural and synthetic diamonds of different dispersity, ultradispersed diamonds produced by detonation synthesis, and diamond films prepared by carbon deposition from the gaseous phase onto different supports. All these materials are characterized by the crystalline diamond structure. The properties of synthetic diamond materials depend substantially on the method of preparation and, which is especially important for ultradispersed diamonds produced by detonation synthesis, on the type of functional groups on the surface.

Therefore, chemical and physicochemical methods for the directed modification of the surface of diamond materials become very significant. The purpose of this modification is the preparation of the predominantly monofunctional layer of a grafted surface compound of organic or inorganic nature on the surface of a diamond material. Thus, chemical modification of diamond powders results in the creation of a new class of promising materials, because they combine the unique properties of diamond and specific properties of the grafted chemical compound.<sup>1</sup>

Halogenation of pre-hydrogenated diamonds is a convenient method for activation of their surface by the creation of electrophilic centers capable of further interacting with a wide set of nucleophilic reagents. This approach provides wide possibilities for the further surface modification of both nanodiamond<sup>2,3</sup> and diamonds of other types.<sup>4</sup> Since quantitative data on the chlorination

of nanodiamond and other diamond materials are virtually lacking, in the present work we aimed at studying the regularities of the liquid-phase chlorination of nanodiamond by molecular chlorine and the interaction of the chlorinated surface with organolithium reagents and  $\text{CN}^-$  ions.

### Experimental

Nanodiamond (UDA-SF trade mark, Joint-Stock Co. "Almaznyi Tsentr," St. Petersburg, Russia) was produced according to technical conditions TU 05121441-275-95. The content of diamond and non-diamond carbon was 98.75 and 0.8%, respectively, and the ash residue was 0.45% (ignoring volatile admixtures). The nanodiamond is a light gray powder with  $S_{\text{sp}} = 284 \pm 1 \text{ m}^2 \text{ g}^{-1}$  and a size of primary diamond particles of ~4–5 nm. Solutions of methyl- and *n*-butyllithium (1.7 and 2.5 mol L<sup>-1</sup>, respectively) were purchased from Aldrich. Solutions of organolithium reagents RLi (R = Me, Bu<sup>n</sup>, *n*-C<sub>6</sub>H<sub>13</sub>, *n*-C<sub>16</sub>H<sub>33</sub>, *n*-C<sub>18</sub>H<sub>37</sub>, *cyclo*-C<sub>6</sub>H<sub>11</sub>, Ph) were synthesized using standard procedures.<sup>5</sup> The concentration of an organolithium reagent in solutions was varied from 0.9 to 1.2 mol L<sup>-1</sup>. Hydrogen was purchased from the Joint-Stock Co. "Balashikhinskii Kislородnyi Zavod" and corresponds to the state technical conditions GOST 3022-80, trade mark A (volume content of H<sub>2</sub> > 99.99%, O<sub>2</sub> + N<sub>2</sub> < 0.01%, H<sub>2</sub>O < 0.02%).

The nanodiamond was treated with hydrogen at 800 °C for 5 h in a flow-type quartz reactor.

Molecular chlorine obtained by the reaction of potassium bichromate with HCl was dissolved in CCl<sub>4</sub> until saturation (5.6 wt.%). Chlorination was carried out at room temperature with continuous stirring. Irradiation with the visible or UV light was used to initiate the photochemical reaction. In the first case, the reaction was conducted in a molybdenum-glass reactor using

a 150-W incandescent lamp remote at 5–6 cm from the reactor. In the second case, a quartz reactor and an SVD-120A UV lamp remote at 10 cm from the reactor were used. In both cases, chlorination was carried out under argon. After chlorination the sample was washed with anhydrous  $\text{CCl}_4$ , and the residue was separated on a centrifuge. It was first dried at 70–80 °C (7–10 Torr) and then kept for 5–6 h at 70–80 °C (0.1–0.2 Torr) to remove adsorbed compounds.

The chlorine concentration in the nanodiamond sample was determined by X-ray fluorescence spectroscopy (Spektroskan-V instrument) using the preliminarily obtained calibration curve.

Reactions of alkyllithium reagents with chlorinated nanodiamond were carried out by the addition of 20 mL of a solution of the corresponding RLi to 300–500 mg of nanodiamond under argon, then the reaction mixture was ultrasonicated (50 W,  $35 \pm 10\%$  kHz) for 1 h and left for 12 h. Then distilled water was carefully added with intense cooling and stirring to the reaction mixture to decompose alkyllithium reagent excess. After the end of the vigorous reaction, concentrated HCl was poured to the resulting suspension. The modified samples were washed and isolated by centrifuging first in aqueous solutions with an addition of 0.1 M HCl to decompose the suspension and then in acetone. Thus prepared samples were kept for 1 h in a vacuum desiccator above  $\text{P}_2\text{O}_5$  and then for 5–6 h at 160–170 °C (0.1–0.2 Torr).

The interaction of chlorinated nanodiamond with sodium cyanide was carried out for 72 h at  $\sim 20$  °C with periodical ultrasonication in DMSO dehydrated by distillation above  $\text{CaH}_2$ .

The modified sample was isolated by centrifuging in water and then in acetone and kept *in vacuo* similarly to the alkylated samples.

IR spectra were recorded on a Thermo Nicolet IR200 FT-IR spectrometer in KBr pellets (resolution  $4\text{ cm}^{-1}$ , scan number 32).

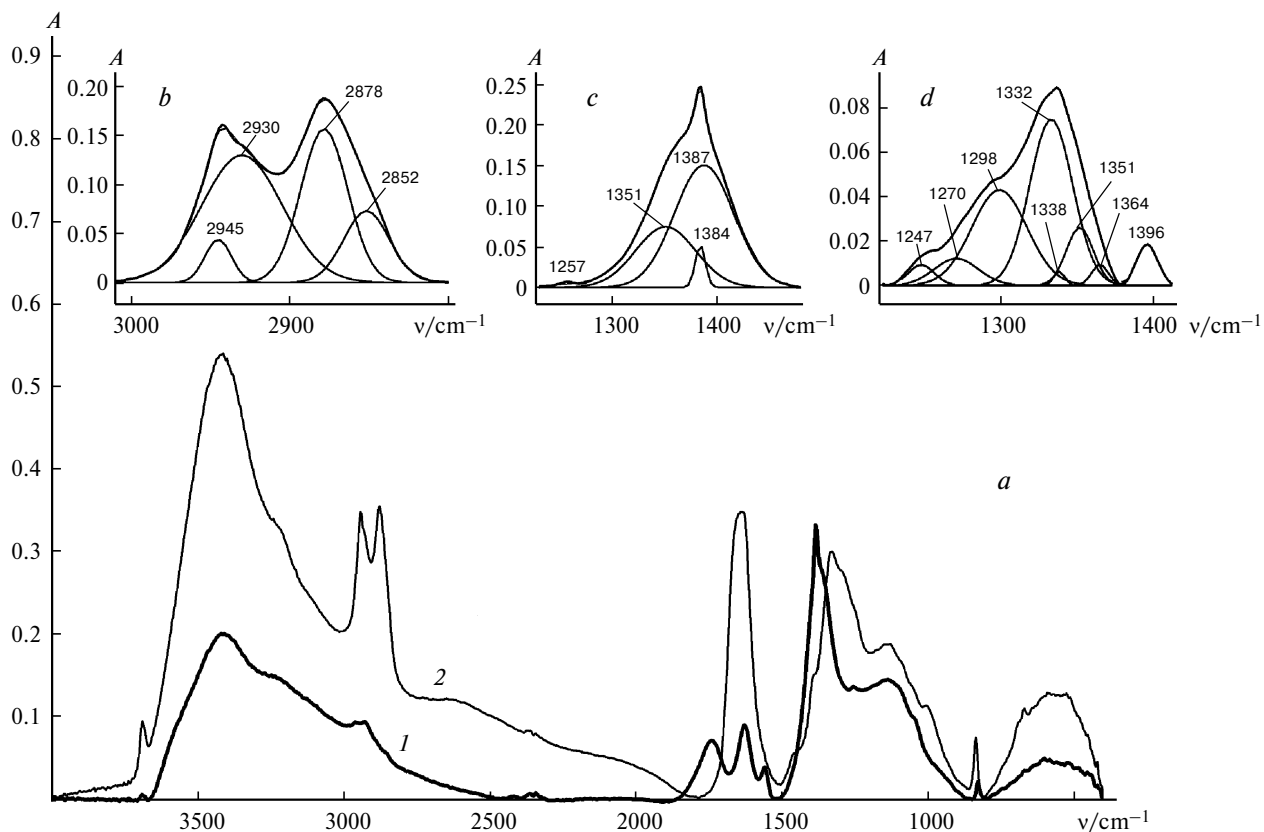
Small sizes of primary nanodiamond particles, a high specific surface, many surface functional groups with characteristic absorption bands in the IR region, and a low intensity of the intrinsic absorption of the diamond at  $4000\text{--}400\text{ cm}^{-1}$  make it possible to use IR absorption spectroscopy for studying the qualitative chemical composition of the nanodiamond surface during its chemical modification.

Standard tabulated data<sup>6,7</sup> were used to assign absorption bands to structural fragments.

Electronic microphotographs were obtained on transmission (LEO912 AB OMEGA, 120 kV) and scanning (Hitachi S520) electron microscopes.

## Results and Discussion

**Chemical composition of the initial nanodiamond surface.** In the IR spectrum of the initial nanodiamond (Fig. 1) the absorption is observed at  $3700\text{--}2800$  and  $1850\text{--}820\text{ cm}^{-1}$ . The high-frequency region contains an intense band of the H-bonded surface hydroxyl groups and adsorbed water with a broad maximum at  $3420\text{ cm}^{-1}$  with a complicated shape and the absorption of the non-



**Fig. 1.** IR spectra of (a) the initial nanodiamond before (1) and after its treatment with hydrogen (2) and the results of deconvolution of the band contour at  $3000\text{--}2800\text{ cm}^{-1}$  (b) and at  $1450\text{--}1250\text{ cm}^{-1}$  for the initial (c) and hydrogenated nanodiamond (d).

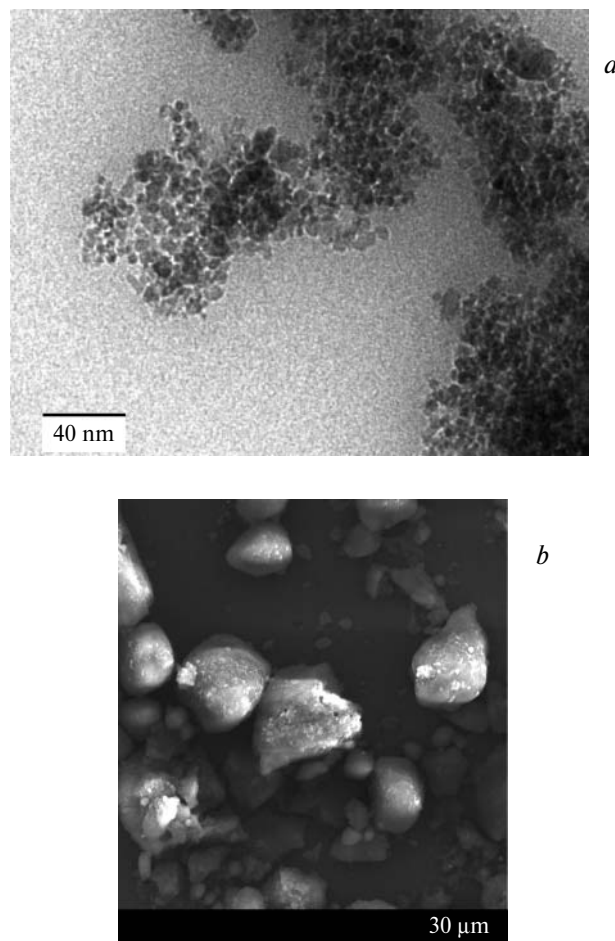
associated OH groups (narrow low-intensity peak at  $3690\text{ cm}^{-1}$ ). Weak bands at  $2953$ ,  $2926$ , and  $2853\text{ cm}^{-1}$  appear in the region of stretching vibrations of the C—H bonds, which indicates that the initial nanodiamond surface contains some amount of hydride groups. The absorption band with a maximum at  $1741\text{ cm}^{-1}$  is caused by the presence of the carbonyl groups on the nanodiamond surface.<sup>8,9</sup> Bending vibrations of adsorbed water molecules are observed at  $1630\text{ cm}^{-1}$  (the frequency of these vibrations usually lies within  $1630\pm 10\text{ cm}^{-1}$ ). The band at  $1560\text{ cm}^{-1}$  belongs, most likely, to the asymmetric vibration of the  $\text{COO}^-$  group; the corresponding band of the symmetric vibration is usually less intense, appears at  $\sim 1400\text{ cm}^{-1}$ , and is overlapped with the more intense absorption of other groups. The narrow intense peak at  $1380\text{ cm}^{-1}$  is likely caused by the presence of nitrates remained on the nanodiamond surface during isolation from the raw materials using nitric acid. The presence of a noticeable amount of nitrogen on the surface of the initial nanodiamond is confirmed by the data of X-ray photoelectron spectroscopy (XPS) (Table 1). The  $1500\text{--}1000\text{ cm}^{-1}$  interval contains a series of overlapped poorly resolved bands, which impedes their detailed assignment. The frequency region below  $1500\text{ cm}^{-1}$  exhibits different stretching and bending skeletal vibrations, including the bending vibrations of O—H bonds in alcohols and C—O—C groups (broad bands at  $1253$  and  $1137\text{ cm}^{-1}$ ). A group of bands caused by defect states of the crystalline diamond lattice appears in the same region ( $1400\text{--}1000\text{ cm}^{-1}$ ).

The presence of these oxygen-containing groups on the surface is mainly responsible for the aggregation of diamond particles. Stability of the aggregates of the nanodiamond particles is provided by intermolecular interactions of these functional groups. The number of these groups is rather large due to a high specific surface of the nanodiamond. The initial diamond particles  $\sim 4\text{--}5\text{ nm}$  in size (Fig. 2, *a*) form aggregates with the size of  $60\text{--}70\text{ }\mu\text{m}$  (according to the data of scanning electron microscopy; Fig. 2, *b*). Therefore, nanodiamond can be disintegrated to the initial particles by a considerable decrease in the number of these groups or their modification.

An analysis of the IR spectrum shows that the surface of the initial nanodiamond is polyfunctional. This

**Table 1.** Elemental composition of the nanodiamond surface upon different treatments (according to the XPS data)

Sample	$T/^\circ\text{C}$	Content of elements (at.%)		
		C	O	N
Initial	—	89	9	2
Treated with $\text{H}_2$	800	98	1	1
	850	98	1	1
	900	98	1	1



**Fig. 2.** Microphotographs of the nanodiamond samples according to the data of transmission (*a*) and scanning (*b*) electron microscopy.

impedes its further directed (selective) chemical modification and results in the necessity of monofunctionalization.

**Chemical composition of the hydrogenated nanodiamond surface.** According to available published data,<sup>4,10,11</sup> the high-temperature treatment with hydrogen is one of the convenient and commonly used methods for the monofunctionalization of the surface of diamond materials, including nanodiamond. During the hydrogen treatment new hydride groups are formed on the nanodiamond surface predominantly due to the reduction and destruction of oxygen-containing groups, which is shown by IR spectroscopy (see Fig. 1) and elemental analysis of the surface based on the XPS data (see Table 1). As can be seen from the IR spectrum, the disappearance of the absorption bands with maxima at  $1740$  and  $1560\text{ cm}^{-1}$  and a substantial increase in the absorption intensity in the region of stretching vibrations of the C—H bonds are the most significant changes in the spectra. At the same time, no substantial changes occur in intensities of the absorption

bands at 3700–3000 and 1400–1000  $\text{cm}^{-1}$ , indicating that the surface OH groups are stable under the conditions of such a hydrogen treatment. Only the band of the C–O–H group shifts to the region of lower wave numbers (from 1360  $\text{cm}^{-1}$  to 1329  $\text{cm}^{-1}$ ), which is related, most likely, to the weakening (after the hydrogen treatment) of intermolecular interactions involving the hydroxyl group. The bands ascribed to stretching vibrations of the C–O and C–O–C bonds (1256 and 1130  $\text{cm}^{-1}$ ) remain unchanged. Several bands appear in the region of in-plane OH vibrations at 1450–1250  $\text{cm}^{-1}$ , and their unambiguous assignment seems difficult. In the region of stretching vibrations of hydride groups, the highest intensity belongs to the bands at 2942 and 2878  $\text{cm}^{-1}$ , which are the superposition of vibrations of hydride groups of several types. These bands can be assigned<sup>4</sup> to vibrations of the C–H bonds on the nanodiamond faces {100} and {111}, respectively. The authors of Ref. 9 distinguished in these bands additional vibrations at 2955, 2927, 2871, and 2852  $\text{cm}^{-1}$ , which are ascribed to  $\nu_{\text{as}}(\text{CH}_3)$ ,  $\nu_{\text{as}}(\text{CH}_2)$ ,  $\nu_{\text{s}}(\text{CH}_3)$ , and  $\nu_{\text{s}}(\text{CH}_2)$ , respectively.<sup>9</sup> We decomposed a complicated superposition of the corresponding bands into four Gaussian components and obtained the following values of absorption maxima: 2945, 2930, 2878, and 2852  $\text{cm}^{-1}$ , which agrees satisfactorily with the earlier<sup>9</sup> published data.

An absorption band at 1458  $\text{cm}^{-1}$ , which is usually assigned to asymmetric bending vibrations of the methyl group or scissors vibrations of the methylene group, appears in the spectrum of the nanodiamond after the high-temperature treatment with hydrogen. It is hardly pos-

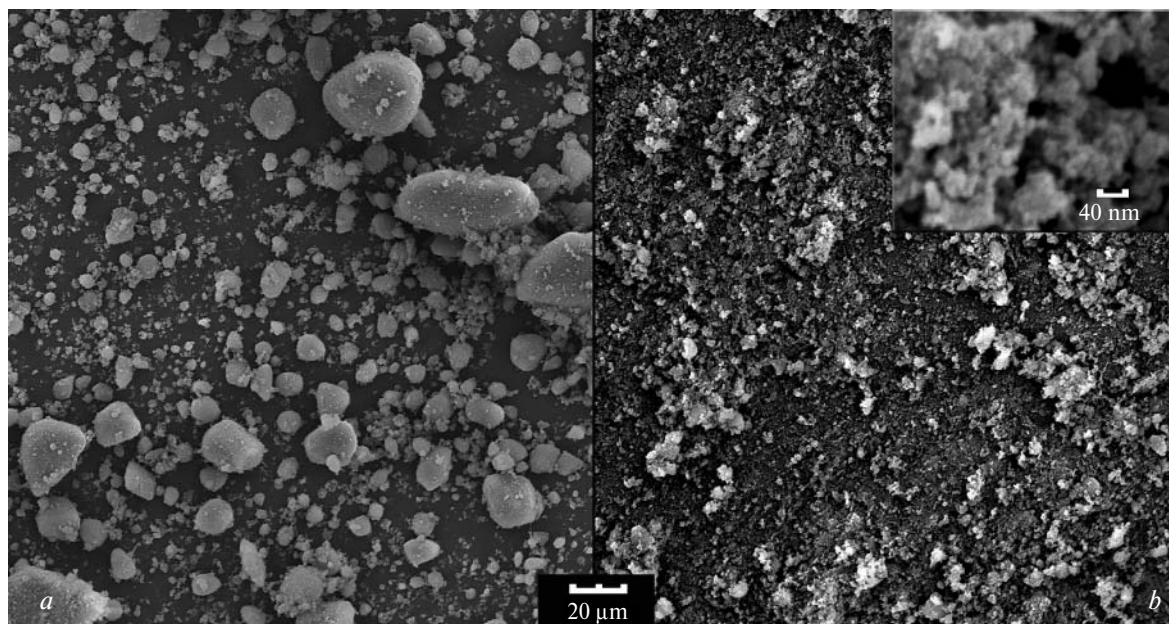
sible to unambiguously assign the absorption bands to vibrations of these or other hydride groups on the nanodiamond surface. This is caused, most likely, by the simultaneous presence of hydride groups of several types on the nanodiamond surface.

The data of the IR spectra of the nanodiamond are well consistent with the results of XPS elemental analysis of the surface. As follows from the data in Table 1, an increase in the temperature of the nanodiamond treatment from 800 to 900 °C exerts no effect on the relative content of the O and N atoms on the surface. In all cases, this content remains at a level of 1 at.%. The measurement of the specific surface by low-temperature nitrogen adsorption for the hydrogenated nanodiamond showed that the specific surface remains almost unchanged, being  $280 \pm 1 \text{ m}^2 \text{ g}^{-1}$ .

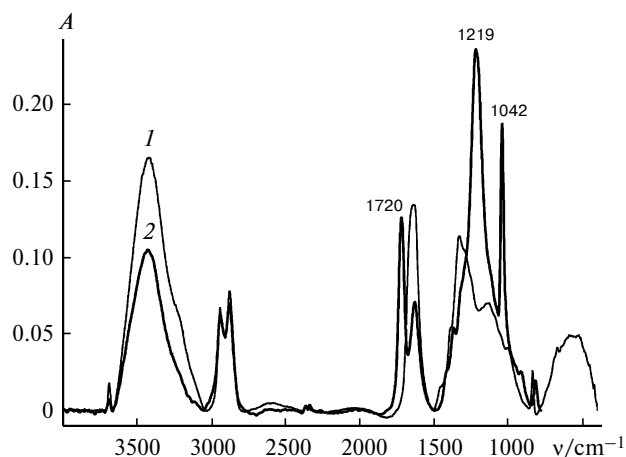
As indicated by the results of scanning electron microscopy, the high-temperature treatment with hydrogen does not substantially change the dispersity of the sample (cf. Figs 2, *b* and 3, *a*).

The presence of the surface hydroxyl groups on the hydrogenated nanodiamond is confirmed by their acylation with acetic anhydride in the presence of catalytic amounts of sulfuric acid or triethylamine (Fig. 4). In both options, the IR spectra of the modified nanodiamond exhibit the bands characteristic of the carbonyl group (1720  $\text{cm}^{-1}$ ) and C(O)–O–C group (1219 and 1042  $\text{cm}^{-1}$ ). Thus, the surface OH groups can be used for the synthesis of grafted surface compounds.

To remove physically adsorbed water, a hydrogenated nanodiamond sample was treated with thionyl chloride



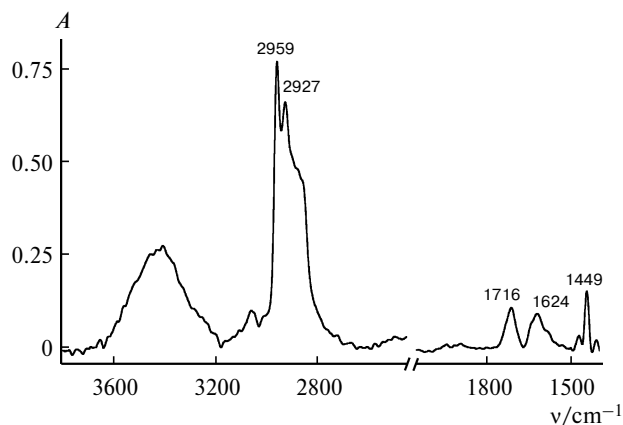
**Fig. 3.** Microphotographs of the nanodiamond samples after the high-temperature treatment with hydrogen (*a*) and subsequent chlorination (*b*) according to the data of scanning electron microscopy, and the amplified fragment is given in inset.



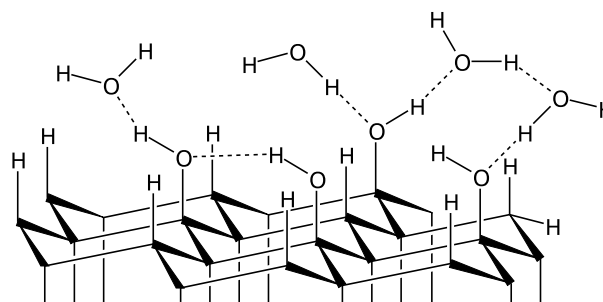
**Fig. 4.** IR spectra of the hydrogenated nanodiamond (1) and nanodiamond acylated with  $\text{Ac}_2\text{O}$  in the presence of  $\text{H}_2\text{SO}_4$  (2).

at 75 °C. It is known that the substitution of the OH groups for Cl using thionyl chloride involves contact ion pairs and, hence, only the removal of adsorbed water molecules can be expected upon this treatment. In fact, as shown by the IR spectrum of the hydrogenated nanodiamond treated with  $\text{SOCl}_2$ , the intensity of adsorption bands decreases substantially in the region of stretching vibrations of OH groups and scissors vibrations of water (Fig. 5). However, although the treatment with thionyl chloride made it possible to remove the significant portion of adsorbed water, thionyl chloride was simultaneously sorbed (both physical sorption and chemisorption) on the surface due to the formation of surface chlorosulfite groups (which is indicated by the absorption bands at 1260 and 1223  $\text{cm}^{-1}$ ).

Thus, the main result of the hydrogen treatment of nanodiamond is the dramatic decrease in the number of oxygen-containing groups (removal of different carbonyl and carboxy groups) on the surface, while hydroxyl groups remain virtually unremoved. Physically sorbed admixtures



**Fig. 5.** IR spectrum of the hydrogenated nanodiamond after its treatment with thionyl chloride.

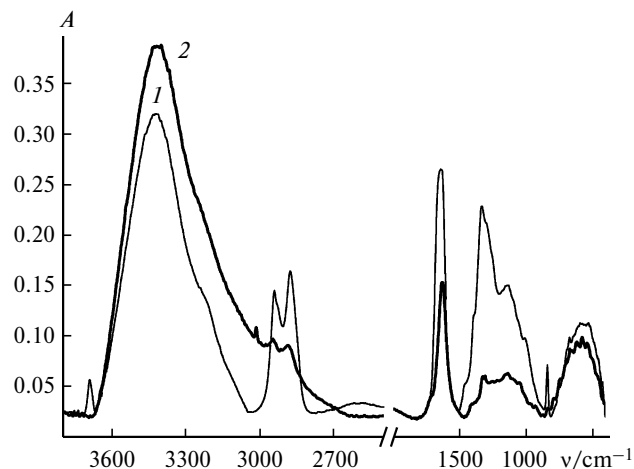


**Fig. 6.** Schematic image of the nanodiamond surface after the high-temperature treatment with hydrogen.

are also removed. A carbon surface is formed, which contains predominantly hydride and hydroxyl groups and adsorbed water molecules (Fig. 6), *i.e.*, in a good approximation this surface can be considered bifunctional.

Reactions, which make it possible to perform covalent grafting to the surface due to C—C bond formation providing the formation of the strongly fixed layer of the grafted surface compound, are of most interest from the viewpoint of chemical modification of nanodiamond and other diamond materials. It is most likely that surface hydride groups are most convenient for such a grafting. However, their reactivity is rather low. Therefore, an additional activation of the surface is necessary; a practical and universal method is the electrophilic activation of the surface by preliminary halogenation, in particular, chlorination, as one of the most accessible processes.

**Regularities of chlorination of hydrogenated nanodiamond.** We found that the 8-h chlorination of the pre-hydrogenated nanodiamond results in the chlorine concentration in the sample equal to 2.9 wt.%. An increase in the chlorination duration to 24 h made it possible to introduce additionally 0.9 wt.% chlorine. Thus, the maximum surface concentration of chlorine that was achieved under these conditions is 2.3 atom  $\text{nm}^{-2}$ . The initial nanodiamond sample that underwent no hydrogen treatment was found to be capable of being chlorinated. However, in this case, the chlorine concentration is 1 wt.%, which additionally indicates the presence of hydride groups in the initial nanodiamond and makes it possible to compare their content before and after the hydrogen treatment. The IR absorption spectra of the nanodiamond samples after chlorination (Fig. 7) exhibit a noticeable decrease in the intensity of absorption bands of hydride groups; however, no their complete disappearance is observed. The absorption intensity also decreases in the region of bending vibrations of OH groups and stretching vibrations of C—O bonds. The band corresponding to the vibration of the free hydroxyl group is absent in the spectrum of the chlorinated sample. It should be mentioned that no absorption of C—Cl bonds is observed in the IR spectrum, which is evidently due to a low intensity of the band of stretching C—Cl vibrations and

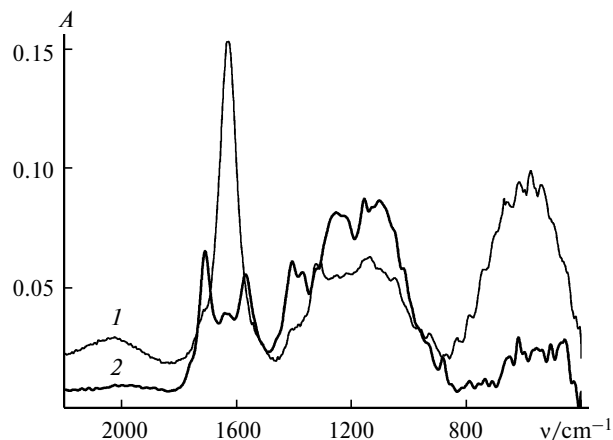


**Fig. 7.** IR spectra of the nanodiamond samples hydrogenated (1) and chlorinated for 2 days (2).

a comparatively low surface concentration of chlorine. The IR spectrum of the nanodiamond after chlorination contains the absorption band corresponding to vibrations of C=O groups. They are formed, most likely, upon the oxidation of the surface C—H bonds by hypochlorous acid (HClO), which is formed *in situ* by the interaction of chlorine with adsorbed water molecules on the hydrogenated diamond surface. This process is favored by photoirradiation.

Published data on the hydrolytic stability of the chlorinated nanodiamond surface are lacking, whereas they are contradictory for micron-size diamond powders. For instance, as mentioned,<sup>4</sup> it is enough to keep a chlorinated diamond sample (the authors used the diamond powder with  $S_{sp} = 21 \text{ m}^2 \text{ g}^{-1}$  and the particle size  $\leq 0.5 \mu\text{m}$ ) in air for several hours to completely remove Cl atoms from the surface. This conclusion<sup>4</sup> is based exclusively on the results of IR spectroscopy without quantitative studies. According to other data,<sup>12</sup> chemisorbed chlorine is hydrolytically stable and can be removed from the surface only upon the prolong treatment with a 1 M solution of NaOH. We have shown that the chlorinated nanodiamond surface is hydrolytically stable in air for at least several days. When the chlorinated nanodiamond was kept in air for 72 h, the decrease in the chlorine content was 0.5 wt. %: from 3.0 to 2.5%. The treatment of the chlorinated sample containing 2.9 wt. % chlorine with a 0.05 M aqueous solution of NaOH for 3 h decreases the chlorine concentration to 0.9 wt. %.

After hydrolysis of the chlorinated surface in an alkaline medium, in the IR spectrum (Fig. 8) the absorption intensity in the region of stretching vibrations of the C=O groups increases and the bands of antisymmetric ( $1567 \text{ cm}^{-1}$ ) and symmetric ( $1406 \text{ cm}^{-1}$ ) vibrations of the COONa groups appear. Evidently, their formation is related to the hydrolysis of the  $\text{CCl}_2$  and  $\text{CCl}_3$  surface groups, respectively. The  $\text{CCl}_3$  groups appear, most likely,



**Fig. 8.** IR spectra of the chlorinated nanodiamond before (1) and after its treatment with 0.05 M NaOH (2).

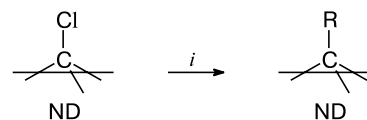
due to the destruction of the C—C bonds during chlorination.

Using scanning electron microscopy, we found that the size of the initial aggregates (less than  $60 \mu\text{m}$ ) decreases ( $100\text{--}200 \text{ nm}$ ) during chlorination (see Fig. 3). In addition, the size distribution of the aggregates becomes narrower. However, we failed to achieve aggregate disintegration to the primary diamond particles  $\sim 5 \text{ nm}$  in size. This is caused, most likely, by strong intermolecular interactions of the surface OH groups of nanodiamond particles, which are not involved in the interaction during chlorination. Thus, radical chlorination is a method for electrophilic activation of the nanodiamond surface and also serves for controlling the dispersity of the sample, *i.e.*, its supramolecular structure.

The method for nanodiamond fluorination by a mixture of fluorine and hydrogen was proposed,<sup>2</sup> which makes it possible to completely decompose the aggregates to form the primary nanodiamond particles with the surface fluorine content 8.6 at. %. As a whole, the formation of the CF groups provides the stabilization of individual nanoparticles preventing their strong aggregation. However, it is obvious that the fluorination process can hardly be considered as commonly used.

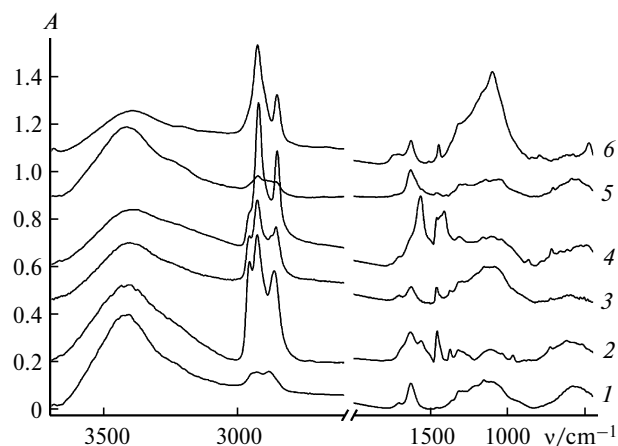
**Interaction of chlorinated nanodiamond with C-nucleophiles.** The chlorinated nanodiamond samples react with the organolithium reagents (Scheme 1).

**Scheme 1**



ND is nanodiamond surface

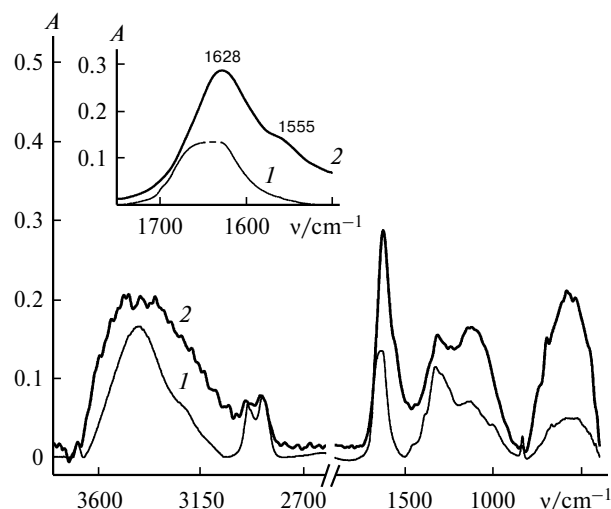
*i.* RLi, hexane,  $\text{Et}_2\text{O}$ , 12 h.



**Fig. 9.** IR spectra of the nanodiamond sample with grafted groups: R = Me (1), Bu<sup>m</sup> (2), *n*-C<sub>6</sub>H<sub>13</sub> (3), *n*-C<sub>16</sub>H<sub>33</sub> (4), *n*-C<sub>18</sub>H<sub>37</sub> (5), and *cyclo*-C<sub>6</sub>H<sub>11</sub> (6).

The spectra of the modified nanodiamonds with alkyl groups (Fig. 9) are characterized by the absorption bands corresponding to stretching (2950–2860 cm<sup>-1</sup>) and bending (1460–1300 cm<sup>-1</sup>) vibrations of the C–H bonds in the alkyl groups. In addition, the strong absorption in the region of stretching and bending vibrations of the OH groups is retained. The peak at 3690 cm<sup>-1</sup>, which appears in the spectra of the initial and hydrogenated nanodiamond samples, is absent in the spectra of the nanodiamonds with grafted alkyl groups. Thus, the nanodiamond surface with grafted alkyl groups is polyfunctional: it contains alkyl groups, OH groups of different nature, and carbonyl groups (the presence of the latter is indicated by the absorption at 1705 cm<sup>-1</sup>). The presence of carbonyl groups on the surface of the modified nanodiamond samples is due, most likely, to the hydrolysis of the CCl<sub>2</sub> groups unreacted with the organolithium reagent, because no absorption in this region is observed in the spectra of the nanodiamond samples after the high-temperature treatment with hydrogen.

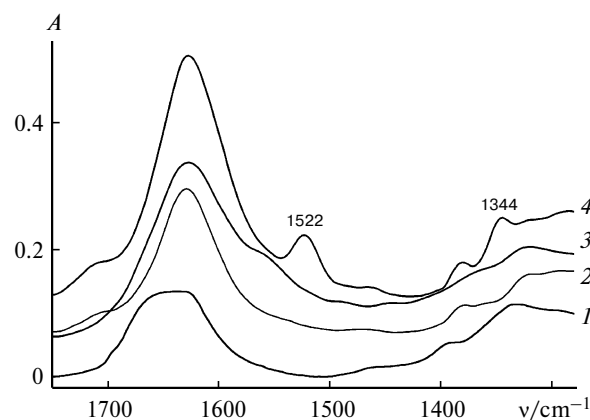
Unlike the IR spectra of the nanodiamond samples with grafted alkyl groups, the identification of grafted phenyl groups on the basis of IR spectra is not so evident. As known, aromatic compounds are characterized by the absorption in the three regions: ~3000, 1600–1500, and 900–600 cm<sup>-1</sup>. Since the intensity of stretching vibrations of the C–H bonds in aromatic compounds is low and the absorption of the nanodiamond at frequencies higher than 3000 cm<sup>-1</sup> is strong due to the hydroxyl groups and adsorbed water molecules (Fig. 10), this spectral region is poorly informative for characterization of grafted phenyl groups. Comparing the spectra of the hydrogenated nanodiamond with grafted phenyl groups at 1600–1500 cm<sup>-1</sup>, one can see the appearance of a medium-intensity band at 1555 cm<sup>-1</sup> on the shoulder of the band at 1628 cm<sup>-1</sup> (see Fig. 10). In the 800–600 cm<sup>-1</sup>



**Fig. 10.** IR spectra of the hydrogenated nanodiamond (1) and nanodiamond with grafted phenyl groups (2).

region the absorption increases compared to that of the spectrum of the hydrogenated nanodiamond. Thus, we found no unambiguous and direct spectral proofs for grafting of phenyl groups.

The presence of grafted phenyl groups on the nanodiamond surface can indirectly be confirmed by nitration under standard conditions used for aromatic compounds.<sup>13</sup> The nanodiamond with grafted phenyl groups and the hydrogenated nanodiamond were treated with a nitrating mixture by a standard procedure under the same conditions. Then the nanodiamond samples were thoroughly washed with a large amount of distilled water, dried, and characterized by IR spectroscopy (Fig. 11). After the nanodiamond sample with grafted phenyl groups was treated with the nitrating mixture, two bands appeared in its IR spectrum: with the frequencies 1522 and 1344 cm<sup>-1</sup>, which can be assigned to  $\nu_{\text{as}}(\text{NO}_2)$  and  $\nu_{\text{s}}(\text{NO}_2)$ .<sup>12</sup> In the

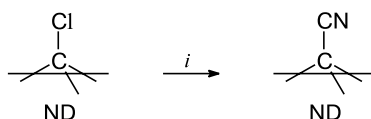


**Fig. 11.** IR spectra of the hydrogenated nanodiamond samples (1) treated with the nitrating mixture (2), containing grafted phenyl groups (3), and containing grafted phenyl groups and treated with the nitrating mixture (4).

IR spectrum of nitrobenzene<sup>7</sup> the corresponding bands are observed at 1542 and 1356  $\text{cm}^{-1}$ . These bands are absent in the IR spectrum of the hydrogenated nanodiamond after the treatment with the nitrating mixture. These experiments indicate the chemical grafting of phenyl groups on the nanodiamond surface.

The preparation of nanodiamond with surface nitril groups provides wide prospects for the further synthesis of various grafted surface compounds due to transformations of the CN group (Scheme 2). At the same time, it is difficult to perform nucleophilic substitution in the nodal positions of polyhedra to which diamond can be assigned because of steric factors (carbocation formation is difficult because a planar structure cannot be formed). The IR spectrum of the nanodiamond thoroughly washed from the initial reactants and by-products contains a medium-intensity band at 2215  $\text{cm}^{-1}$ , which corresponds to the absorption of the nitril group.

Scheme 2



ND is nanodiamond surface

*i.* NaCN, DMSO, 72 h.

Thus, the high-temperature treatment of nanodiamond produces a bifunctional surface that can further be modified due to both hydride and hydroxyl groups, and an additional activation of the surface is required in the first case. For this purpose we proposed a procedure of liquid-phase photochemical chlorination of the nanodiamond pre-hydrogenated by molecular chlorine. Under these conditions, the maximum possible chlorine concentration in the sample was found to be 3.8 wt.% or 2.3 atom  $\text{nm}^{-2}$ . It has been found for the first time that the chlorinated nanodiamond surface is hydrolytically stable in air for a long time. The chlorination results in the dispersion of the initial nanodiamond aggregates to finer aggregates with simultaneous narrowing of their size distribution. It is shown that the chlorinated diamond surface is capable

of interacting with a series of organolithium reagents and cyanide anion.

The authors are grateful to A. P. Dement'ev for recording X-ray photoelectron spectra.

## References

- G. V. Lisichkin, A. Yu. Fadeev, A. A. Serdan, P. N. Nesterenko, P. G. Mingalev, and D. B. Furman, *Khimiya privitykh poverkhnostnykh soedinenii* [Chemistry of Grafted Surface Compounds], Fizmatlit, Moscow, 2003, 592 pp. (in Russian).
- Y. Liu, Z. Gu, J. L. Margrave, and V. N. Khabashesku, *Chem. Mater.*, 2004, **16**, 3924.
- Y. Liu, V. N. Khabashesku, and N. M. Halas, *J. Am. Chem. Soc.*, 2005, **127**, 3712.
- T. Saito, Y. Ikeda, and S. Egawa, *J. Chem. Soc., Faraday Trans. 1*, 1998, **94**, 929.
- T. V. Talalaeva and K. A. Kocheshkov, in *Metody elemento-organicheskoi khimii. Liti, natrii, kalii, rubidii, tsezii* [Methods of Organoelement Chemistry. Lithium, Sodium, Potassium, Rubidium, Cesium], Ed. A. N. Nesmeyanov and K. A. Kocheshkov, Nauka, Moscow, 1971, Books 1–2, 1192 pp.
- L. J. Bellami, *The Infra-Red Spectra of Complex Molecules*, Methuen and Co, Ltd., J. Wiley and Sons, Inc., London—New York, 1960, 462 pp.
- E. Pretsch, P. Bühlmann, and C. Affolter, *Structure Determination of Organic Compounds. Tables of Spectral Data*, Springer, Berlin—Heidelberg, 2000, 421 pp.
- I. I. Kulakova, B. N. Tarasevich, A. P. Rudenko, N. Dorzhpalamyn, and T. M. Gubarevich, *Vestn. Mosk. Gos. Univ., Ser. 2. Khim.*, 1993, **34**, 506 [*Vestn. Mosk. Univ., Ser. Khim.*, 1993 (Engl. Transl.)].
- T. Jiang and K. Xu, *Carbon*, 1995, **33**, 1663.
- T. Tsubota, S. Tani, S. Ida, M. Nagata, and Y. Matsumoto, *Diamond and Related Materials*, 2004, **13**, 1093.
- Y. Ikeda, T. Saito, and K. Kusakabe, *Diamond and Related Materials*, 1998, **7**, 830.
- E. P. Smirnov and S. K. Gordeev, *Almaz: poluchenie, svoistva, primeneniye* [Diamonds: Preparation, Properties, Application], Len. Tekhn. Inst. im. Lensovet, Leningrad, 1984, 73 pp. (in Russian).
- H. Becker, W. Berger, G. Domschke, E. Fanghänel, J. Faust, M. Fischer, F. Gentz, K. Gewalt, R. Gluch, R. Mayer, K. Müller, D. Pavel, H. Schmidt, K. Schollberg, K. Schwetlick, E. Seiler, and G. Zeppenfeld, *Organikum*, Veb Deutscher Verlag Wissenschaften, Berlin, 1976.

Received August 3, 2006