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Surface modification of detonation nanodiamond with ethylenediamine and hexamethylenediamine

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The surface of chlorinated and fluorinated nanodiamond obtained by detonation synthesis was modified with ethylenediamine and hexamethylenediamine. Nanodiamonds with grafted diamines were found to manifest photoluminescence in Raman spectra; the occurrence and intensity of luminescence depended on the chemical nature of the diamines.

The chemical surface modification of detonation nanodiamond (ND) is a problem of current interest, particularly in terms of development of efficient drug delivery systems based on NDs.[1] The presence of functional groups on the ND surface enables the covalent grafting of various chemical compounds that can also serve as spacers for subsequent grafting of bioactive compounds.[2] The structure and length of the spacer can change the conformational mobility of the grafted molecules and the capability for adaptational tuning of the substrate to the receptor, thus affecting their pharmacological and biopharmaceutical characteristics.

A monofunctional ND surface is the main condition for a successful chemical modification. The latter includes the following stages: the unification of functional groups on the diamond surface, the surface activation by halogenation with Cl or F, and the covalent grafting of compounds. The surface layer unification is performed by ND reduction with hydrogen. As shown previously,[3] this creates a bifunctional layer of H atoms and OH groups on the diamond surface; however, these groups are insufficiently reactive in covalent grafting reactions. Therefore, the surface is activated by halogenation.[3,4]

The aim of this work was to synthesize and study the physicochemical properties of NDs[†] with grafted ethylene- and hexamethylenediamine, *i.e*., potential spacers of various lengths, where one NH_2 group is the anchor group while the other one is the functional group for subsequent covalent bonding with modifiers, in particular, bioactive compounds.

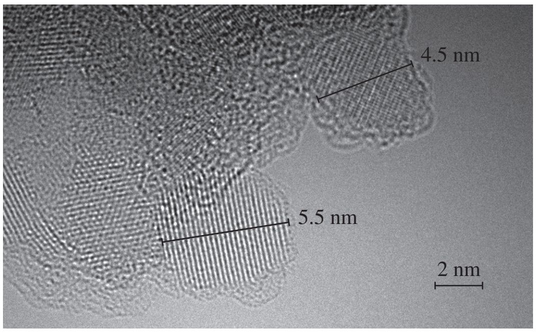
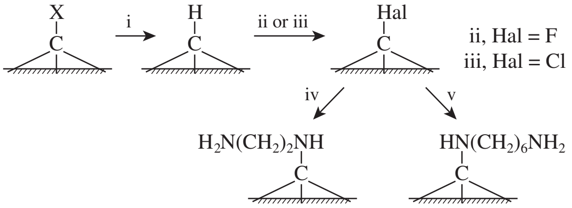


Figure 1 TEM micrograph of nanodiamond particles.

Figure 1 shows the image of primary ND particles. The NDs were modified using the following procedure (Scheme 1): treatment with hydrogen; fluorination in an SF_6 : Ar (1 : 3) plasma or chlorination in a CCl_4 plasma; covalent grafting of diamines. The halogenation techniques are described elsewhere.[6,7] Diamine grafting was performed concurrently on two fluorinated and chlorinated ND specimens.[‡]

The chemical state of the ND surface was monitored using XPS, IR and Raman spectroscopy.[§] The amount of grafted



Scheme 1 Nanodiamond surface modification. *Reagents and conditions*: i, H_2 (~2 dm^3 h^{-1}), 800 °C, 5 h; ii, plasma SF_6 : Ar (1:3), 20 °C, 133 Pa, 2.5 h; iii, plasma CCl_4, 20 °C, 133 Pa, 6 h; iv, $NH_2(CH_2)_2NH_2$, DMSO, Py, 117 °C, 24 h; v, $NH_2(CH_2)_6NH_2$, Py, 120 °C, 24 h.

[†] UDA-TAN NDs manufactured at the Tekhnolog Federal State Unitary Enterprise (St. Petersburg) were used after industrial chemical cleaning (50–60% nitric acid, 230–240 °C, 80–90 atm) and additional treatment with aqueous ammonia at pH 9–10[5] to neutralize residual acids on the surface and in the micropores of the ND aggregates. Subsequent heating in an ammonia medium under pressure at 200–240 °C for 30 min allowed nitrogen oxides to be removed from the NDs; under these conditions, harmless N_2 and H_2O are formed and partial destruction of the aggregates occurs. According to specification, the resulting ND contained 0.7 wt% non-combustible admixtures and was a grey powder with aggregates of primary particles 10–100 nm large and with $S_{specific}$ = 296±1 m^2 g^{-1} (BET surface area was determined on the basis of the low-temperature adsorption of nitrogen on a Gimini 2390 V1/02t instrument). TEM images were obtained on a JEM-2100F ultra-high resolution transmission electron microscope (JEOL, Japan).

[‡] DMSO (50 ml) was added to a thoroughly dried flask, and then a weighed ND specimen (500 mg) and ethylenediamine (2.5 ml) were added, followed by a few drops of pyridine to bind HCl or HF liberated during the reaction. The mixture was refluxed for 24 h at 117–120 °C in a setup equipped with a calcium chloride tube. The resulting product was repeatedly washed with water and acetone and dried in a rotary evaporator.

In order to graft hexamethylenediamine to the ND surface, hexamethylenediamine (5 ml) warmed to 50–60 °C was added to ND (500 mg) and the synthesis was carried out for 24 h at 120 °C. The product was repeatedly washed with water and acetone and dried in a rotary evaporator.

Table 1 Concentrations of halogens and nitrogen (according to XPS data) in ND before and after modification with ethylenediamine.

ND specimen	Element content (at%)				$\frac{\mathrm{Hal}_{\mathrm{before}} - \mathrm{Hal}_{\mathrm{after}}}{\mathrm{N}_{\mathrm{before}} - \mathrm{N}_{\mathrm{after}}}$
	$\mathrm{Hal}_{\mathrm{before}}$	$\mathrm{N}_{\mathrm{before}}$	$\mathrm{Hal}_{\mathrm{after}}$	$\mathrm{N}_{\mathrm{after}}$	
Fluorinated	14.5	1.9	4.4	3.5	6.3
Chlorinated	8.7	1.9	<3	2.9	5.7

diamines was assessed from the increase in the amount of nitrogen and the decrease in the halogen content on the ND surface. The relatively high content of halogens in the specimens after the modification may be due to the presence of $\mathrm{CHal_2}$ and $\mathrm{CHal_3}$ groups on the ND surface, where only one halogen atom is replaced by a diamine molecule. Table 1 presents data for ND grafted with ethylenediamine as an example.

It follows from Table 1 that the ratios of the number of halogen atoms removed from the surface to the increase in the number of nitrogen atoms in the chlorinated and fluorinated ND specimens are 5.7 and 6.3, respectively. This suggests that the extent of ethylenediamine grafting to the surface of halogenated specimens is approximately the same. Furthermore, the ratio of the number of halogen atoms on the original fluorinated and chlorinated specimens (1.67) is almost equal to that of the increase in the number of nitrogen atoms after grafting (1.6). This may suggest that the C–F and C–Cl bonds on the ND surface have the same reactivity.

When hexamethylenediamine is grafted to the ND surface, its amino group manifests itself in the IR spectrum as bands at 1660 and 1573 cm^{-1} characteristic of deformation vibrations of the N–H bond. They are observed both on the chlorinated and fluorinated ND specimens. In addition, the intensity of bands at 2927 and 2857 cm^{-1} corresponding to the vibrations of the C–H bonds increases due to the grafting of the $\mathrm{NH(CH_2)_6NH_2}$ group to the ND surface.

We also revealed that the covalent grafting of diamines on an ND surface dramatically changes the Raman spectra of the ND specimens (see Online Supplementary Materials). In fact, the spectrum of the original ND contains two broad bands with maxima at 1332 and 1632 cm^{-1}. For all the ND specimens studied, the band corresponding to *sp*^{3} carbon of the diamond lattice manifests itself at the same frequency of 1332 cm^{-1}. The broadening and asymmetry of this band is due to the nanosize of the diamond particles. According to published data,[8] a theoretical calculation of the mean ND size based on its Raman spectrum gave 4.9 ± 0.1 nm. The second band corresponding to *sp*^{2} carbon is observed at 1632 cm^{-1}. The graphite component in carbon materials usually has a maximum at 1580 cm^{-1} in the Raman spectra.[9] Perhaps, such a shift in the maximum is not due to the graphite component in ND, as that component was not detected in these ND specimens by other methods. More likely, it is caused by surface functional groups[10] containing *sp*^{2} carbon. This is supported by a shift of the maximum at 1632 cm^{-1} to a longer-wave region upon chemical modification of the ND surface.[11]

The Raman spectrum of the ND specimen with grafted hexamethylenediamine retains the two main bands characteristic of *sp*^{3} and *sp*^{2} carbon on the ND surface, while their relative intensities and the position of the second maximum (1600 cm^{-1}) change. The shift of the *sp*^{2} carbon peak is due to the preliminary hydrogen treatment of the specimens, which resulted in the reduction of carbonyl groups. The ND specimen with grafted ethylenediamine exhibited strong luminescence during the recording of the Raman spectrum; the intensity of the latter exceeded the intensity of the Raman spectrum of the original ND by a factor of more than 50. The occurrence of luminescence (photoluminescence) may be owing to an increase in the surface defectness because of chemical grafting of conformationally rigid ethylenediamine to the ND surface, accompanied by formation of C–N bonds, in agreement with previous data.[12] The ND with grafted hexamethylenediamine showed some broadening of the band at 1332 cm^{-1} in the Raman spectrum and changes in the positions of the peak maxima, whereas no photoluminescence effect was observed.

In addition, the luminescence excitation and emission spectra of ND specimens were studied (LS-55, PerkinElmer, USA). It was shown that luminescence as a broad band in the region of 500–620 nm with a maximum at 573 nm occurred in the emission spectrum of an ND specimen with grafted ethylenediamine. The excitation spectra contain two maxima at 280 and 380 nm, the second maximum being of a higher intensity.

Thus, we synthesized NDs with grafted ethylenediamine and hexamethylenediamine and demonstrated that they manifested a considerable luminescence. It was found that the occurrence and intensity of photoluminescence depended on the chemical nature of the diamines. Application of this phenomenon may be promising in studies on the physicochemical and spectral properties of drug delivery systems based on detonation nanodiamonds.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2012.06.015.

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[§] IR absorption spectra were recorded in KBr pellets using an FTIRS IR200 instrument (Thermonikolet, USA) with 4 cm^{-1} resolution. Raman spectroscopic measurements were carried out using a Ramanor U-1000 spectrometer (Jobin Yvon, France) with excitation by an argon laser at a wavelength of 514.5 nm. The elemental composition of the ND surface before and after the modification with amines was determined by XPS with a Riber instrument.