Detecting Nanodiamonds With DNP

David E J Waddington[1,2], Mathieu Sarracanie[1,3], Huiliang Zhang[3,4], David Reilly[2], Ronald L Walsworth[3,4], and Matthew S Rosen[1,3]

[1]MGH/A.A. Martinos Center for Biomedical Imaging, Charlestown, MA, United States, [2]ARC Centre of Excellence for Engineered Quantum Systems, School of Physics, University of Sydney, Sydney, NSW, Australia, [3]Department of Physics, Harvard University, Cambridge, MA, United States, [4]Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, United States

Purpose

This work aims to develop a new bio-probe based on the detection and tracking of nontoxic nanoparticles in biological environments [1]. Nanodiamond (ND), shown to be nontoxic [2], has found applications as a vector for therapeutic drug delivery [3,4] and as an optically addressable bio-probe for investigating sub-cellular processes [5]. The development of ND as an MR contrast agent has focused on the direct hyperpolarization and detection of long-lived ^{13}C nuclear spins in the ND core [6]. Investigations into the possibility of using ND as a nontoxic dopant in hyperpolarized hydrogen MRI were presented in [7].

We report the first DNP enhancement of ^{1}H in a nanodiamond/water solution at very low magnetic field. Overhauser-enhanced MRI (OMRI) utilizes the nuclear hyperpolarization of hydrogen to detect paramagnetic species. The high electronic gyromagnetic ratio (~28 GHz/T) necessitates that OMRI scanners operate at ultra low magnetic fields (~10 mT) to maximize RF penetration depth and minimize RF heating. Our result at 6.5 mT is a crucial step towards *in vivo* nanoparticle tracking with Overhauser-enhanced MRI (OMRI) based methodologies [8].

Methods

A spectroscopic DNP probe (shown in Figure 1) was constructed for use in our 6.5 mT MRI scanner [9], consisting of an NMR solenoid inside an Alderman-Grant resonator The high sensitivity NMR solenoid (276 kHz) consists of ~200 turns of 40/38 Litz wire. The Alderman-Grant resonator is tuned to f_{1e} = 130 MHz or f_{1e} = 190 MHz. A Branson 450 probe sonicator was used at 120 W average power for 20 minutes to disaggregate ND clusters. Particle size was measured before and after sonication using Dynamic Light Scattering. In DNP scans, 40 W of RF power was applied to the Alderman-Grant Resonator for 500 ms before proton magnetization was measured using a $\pi/2$ pulse.

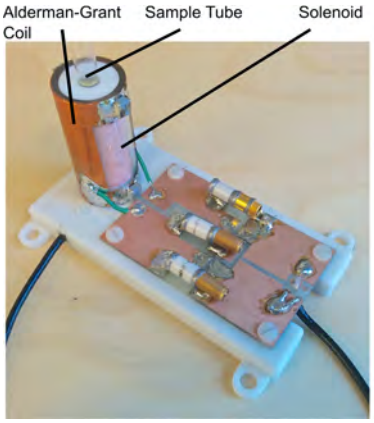

Figure 1: NMR/ESR spectroscopic probe: litz NMR solenoid (276 kHz) and ESR Alderman-Grant resonator (130 MHz). B_0, B_{1e} and B_{1H} are mutually orthogonal.

Results

A –1.36 times enhancement of the ^{1}H signal has been demonstrated in a 10%/wt solution of 100 nm natural nanodiamonds (Microdiamant) and DI water, as shown in Figure 2. Before probe sonication the average aggregate size was 2170 +/- 280 nm and our hyperpolarization experiment yielded an enhancement of 0.23. After sonication, the average aggregate size was reduced to 220 +/- 90 nm and the enhancement reached –1.36.

Discussion

The increase in enhancement with reduced aggregate size suggests that the increase in signal magnitude is due to coupling between ^{1}H in water and paramagnetic impurities on the diamond surface. Details of the enhancement mechanism will be determined by performing the DNP experiment over a wider range of *g* factors. Previous work suggested that DNP enhancement occurs via the solid effect [7] due to water adsorbed to the ND surface [10] but these measurements yielded a much smaller enhancement in a different regime (B_0 = 330 mT using different NDs at much higher ND concentration). Mapping of the DNP enhancement over a wide range of *g* values will be achieved by sweeping B_0 from 4 mT (f_H = 171 kHz) to 7 mT (f_H = 299 kHz). This measurement has thus far been hampered by poor S/N due to the large bandwidth required of the detection coil.

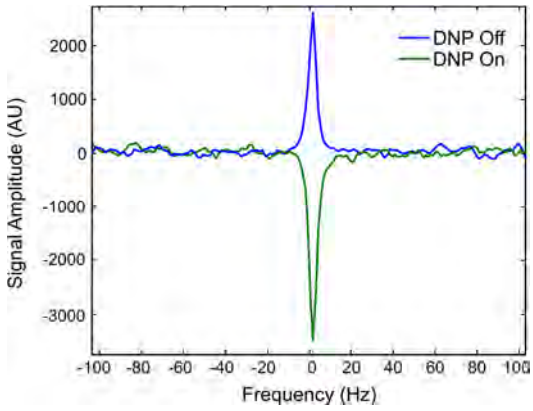

Figure 2: The thermal ^{1}H signal at 6.5 mT (276 kHz) in blue is enhanced by a factor of –1.36 after 500 ms of 191 MHz RF was applied to the ND solution (green)

Conclusion

We have demonstrated a DNP enhancement of the ^{1}H signal in water due to the presence of nanodiamonds. This result will drive further research into the use of OMRI methodologies as a means of tracking nanoparticles *in vivo*.

References

[1] M. C. Cassidy *et al.*, Nature Nano. 8, 363-368 (2013). [2] A. Schrand *et al.*, J. Phys. Chem. B., 111, 2-7 (2007). [3] H. Huang *et al.*, Nano Lett., 7, 3305-3314 (2007). [4] E. K. Chow *et al.*, Sci. Trans. Med., 73, 3, 73ra21 (2011). [5] L. P. McGuinness *et al.*, Nature Nano, 6, 6, 358-63 (2011). [6] L. B. Casabianca *et al.*, J. Phys. Chem. C, 115, 19041-19048 (2011). [7] E. Rej *et al.*, 4th Int. DNP Symposium, p30 (2013). [8] M. Sarracanie *et al.*, Magn Res. Med., 71, 735-745 (2014). [9] Tsai *et al.*, J. Mag. Res., 193, 274-285 (2008). [10] Korobov *et al.*, J. Phys. Chem. C, 111, 7330-7334 (2007).

Acknowledgement: This research was supported by the DOD DMRDP Award W81XWH-11-2-0076 (DM09094). DW was supported by ANSTO and the Australian-American Fulbright Commission.