

Evolution of magnetic properties of manganese oxide nanoparticles during dissolution

Alexander Omelyanchik¹, Gurbinder Singh², Birgitte Hjelmeland McDonagh³, Valeria Rodionova^{1,4},
Dino Fiorani^{1,5}, Davide Peddis⁵ and Sara Laureti⁵

¹ Center for Functionalized Magnetic Materials (FunMagMa), Immanuel Kant Baltic Federal University, 236041, Kaliningrad, Russia

² Department of Materials Engineering, Norwegian University of Science and Technology (NTNU), 7491, Trondheim, Norway

³ Ugelstad Laboratory, Dept. Of Chemical Engineering, Norwegian University of Science and Technology (NTNU), 7491 Trondheim, Norway

⁴ National University of Science and Technology "MISiS", 119049 Moscow, Russia

⁵ Istituto di Struttura della Materia – CNR, CNR, 00016, Monterotondo Stazione, Roma, Italy

Magnetic resonance imaging (MRI) is a very powerful method in modern medicine, allowing the diagnosis of a wide range of diseases. The method is based on the resonance absorption of microwave radiation by protons in an aqueous system under a strong external field. The use of contrast agent (CA) allows improving the precision of method by change of spin–lattice (T1) or spin–spin (T2) relaxation time of waters protons. Magnetic nanoparticles (NPs) are considered as effective T2-CAs, due to their high value of magnetization and possibility to be dispersed in stable suspension for long circulation-time in the blood.

The great advantage of the high surface-to-volume ratio characteristic of NPs can be further exploited by the synthesis of hollow NPs. An increased surface allows to additional improve the both T1 and T2 signals, thus to increase the contrast and to reduce the dose with a significant neutralization of toxicity.

It has been recently demonstrated that manganese oxide nanoparticles (MONPs) are effective as dual-CAs [1], thanks to a degradation process that occurs when they are dispersed in an aqueous medium and that brings to hollow nanoparticles (Kirkendall effect) [2]: indeed, immediately after injection into the blood, MONPs are able to increase the T2 relaxation time, while after dissolution the released Mn²⁺ ions leads to a decrease of the T1 relaxation time. Such a dissolution process has been demonstrated to produce hollow nanoparticles with a significant reduction of their diameter [1].

In this work, magnetic properties of L-3,4-dihydroxyphenylalanine (L-DOPA) stabilized core/shell MONPs (Mn₃O₄/MnO) were investigated during the process of degradation. The surface of MONPs was functionalized by L-DOPA for two goals: stabilization of suspension and therapeutic effect. The magnetic properties of as-prepared Mn₃O₄/MnO nanoparticles gave evidence of the interface exchange coupling (Exchange Bias effect) between the ferrimagnetic Mn₃O₄ core, (T_C^{Mn₃O₄}=43K) and the antiferromagnetic MnO shell (T_N^{MnO}=118K). The vanishing of the EB effect and dramatic change in the remanent magnetization and coercivity values were observed after the degradation process and correlated to the microstructural features.

References

- [1] B.H. McDonagh, G. Singh, S. Hak, S. Bandyopadhyay, I.L. Augestad, D. Peddis, et al., , Small. 12, 301 (2016).
- [2] Y. Yin, R.M. Rioux, C.K. Erdonmez, S. Hughes, G. Somorjai, A.P. Alivisatos, Science. 304, 711 (2004).

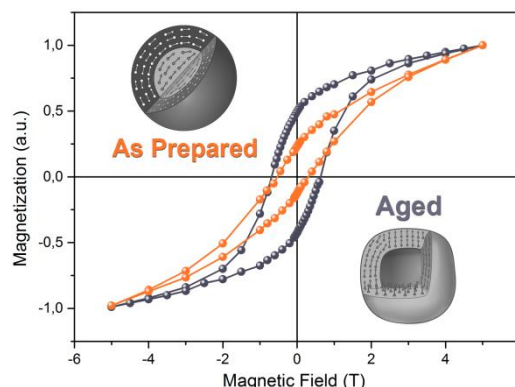


Fig. 1. FC-hysteresis loops at 5K for as-prepared and aged in an aqueous medium samples.