Gadonanotubes as a Dual Modal T_1 and T_2^* MRI Contrast Agent: Magnetic Property Characterization by SQUID Magnetometry

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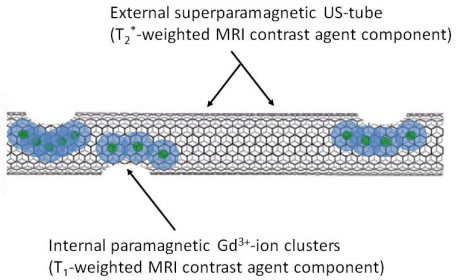

Figure 1. Illustrated diagram of Gadonanotube.

Introduction

Ultra-short, single-walled carbon nanotube capsules internalized with paramagnetic gadolinium-ion clusters (Gadonanotubes), see Figure 1, possess the unusual ability to cause marked shortening of both T_1 and T_2^*(1,2). In this work we report the magnetic properties of the Gadonanotubes that underlie the significantly shortened T_1 and T_2^* relaxation times. Thus, the Gadonanotubes represent a new paradigm in MRI contrast agent design.

Methods

Sample Preparation

Single-walled carbon nanotubes (SWNTs) created from two different synthetic methods, arc discharge (Arc) and high pressure decomposition of carbon monoxide (HiP_{CO}), were purchased from CarboLex Inc. and Rice University, respectively. Each synthesis utilizes different catalyst particles for SWNT production, Ni and Y for Arc SWNTs and Fe for HiP_{CO} SWNTs. These tubes were further purified of residual catalyst particles via bath sonication in HCl (conc.). Next, ultra-short SWNTs (US-tubes) were created via fluorination and pyrolysis following previously established methods (1). The hydrophobic US-tubes exist as bundles, yet reduction of the tubes via metallic sodium in aprotic solvent causes exfoliation of the bundles yielding individualized US-tubes (3). Finally, the US-tubes are bath sonicated in $GdCl_3$ (*aq*) rendering individual Gadonanotubes.

Magnetic Property Measurements

Approximately 10 mg of each of the above prepared samples were encapsulated within diamagnetic low density polyethylene. These samples were placed in a diamagnetic mounting straw and their magnetic properties were measured using a Quantum Design SQUID magnetometer. The samples then underwent a demagnetization sequence before being cooled to 2K and varying the field strength from 0 to 5 T creating M-H curves at 2 K. Next, the samples underwent another demagnetization before creating zero field cooled (ZFC) and field cooled (FC) samples under 1000 Oe (0.1 T) varying the temperature from 5 K to 300 K.

Results

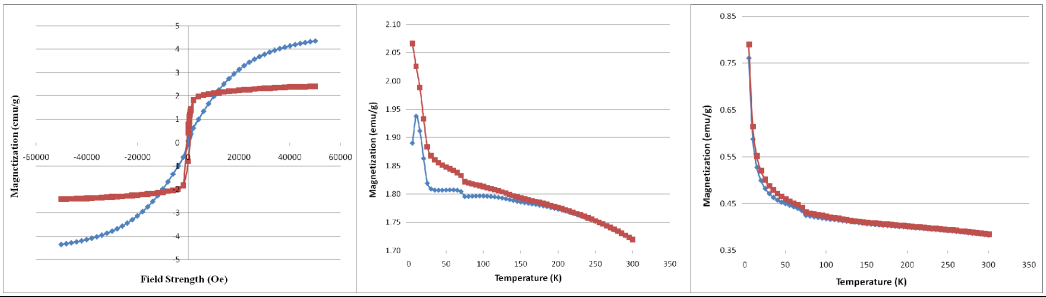

Figure 2. MPMS Results. **[Left]** M-H curve at 2 K. Red: US-tubes (Arc), Blue: Gadonanotubes (Arc). **[Center]** M-T curve of US-tubes (Arc) at 0.1 T. Red: Field cooled (100 Oe), Blue: Zero Field Cooled. **[Right]** M-T curve of Gadonanotubes (Arc) at 0.1 T. Red: Field cooled (100 Oe), Blue: Zero Field Cooled

	Full-length	Purified Full-length	US-Tubes	Purified US-Tubes	Individual US-tubes	Gadonanotubes
% Ni by mass (%)	32.14	18.26	15.78	4.97	2.32	1.95
Hysteresis (Oe)	1351	1318	1200	995	200	0

Table 1. Table denoting the % Ni catalyst remaining in the nanotube sample, as well as the amount of hysteresis present in the M-H curves for Arc tubes.

Discussion and Conclusion

US-Tubes

For both the Arc and HiP_{CO} synthesized tubes, the catalyst % (Ni and Fe, respectively) decreased at each step of preparation in that there is a direct correlation seen between the catalyst % and the degree of hysteresis as shown in Table 1. The catalyst particles likely exist in multiple domains, with each purification step causing the remaining catalyst to become closer to a single-domain system, hence the decrease in hysteresis (4). Furthermore, the step function M-H curve (Fig. 2 – left) and the delineated ZFC and FC curves on the M-T curve with a categorical blocking temperature around 100 K (Fig. 2 – center) suggest that empty US-tubes are predominately superparamagnetic (5). At clinical field strength (1.5 T), the US-tubes are magnetically saturated; the resulting perturbing dipolar field explains the significant reduction in T_2*. Further experiments are required to determine whether the superparamagnetism stems from nanoscale catalyst clusters or defect sites along the carbon sidewalls.

Gadonanotubes

The Gadonanotubes show a strong increase in magnetization (emu/g), and their M-H curve changes from the step function of the US-tubes to a more sigmoidal curve with no hysteresis or magnetic saturation (Fig. 2 – left). This change is indicative of the sample becoming more paramagnetic when internally loaded with aquated Gd^{3+}-ion clusters (4). Furthermore, the M-T curve shows a reversible ZFC/FC cycle, with the sharp upward curve also indicative of paramagnetism (Fig. 2 – right). The strong paramagnetic domain of the Gadonanotube's internalized Gd^{3+}-ion clusters explains the large decrease observed in T_1 relaxation times (1). This paramagnetic domain, coupled with the superparamagnetic domain of the US-tube nanocapsule shell, produces Gadonanotubes that are a dual modal MRI contrast agent capable of decreasing both T_1 and T_2*.

References

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