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Halogenation of detonation-synthesised nanodiamond surfaces

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Comparative chlorination and fluorination of detonation-synthesised nanodiamond surfaces was carried out by various methods and the hydrolytic stability of the halogenated surfaces was studied.

The properties of nanosized objects are often determined by the properties of their surfaces; hence, the physicochemical properties of a material can be controlled by varying the composition and structure of a grafted layer. In the past decade, increasing interest was felt in studies on a new carbon material, *viz.*, detonation-synthesised nanodiamond (ND), and in modifying its surface. This is due to both the necessity of increasing the efficiency of its use in traditional areas and to a search for new fields of application of this material. From the point of view of chemical modification, the most interesting are reactions that provide covalent grafting to the surface by formation of a C–C bond between the group being grafted and the surface, which ensures the formation of a strongly bound layer of a grafted surface compound.[1]

The surface of commercial nanodiamond is polyfunctional.[2,3] Reducing treatment with hydrogen at elevated temperatures is commonly used to make it monofunctional.[4] However, we have found[5] that in this case a bifunctional coating of H and OH groups is formed on the ND surface; these groups are insufficiently reactive in covalent grafting reactions. Halogenation is used to activate such a surface, particularly with respect to C-nucleophilic agents.[6–9]

The aim of this study was to compare the results of ND halogenation *versus* the halogen nature and halogenation technique, as well as to assess the hydrolytic stability of halogenated samples.

In this study, we used ND of trademarks UDA-TAN and UDA-SF manufactured by Federal State Unitary Enterprise 'Tekhnolog' (St. Petersburg), which contained 0.4 and 0.7 wt% of incombustible impurities, respectively, according to specification. The ND surface was halogenated using newly developed techniques. The halogen concentration on the surface was evaluated using XPS, IR spectroscopy (see Online Supplementary Materials) and X-ray fluorescence analysis (XRF).

ND surfaces were fluorinated (i) with molecular fluorine and (ii) in SF_6 plasma. To fluorinate with gaseous fluorine, a weighed portion of ND in a Teflon boat was placed in an evacuated Teflon reactor and kept for 48 h at room temperature and a pressure of ~50 kPa. The resulting fluorine concentration on the sample surface was 12.5 at% (XPS).

Fluorination in SF_6 plasma was carried out in a device based on a rotary evaporator. High-frequency glow-discharge plasma was ignited in a stream of an SF_6 + Ar (1:3) gas mixture. The generator working frequency was 13.56 MHz and the maximum power was 50 W. The mixture pressure and flow rate were controlled using fine adjustment valves. Fluorination was carried out for 2.5 h at room temperature and a pressure of ~133 Pa. The inside surface of the flask (0.5 dm^3) was coated with Teflon to prevent fluorine from reacting with the glass. Nanodiamonds were stirred by means of glass balls (D_{ball} = 0.3–0.5 mm) also coated with Teflon (< 2 μm). After fluorination, ND powder was separated from the balls by sieving. The fluorine concentration on the surface was 14.5 at% (XPS). Electron micrographs of the original (*a*) and fluorinated (*b*) nanodiamonds are shown in Figure 1. Treatment of the sample with fluorine results in a noticeable disaggregation of ND grains. However, rather large aggregates remain that are not destructed during the synthesis. The surface of fluorinated ND grains contains no adherent small diamond particles, which might be due to their strong electrostatic repulsion owing to the fluorine-containing groups on the surface. Fluorinated ND itself is not wetted with water at all.

Chlorination of ND was also performed in two ways. Liquid-phase chlorination of reduced ND was carried out for 72 h in a chlorine-saturated carbon tetrachloride (5.6 wt%) at room temperature and with permanent agitation. The photochemical reaction was initiated by irradiation. Since the use of UV irradiation and quartz reactor proved to be inefficient, the process was carried out in a molybdenum glass reactor under visible light irradiation (using a 150 W incandescent lamp located at a distance of 5–6 cm from the reactor). After chlorination, ND was washed with dry carbon tetrachloride, the precipitate was separated by centrifugation and dried for 5–6 h at 13–26 Pa and 70–80 °C to remove adsorbed compounds.

It was found by XRF that addition of chlorine onto the surface of reduced diamond by radical photochemical chlorination in liquid phase makes it possible to reach a chlorine concentration of up to 3.8 wt% in the sample. Thus, the maximum surface concentration of chlorine that we were able to reach under the specified conditions was 12 at%. The resulting samples were studied by scanning electron microscopy;[5] the data obtained suggested that ND powder underwent disaggregation during liquid-phase chlorination.

Chlorination in a CCl_4 plasma was performed in a device described above for fluorination but the treatment duration was 6 h (the flask walls were not protected with Teflon). According to XPS data, chlorination in a CCl_4 plasma provides a concentration of chlorine on the surface equal to 8.7 at%, which is a bit less than the maximum amount reached by liquid-phase halogenation.

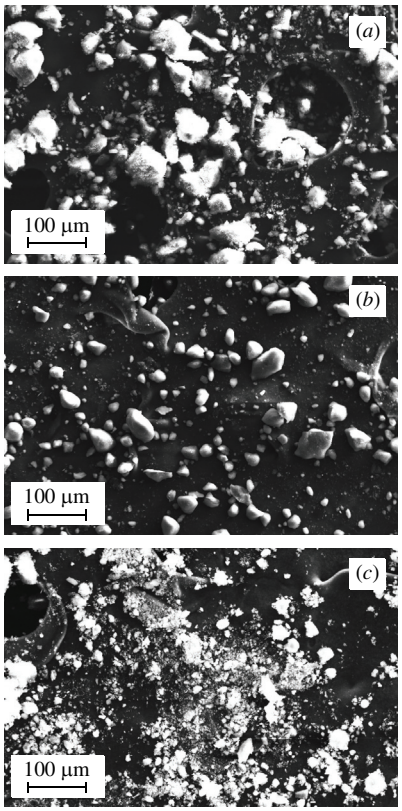

Figure 1 Micrographs of nanodiamond samples: (*a*) original, (*b*) fluorinated and (*c*) chlorinated.

Chlorination in a CCl_4 plasma, similarly to liquid-phase chlorination,[3] results in intense destruction of large ND aggregates [*cf.* Figures 1(*a*),(*c*)]. Medium-sized aggregates are present, but there are rather few of them, and large aggregates are not present at all. Halogenation of ND can be used successfully for disaggregation of particles, which is required for subsequent ND modification and application in various technological and medical areas.

Note that washing off the remaining chlorinated nanodiamonds from the reactor walls with water results in stable suspensions with pH 5. The mean particle diameter of these particles determined by dynamic laser light scattering was 70 nm if the suspension was studied one month after the synthesis or 180 nm if studied nine months later. The particle size distribution is rather narrow.

The resulting chlorinated and fluorinated ND samples were studied by IR spectroscopy. The bands corresponding to grafted chloro- and fluoro- groups had low intensity and overlapped with absorption bands of other groups, and we were unable to make reliable correlations of the signals in the resulting spectra. However, the replacement of surface hydrogen atoms with halogen atoms could be monitored by a decrease in the absorption intensity of bands at 2800–3000 cm^{-1} corresponding to the stretching vibrations of C–H groups. Analyses of XPS spectra indicated that the existing halogen atoms were bound to surface carbon atoms.

Table 1 Hydrolytic stability of halogenated ND.

Treatment	Halogen content on ND surface (at%)	
	Cl	F
After halogenation	12.0	14.5
Air exposure	10.0 (3 days)	14.5 (75 days)
Treatment with 0.05 M NaOH	4.0 (2.5 h)	4.5 (2.5 h)

The chlorinated and fluorinated ND samples were studied for hydrolytic stability of ND–Hal bonds in an alkaline medium and in air (Table 1).

As follows from the above data, the ND–Cl bond has lower hydrolytic stability in air compared to the ND–F bond, whereas the loss of a halogen upon alkaline treatment is the same for both fluorinated and chlorinated nanodiamond. Furthermore, the maximum number of fluorine atoms that can be grafted to the ND surface exceeds the number of chlorine atoms, which may be favourable for subsequent covalent grafting reactions on fluorinated nanodiamond surfaces. This makes it possible to obtain grafted layers with predefined hydrophilic-lipophilic balance on ND, thus expanding the application range of this promising carbon material.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2009.11.004.

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