



Nuclear magnetic resonance studies of nanodiamond surface modification



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ABSTRACT

We review Nuclear Magnetic Resonance (NMR) studies of surface modification of nanodiamonds (ND). The spectra of chemically functionalized – fluorinated, chlorinated, hydroxylated, carboxylated and hydrogenated ND show formation of C–F, C–Cl, C–OH, C–COOH and C–H covalent bonds with the surface carbon atoms, respectively. These bonds reveal different chemical shifts that allow distinguishing between them in the NMR spectra. The NMR data are well supported by XPS measurements.

Nanodiamond annealing above 600 °C results in a surface graphitization, which increases with increasing the annealing temperature.

ND particles with grafted paramagnetic copper, cobalt and gadolinium ions are prepared by mixing of aqueous ND suspension with aqueous solutions of transition metal nitrates. Dissociated cations in this mixture undergo ion exchange with hydrogen atoms of the surface carboxyl groups. To evidence the ion grafting to the surface, we developed an effective approach based on the analysis of nuclear spin-lattice relaxation data. These data show noticeable acceleration of ^{13}C and ^1H nuclear spin-lattice relaxation, which results from the interaction of carbon and hydrogen nuclear spins of diamond with the unpaired electron spins of paramagnetic ions. This finding provides clear evidence of the binding of Cu^{2+} , Co^{2+} and Gd^{3+} ions to the ND surface. The aforementioned approach allows calculating distances between the ions and surface. A model of the positioning of transition and rare-earth metal ions on the ND surface is presented. The NMR data obtained are supported by EPR measurements. Biomedical applications of the studied nanomaterials are discussed.

1. Introduction

Due to their high biocompatibility and non-toxicity, nanodiamonds (ND) are promising multi-functional systems for drug delivery, cancer therapeutics, fluorescence probes and biomarkers for medical imaging [1–5]. Nanoscale diamonds are important physical systems for various nanotechnologies such as quantum computing and metrology, nanophotonics, information processing and communications [6–9]. ND applications also include galvanic coatings, polishing pastes and suspensions, polymer composites, lubricating oils, greases and cosmetic products.

Nanodiamonds are mainly produced by detonation technique from a mixture of carbon-containing trinitrotoluene (TNT) and RDX (initialism for Research Department eXplosive, also known as hexogen, whose chemical name is cyclotrimethylenetrinitramine) explosives, laser assisted technique from graphite, chemical vapor deposition from a hydrocarbon gas mixture, and by milling of synthetic diamonds produced from carbon sources by high pressure – high temperature (HPHT) and shock wave compression methods. Herewith the detonation technique is the most prevalent due to inexpensive large scale synthesis, primary particle size (4 to 5 nm) with narrow size distribution and facile surface

functionalization. The detonation nanodiamond (DND) particle consists of a mechanically stable and chemically inert diamond core and chemically active surface that can be modified/functionalized by various methods, enabling its conjugation to a wide variety of specific molecules, functional groups, linkers and biomarkers. Numerous applications of DND are just a result of such surface modification, which allows controllable preparation of DND with specified chemical, physical and electronic properties [1–5,9].

The DND surface functionalized by carboxyl groups allows grafting of the transition and rare-earth metal ions [10–17]. Such grafted nanoparticles are suggested to be used in spintronics, magnetic recording and especially as contrast agents for magnetic resonance imaging (MRI), since they reduce the relaxation time of water protons and thus enhance the local signal intensity in the examined cells and tissues that are magnetically similar but histologically distinct. Particularly promising for this purpose are Gd^{3+} ions as they have a large unpaired electron spin of $S = 7/2$ and exhibit fast spin dynamics in the gigaHertz frequency range. Several ND with conjugated Gd-containing molecular complexes were synthesized [10,16,17]. Such complexes contain one or more coordination sites available for water to interact with the unpaired electrons of the Gd(III) ion, which results in a relatively high

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water proton relaxivity of this complex in aqueous solution. Such compounds are aimed to be used as MRI contrast agents.

An important stage in this matter is a detailed characterization of the surface after its modification. Among a variety of techniques, nuclear magnetic resonance (NMR) spectroscopy is an excellent tool for solving this problem [18]. This technique allows distinguishing between different atomic and molecular groups of the same chemical element by measuring chemical shifts, i.e., deviations of the NMR frequency from the Larmor frequency caused by (i) the orbital circulation of an electron cloud induced by applied magnetic field and (ii) the mixing between the ground and excited states due to the partial unquenching of the orbital angular momentum of the electrons in the magnetic field. While the first term (called diamagnetic contribution) is due to inner electrons and is the same for all atoms of a particular chemical element, the second term (paramagnetic contribution) strongly depends on the chemical environment of the atom and on the structure of external molecular orbitals taking part in chemical bonding. Therefore it is sensitive to the nature of the chemical bond and varies from one chemical compound to another, making possible to obtain information on the studied compounds at the atomic level [18,19]. Magic angle spinning (MAS) of samples results in narrow, high-resolution NMR spectra. ^1H – ^{13}C cross-polarization (CP) MAS technique, a transfer of polarization of ^1H nuclei with high natural abundance to ^{13}C nuclei with low natural abundance, selectively brings out carbon atoms having neighboring hydrogen atoms. Some more elaborate 1D and 2D pulse sequences based on dipolar and scalar (or J) spin-spin couplings are often needed to complement the assignment of the signals.

The next important NMR parameter (especially in the context of ND) is nuclear spin-lattice relaxation time T_1 , at which, after excitation to the upper energy level, the nuclear spins return to the equilibrium state, exchanging their energy with the environment [18,19]. This process is sensitive to atomic and molecular motions and nuclear spin interaction with paramagnetic centers & defects, which creates an additional channel of nuclear spin-lattice relaxation.

In this paper, we review the recent advances in NMR characterization of the DND surfaces functionalized by fluorine, chlorine, hydroxyl, carboxyl groups and atomic hydrogen, of the DND with grafted copper, cobalt and gadolinium ions, as well as NMR studies of the nanodiamond surface purification and effects produced by ND milling and annealing.

2. NMR spectra of initial and purified nanodiamonds

Under ND production, carbon atoms do not fully crystallize in the diamond structure at the nanoscale. This is especially true for DND. During the detonation, sp^3 carbon is energetically preferred only for the first $\sim 0.5 \mu\text{s}$. For the rest of the detonation time, sp^2 carbon is the energetically preferred configuration. Such sp^2 carbons can cover the diamond core and fasten together primary ND particles forming ND aggregates, possibly by means of interparticle C–C bonds. A similar situation is implemented in ND prepared by shock wave compression and laser assisted techniques. The aforementioned sp^2 carbons can be removed by purification, which increases the cost of production and, therefore, is quite moderate with vendors selling “pristine purified NDs”. Typically such as-received samples show some sp^2 carbon shell or flakes on the diamond surface, which are detected in HRTEM, XPS, Raman and NMR measurements [18,20 and references therein]. To get rid of these sp^2 carbon components, an additional deep purification is needed, which usually includes a disintegration of the ND aggregates followed by a thorough boiling acid washing [18,20–23] (see Fig. 1a). As an example, we show the ^{13}C MAS NMR spectrum of a ND sample synthesized by shock wave compression technique (Fig. 1b) and purified by the manufacturer, which is deconvoluted into three components [22]. The intense component with chemical shift $\delta = 36 \text{ ppm}$ characteristic of carbon atoms in bulk diamond [18] is attributed to the sp^3 -hybridized carbons of the diamond core. Two other components

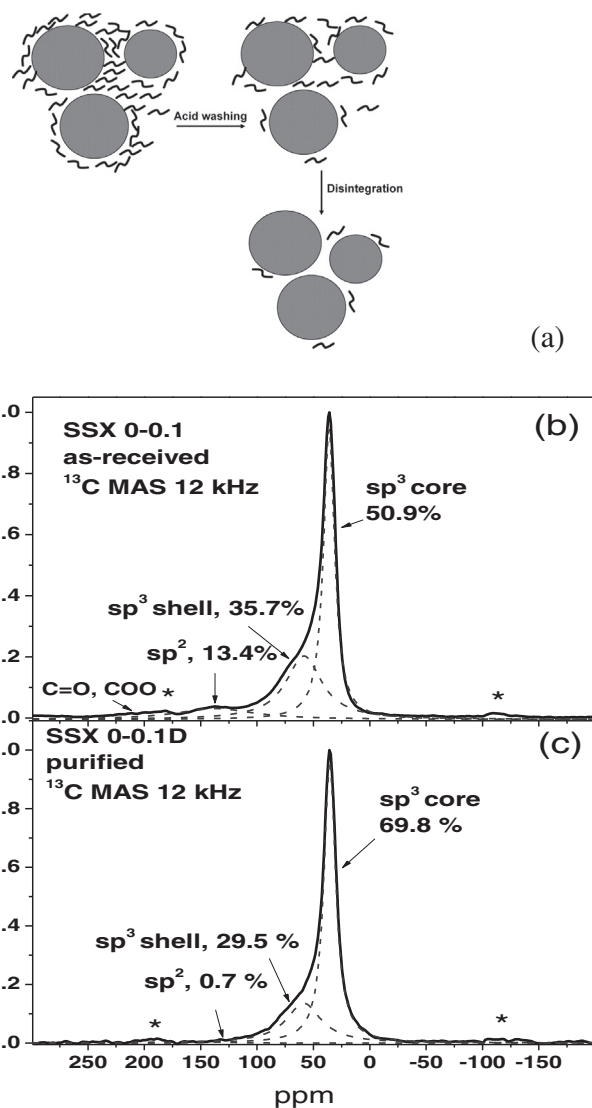


Fig. 1. Sketch of acid washing and disintegration of detonation nanodiamonds (a) (Reprinted with permission from Dubois et al. [23] Copyright 2009: American Chemical Society) and ^{13}C MAS NMR spectra of nanodiamond samples prepared by a shock wave compression method: as-received ND sample purified by manufacturer (b) and ND sample after additional deep purification (c). Deconvolutions of the spectra into three components are shown by blue dashed lines; the fractions of the components are given in Figure. Asterisks indicate spinning sidebands. (Reprinted with permission from Shames et al. [22] Copyright 2015: Wiley).

with $\delta \sim 58$ and $\sim 135 \text{ ppm}$ belong to a partially disordered sp^3 carbon shell and sp^2 carbons, respectively. Very weak signal coming from carboxyl and carbonyl groups, which overlaps with the sideband, appears at $\sim 200 \text{ ppm}$. The signal of sp^2 carbons apparently arises from the graphitic-like fragments on the periphery of aggregated diamond nanoparticles. This finding is in a good agreement with the XRD data showing broad peak at $2\theta \approx 25^\circ$ that comes from graphitic fragments (nanocaps and discontinuous sp^2 graphitic layers) on the surface of diamond nanoparticles [22]. At that, the ^{13}C MAS spectrum of the additionally highly purified ND sample (Fig. 1c) practically does not exhibit the line of sp^2 carbons, the amount of which is estimated as $\sim 0.7\%$ of all carbon atoms. Herewith the graphitic XRD peak disappears after deep purification as well, indicating nearly complete removal of the aromatic carbons in agreement with the NMR finding.

Intense ^{13}C NMR line coming from sp^2 carbons was also detected by Zagrebina et al. in as-received ND with average diameter of 50 nm prepared by a shock wave compression method [24]. Similarly, the

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