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Irradiation of detonation nanodiamonds with γ-rays does not produce long living spin radicals

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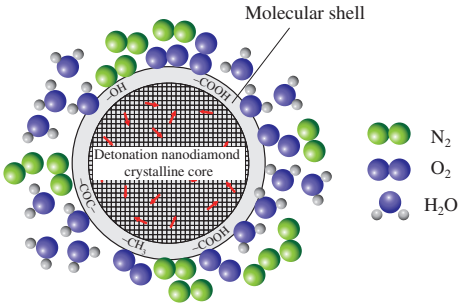
Detonation nanodiamonds of 5 nm size with the surface terminated by carboxyl and/or hydroxyl groups, which act as radical scavengers, represent promising nanofillers for polymer composites. Irradiation of the nanodiamonds with ^{137}Cs γ-rays does not produce long living paramagnetic species both inside the crystalline core and in the outer molecular shell. The reason is rapid interaction of the radiation-induced surface radicals with physisorbed water, molecular oxygen and oxidizing products of their radiolysis.



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Diamond is known to be a radiation-hard material. Isolated vacancies in its lattice or atoms knocked out of their regular position can be produced exclusively by high-energy electrons or neutrons as well as by γ-radiation of 1–2 MeV energy, with treatment at the lower limit of this range resulting in only 0.003 vacancy per millimeter depth per one photon.[1,2] Detonation nanodiamonds (DNDs) of ~5 nm size represent promising nanoplatforms for binding various molecular agents to their easily modifiable molecular shell[3–5] as well as effective nanofillers for polymers, for example poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-vinylene] (MEH-PPV), to improve the mechanical properties and wear resistance.[6–10] Contrary to ordinary fillers, DND particles are covered with carboxyl, hydroxyl and other oxygen-containing groups, which can effectively bind the surrounding polymer chains.[11–13] It is known that intensive γ-irradiation of polymers themselves can change considerably their properties due to bonds breaking, generation of free radical centers and formation of new bonds.[14,15] The same occurs between the polymer chains and nanoparticles having the molecular shells. Thus, it is promising to explore DND particles with the oxygen-containing shells subjected to high-dose γ-irradiation. The expected formation of dangling bond spins in the molecular environment of DND particles would promote an improvement of DND–polymer composites. Although paramagnetic properties of DNDs related to spin-radicals inside their crystalline cores are well described, the external paramagnetic species located in the molecular shells have not been investigated in detail, in particular, no information is available concerning their stability to γ-irradiation. In our works,[16,17] we clarified in detail oxygen-containing functional groups on the DND surface. Nitrogen atoms are contained inside the sp^3 diamond crystallites both in isolated and aggregated forms in a relatively large content up to 2.5 at%.[18,19] As has been established, substitutional nitrogen, the NN^+ charged pairs and interior dangling bonds all represent paramagnetic species located inside the crystalline core of the nanodiamond particles,[20] these species being partially responsible for the main intensive ESR signal of DND with $g = 2.0027$.

In this work, for DND particles subjected to heating at 430 °C *in vacuo* (1.2×10^{-5} Torr) to remove adsorbed water, triplet oxygen and other chemisorbed molecules, the presence of only spin-half species inside the cores was established from the magnetization curve of localized spins after correction (Figure 1, for details, see Online Supplementary Materials). As is known,[21] the full magnetization of pristine DND consists of two contributions, namely magnetization related to the Curie paramagnetism of only interior DND spins (term 1) and the diamagnetism of diamond lattice (term 2) (for details, see Online Supplementary Materials). The plot of magnetization of the only interior localized spins $S_1 = 1/2$ *versus* the magnetic field was obtained after subtraction the term 2 from the full magnetization:

$$M_{S_1=1/2}(H) = M(H) - \chi_0 H, \quad (1)$$

where $\chi_0 = -4.18\times10^{-7}$ emu g^{-1} was diamagnetic susceptibility of carbon atoms cores C^{4+} calculated as a fitting parameter (for details, see Online Supplementary Materials). It was found that the shape of resultant magnetization curve of only localized spins (see Figure 1, black circles) corresponded to the ensemble of localized spins with only spin value $S_1 = 1/2$,[21] because the most appropriate spin value S_1 found in the course of the experimental data fitting using the Brillouin formula (see Figure 1, red curve) was 1/2 (for details, see Online Supplementary Materials).[22,23] Moreover, candidates for paramagnetic centers with spins greater

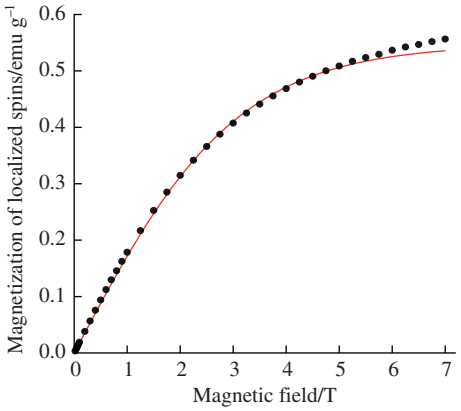

Figure 1 Magnetization curve for DND particles at 2 K. The black circles indicate paramagnetic contribution of only $S_1 = 1/2$ interior carbon-inherited spins to the total magnetization of sample (see the text). The continuous line represents fitting by means of the Brillouin formula for $S_1 = 1/2$ spins.

than or equal to one seem unlikely. The best fit was achieved for a temperature of 2.07 K, although in the experiment, according to a temperature sensor, it was 2.0 K. The concentration of spin-half units per carbon atoms was found as a second fitting parameter in the Brillouin formula as $N_s = 5.90 \times 10^{19}$ g^{-1} or 7.09×10^{20} mol^{-1}, which corresponded to ~13–14 spins 1/2 per one 5 nm particle. It means that each interior spin-half corresponds to a diamond lattice piece consisting of ~850 carbon atoms. The value of N_s is known to be $(5.7–7.3) \times 10^{19}$ g^{-1} for the standard DND made from trinitrotoluene–hexogen mixture (40 : 60 wt) of less than 2 kg detonated in a chamber of 1–3 m^3 volume (for details, see Online Supplementary Materials), and our experimental N_s value falls within this range.

Then we compared ESR data for two DND powder samples (Figure 2), namely pristine acid-purified one, designated as DND-ini, with the content of nitrogen and surface oxygen of ~2.1 and 8.5 at%, respectively, according to our work,[21] as well as the sample exposed to ^{137}Cs γ-radiation in air for three months (total absorbed dose 13 MGy) and designated as DND-irr.

For the DND-ini sample (see Figure 2, curve *1*) the *g*-factor of 2.0027 and linewidth of the ESR signal $\Delta H_{pp} = 7.5$ G were found. This signal corresponds to the total concentration of spins $S = 1/2$ of $\sim 7.8 \times 10^{20}$ mol^{-1}, which is very close to the one found above using low-temperature magnetometry. This linewidth value originates from an exchange and dipole–dipole interaction of all groups with paramagnetic spins 1/2 inside the crystalline core. Note that for the commercial synthetic high pressure–high temperature (HPHT) diamonds of type Ib with concentration of paramagnetic nitrogen ~100 ppm, the linewidth of the main central ESR signal ($g = 2.0024$) equals ~1 G, *i.e.,* is much smaller.

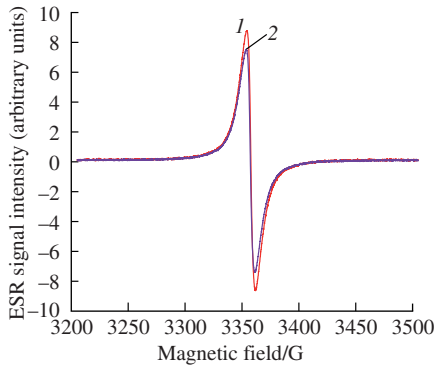

Figure 2 ESR spectra of DND samples at microwave frequency 9.4023 GHz: (*1*) initial sample and (*2*) the same sample after γ-irradiation. Microwave power is 0.03 mW.

This comparison is in favour of a huge concentration of spin-radicals inside the DND particles, whose origin has been discussed[16,17,20] as related to various dangling C–C bonds and substitutional nitrogen atoms in the diamond lattice. We also cannot exclude the presence of various vacancy-based paramagnetic centers carrying the spin 1/2. It is known that the most part of radicals is buried in the depth of less than 1.5 nm below the particle surface.[17]

ESR spectrum of the sample DND-irr was taken within one day after the end of irradiation (see Figure 2, curve *2*), with its peak intensity being slightly less than that of the DND-ini one. The spectra for both samples are enough well coincided in their positions on the magnetic field scale and in their *g*-factors. The linewidth for the DND-irr sample (~7.6 G) is the same with accuracy of ~2% as that for the DND-ini one, but its double integrated intensity, roughly evaluated as $\sim I_{pp} \times \Delta H_{pp}^2$, is ~15% less. Such a small difference between both spectra means that the concentration of spin-radicals in the irradiated sample is only slightly lower than that of the initial one and new spin-radicals do not appear or exist in the system for no more than a few hours after the end of irradiation. Usually the sp^3 covalent diamond lattice is quite resistant to the appearance of defects after irradiation with energy less than 2 MeV,[1,2] but this is not the case for the molecular shell. The functional groups standing alone on the DND surface are very flexible and undergo bending, stretching and torque vibrations, whose intensity depends on temperature, thus the probability of reaction between the dangling bonds created by γ-radiation and the surrounding alien species increases with temperature. We can conclude that even spin-radicals appearing in the molecular shell of DND for a short time recombine very quickly through reaction of sp^3-C$^{\cdot}$ and other radicals with alien mobile species, namely molecular oxygen, water and the products of their radiolysis.[24] Thus, the DND terminated by oxygen-containing groups acts as a radical scavenger, and this results in the formation of sites such as sp^3-C–OH, sp^3-COOH and intermediate sp^3-COO$^{\cdot}$ radicals, which undergo subsequent transformation. These reactions are highly probable in the presence of air and traces of moisture in the irradiation chamber as well as taking into account the flexibility, namely stretching and bending vibrations, of the functional groups at room temperature. Radiolysis of adsorbed water[†] also promotes the oxidation of DND surface with formation of sp^3-C–OH sites. Here we do not consider reactions between the oxygen and nitrogen radiolysis products in the N_2–O_2–H_2O system on the DND surface, which can proceed with generation of nitrogen oxides and/or nitric acid. In general, we assume that the surface radicals formed *via* breaking of the surface C–C and C–O bonds cannot be stabilized and thus recombine within the nanoparticle surface even if there is a migration of free valences far away from the primary sites of the C–C and C–O bonds disruption. As well, DND powder is not dense, so oxygen and the majority of the mobile water radiolysis products easily diffuse to the reaction centers with formation of carbonyl and carboxyl groups. Therefore, γ-radiation promotes the partial oxidation of material surface and changes the strength of covalent bonds between the neighbouring DND particles. We also assume that the experimentally observed ~15% drop in the ESR signal intensity is related to saturation of some shallow

[†] The radiolysis of water is known to give the following long-lived chemical species that appear 0.1 μs after their excitation and ionization: H$^{\cdot}$, OH$^{\cdot}$, $HO_2^{\cdot}$, e_{aq}^-, OH^-, H_3O^+, H_2 and H_2O_2, with OH$^{\cdot}$ being the most effective free radical oxidant for the shells of nanoparticles and bio-molecules.[24] The ability of DND particles to scavenge e_{aq}^- and OH$^{\cdot}$ radicals is described[25] along with the significant degree of water adsorption by DND.[26]

dangling bonds on the surface by the products of water and/or air radiolysis. It has been found that the IR absorption spectrum of DNDs with oxygen-containing functional groups reminds the one for cellulose,[12] which is notable because the natural polysaccharides like cellulose, chitin and chitosan are prone to radiation-induced degradation, and the degree of destruction is 4–5 times less for biopolymers with MeCONH groups like chitin compared with cellulose.

The analysis of known data on γ-radiation of various carbon materials[10,27–33] (for details, see Online Supplementary Materials) allows one to conclude, that γ-radiation typically promotes the formation of crosslinks between the molecular groups on the particle surface/periphery and other surrounding moieties like polymer chains, organosilanes and/or active forms of oxygen. For DND, the most protruding surface groups are carboxyls, therefore, these groups belonging to neighboring DND particles can form an anhydride link, the same is possible for the bond between the DND particle and a third alien molecule with a carboxyl group. Hyperbranched chains having carboxyl groups can easy bind to the surface of a DND particle. Thus, the processes occurring on the DND surface during γ-irradiation are the following: (i) radiation-induced destruction and breaking of the surface C–O, C–C and C–H bonds as well as (ii) recombination of the dangling bond radicals with free ions and radicals generated by the radiolysis of physisorbed water and oxygen originated from the ambient air, with subsequent formation the new molecular products on the DND surface, including sp^3-C–OH and sp^3-C–H groups. This makes DND a promising nanofiller for some polymers with potential crosslinking between the DND particles and the polymer chains after γ-irradiation.[10]

In summary, we have not found any raise in the concentration of interior $S_1 = 1/2$ spins inside DND after prolonged γ-irradiation, *i.e.*, all the paramagnetic spin-half species located in the bulk of DND particles are sufficiently stable to such an aggressive influence. We also have not detected any contribution from other paramagnetic spin-half species with a *g*-factor that differs from 2.0027. This follows not only from rough coincidence of the ESR spectra before and after irradiation, but also from the evaluation of double integrated intensity of the signal with $g = 2.0027$ and the 15% decrease in its intensity found after the irradiation. Thus, ^{137}Cs γ-irradiation of the DND sample at room temperature in air does not create new long-living paramagnetic species, at least such centres have not been detected by ESR few hours after the end of irradiation. It confirms, that the paramagnetic species appeared on the surface through breaking of C–C and C–O bonds in the DND molecular shell quickly recombine with other mobile paramagnetic species as well as alien molecules like physisorbed H_2O, O_2 and the products of their radiolysis. It also means in principle that DND particles may form star-like (*i.e.*, radial) covalent links with polymer chains as a result of γ-irradiation, which can improve the mechanical characteristics of the polymers, including wear resistance. As well, the robustness of DNDs to the appearance of long-lived spin radicals after γ-irradiation makes them a good standard for calibration of ESR spectrometers in precise magnetochemical investigations related to counting the absolute number of spin-radicals.

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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.2021.03.027.

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