Electron Paramagnetic Spectroscopy Study on Nanodiamonds

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I. Context
Recent advances in nanotechnology have attracted considerable interest for nanodiamonds (NDs) thanks to their remarkable intrinsic properties (e.g., chemical stability, magnetic and optical properties). The relative stability of radical-like centers entrapped inside NDs constitutes a main interest for versatile applications such as EPR imaging. Here, we describe the development and design of a nanodiamond strategy (e.g., particle origin, surface oxidation, size exclusion) to demonstrate high EPR spectroscopic and imaging feasibilities. To achieve this, mathematical and IT procedures were developed and allowed experimental evidence of the conditions required for optimal phantom images resolution. The ability to perform low frequency EPR resolution imaging in combination with the stable intrinsic properties of NDs, raises the possibility of performing non-invasive tracking for biological purposes.

II. Objectives
• Study of two types of NDs as platform
• Evaluation of intrinsic EPR properties
• Physicochemical treatments to decrease the broad EPR contribution
• L-band EPR imaging optimizations
• Phantom imaging feasibility studies
• Surface grafting procedure
• Further use as an EPR imaging platform for biomedical applications
• Commercial nanodiamond particles (size smaller than 100 nm)
• EPR study
• Detectors
• Gridding of µ-sized HPHT diamonds

III. Methodology and Results

A. General scheme of a ND as an unpaired \( ^{14} \) centre
- Oxidation by air-annealing
- Controlled annealing in air leads to efficient purification of the carbon ND shells
- Structural and chemical correlations confirm surface modification for DET while no significant differences were observed for HPHT
- Surface carboxylic acid functions
- HPHT size below 10 nm may facilitate easier cell penetration for (in vitro) medical imaging and to decrease EPR linewidth

B. X-band EPR spectra
Electron spin resonance spectroscopy was performed to evaluate the influence of the treatments. Their experimental EPR spectrum can be assumed as a sum of two components of single lines with the same g-factor (\( g \approx 2.0023 \)) but having different line-width contributions: a broad spin-1/2 Lorentzian component assigned to carbon dangling bonds on the particle surface and a narrow spin-1/2 Lorentzian component attributed to defects within the diamond lattice. The observed EPR line shapes were characterized with peak-to-peak resonance width (\( \Delta H_{pe} \)) according to some parameters (e.g., NDs origin, treatments). Since the resolution in EPR imaging is closely proportional to:

\[ \Delta H_{pe} = \frac{1}{2T} \]

Thus, linewidth values were studied and modified by applying surface modification and size exclusion to reduce the broad component of the signal (TEM, Unitar, Belgium).

C. L-band EPR phantom images
Electron paramagnetic resonance imaging experiments (1 MHz) were evaluated and optimized using:
- Adequate mathematical procedures
- PTFE capillaries with different Ø (X-scanner)

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References:

Table of the 39.9 ± 0.62 conductance values of the plasma components at the NMR peak

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Surface (ppm)</th>
<th>Conductance (Ω)</th>
<th>Size (mm)</th>
<th>Peak</th>
<th>HPHT data (mV)</th>
<th>20 MHz, 37°C (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DET-asrec</td>
<td>11.9 ± 0.7</td>
<td>12.8 ± 0.7</td>
<td>5.2 ± 0.7</td>
<td>1.4</td>
<td>9.8</td>
<td>0.61 ± 0.01</td>
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<tr>
<td>DET-xrec</td>
<td>11.9 ± 0.7</td>
<td>12.8 ± 0.7</td>
<td>5.2 ± 0.7</td>
<td>1.4</td>
<td>9.8</td>
<td>0.61 ± 0.01</td>
</tr>
<tr>
<td>HPHT-18</td>
<td>11.9 ± 0.7</td>
<td>12.8 ± 0.7</td>
<td>5.2 ± 0.7</td>
<td>1.4</td>
<td>9.8</td>
<td>0.61 ± 0.01</td>
</tr>
<tr>
<td>HPHT-xrec</td>
<td>11.9 ± 0.7</td>
<td>12.8 ± 0.7</td>
<td>5.2 ± 0.7</td>
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</tbody>
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Summary of the presented work
- HPHT have better structural quality than DET with HPHT size approaching that of DET (5 nm size) after HPHT size exclusion
- EPR linewidth associated with surface and near defects induced by grinding (dangling bonds) decreases the broadening EPR lines
- Functional groups (e.g., carboxylic acid functions)
- HPHT-10nm and ultramall HPHT (<10nm) are more convenient for EPR imaging
- Stable radical-like centers
- Optimized mathematical procedures prior to imaging acquisitions

Future outlook
- Surface stabilization procedure for their use in biomedical applications