Experimental report

05/02/2024

Proposal: DIR-297 **Council:** 4/2023

Title: Unmasking the Complex Core-Multishell Morphology of Magnetic Nanoparticles

Research area: Materials

This proposal is a new proposal

Main proposer: Stefan HRICOV

Experimental team: Stefan HRICOV
Dominika ZAKUTNA
Ondrej KAMAN
Sara ZOUGGAGH

Local contacts: Nina-Juliane STEINKE

Samples: Fe3N

Instrument	Requested days	Allocated days	From	To
D33	3	3	21/09/2023	24/09/2023

Abstract:

This proposal aims to investigate the correlation of the chemical and magnetic morphology of ¿-Fe3N magnetic nanoparticles (MNPs) encapsulated in SiO2 with a complicated organic bridge (using the SANSPOL) with their macroscopic performance. SANSPOL measurements will enable us to precisely determine very complex chemical morphology and, furthermore, to unveil the magnetization distribution of MNPs with spatial resolution. A possible formed oxidic layer at the MNPs surface can be revealed solely by SANSPOL due to the enhanced scattering contrast not achievable by X-rays. Moreover, by investigating the nuclear-magnetic interference term will unambiguously allow us to disentangle the core and oxidic shell magnetization contributions to the total magnetization and reveal the possible presence of surface effects (spin disorder or canting). This study will ultimately uncover the connection between the physical properties (magnetization and surface disorder) and the complex core-multishell structure highly desirable for the explanation of the macroscopic performance of ¿-Fe3N MNPs in MRI, MPI, and magnetic hyperthermia.

Unmasking the Complex Core-Multishell Morphology of Magnetic Nanoparticles

Introduction

Nanoscale magnetism exhibited by magnetic nanoparticles (MNPs) is currently under high research demand, especially for their heating performance in magnetic hyperthermia cancer treatment. One of the promising nanomaterials as a heat generator is ferromagnetic ε-Fe_3N NPs. However, due to the presence of Fe2+ inside of the material, the NPs' encapsulation with the silica shell is necessary to avoid further oxidation of the NPs that leads to the diminution of the heat release. Nevertheless, since their complex nanoscopic chemical and magnetic nature, one cannot rely solely on averaged magnetization measurements or Mössbauer spectroscopy. To fully understand the connection between the performance of MNPs, their chemical and magnetic morphology at the microscopic level must be uncovered, and thus a probe that can spatially resolve nuclear fluctuations and magnetization through the NPs is necessary. Half-polarized small-angle neutron scattering (SANSPOL) is a technique that permits to probe nuclear and magnetic fluctuations at the nm-length scales allowing to unravel not only the complex chemical but also magnetic morphology [1]. In this proposal, we aim to study the chemical and magnetic morphology of core@shell-like NPs encapsulated in a silica layer via an oleic acid – oleylamine – igepal CO-520 (OA-OAM-IGP) bridge and correlate it with their macroscopic responses. The obtained information will be highly essential to properly understand the heating performance of NPs highly demanding in hypothermia cancer treatment, drug (gene) delivery, MRI, or magnetic separation.

Results

Magnetic Small-angle neutron scattering without spin polarization analysis (SANSPOL) was done at the D33 instrument at ILL, Grenoble, France. The experiments were performed at a detector distance of 2 m (5 m collimation) and 10.3 m (10.3 m collimation) and using 6 Å neutron wavelength (wavelength spread of $\Delta\lambda/\lambda$ = 10 %) and 6x10 mm beam aperture. The neutrons were polarized by a V-shape polarizer (efficiency of 0.9148), and the polarization of neutrons was changed by a radiofrequency flipper (efficiency of 0.9978). The samples were placed in 1 mm rectangular Hellma cells, and a magnetic field was applied perpendicularly to the incoming neutron beam in the horizontal direction by an HTS magnet (max. field of 2 T). The data were corrected to the background scattering, blocked beam, and polarization efficiency of the V-shaped polarizer (0. 9148) and flipper (0.9978).

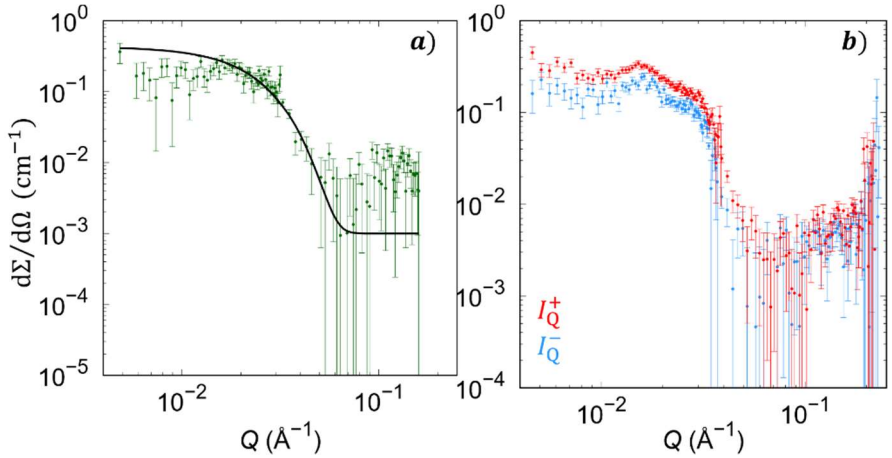

Figure 1 a) Nuclear scattering cross-section of the NSH9.H1 sample in H_2O:D_2O (32:68 by volume). The black line represents Guinier law fit. **b)** Two scattering cross-sections with different incident beam polarization (I_Q^-, I_Q^+).

To contrast match the large SiO_2 shell (SLD = $4.186 \cdot 10^{-6}$ Å^{-2}), the sample was measured in the mixture of H_2O:D_2O (32:68 by volume), and we solely focused on the magnetic core-shell nanoparticle part. The pure nuclear scattering cross-section (**Figure 1 a)**) was extracted by sector averaging (with a total opening of 20 degrees) in the magnetic field direction (horizontal, perpendicular) at the saturating magnetic field of nanoparticles (2.8 T). The sample shows unambiguous magnetic scattering visible as the splitting of

radially averaged I_Q^+, I_Q^- scattering cross-sections (**Figure 1 b)**). In the first approach, the data were described with simple Guinier law, leading to a radius of gyration of 7.5(2) nm, which agrees with the size of spherical particles obtained from TEM analysis. In the second approach, data were analyzed with the core-shell-shell model (**Figure 2 a)**) where nuclear scattering length densities were fixed from previous knowledge ($SLD_{\varepsilon-Fe3N}$ = 8.994·10^{-6} Å^{-2}, SLD_{FexOy} = 7.190·10^{-6} Å^{-2}, SLD_{SiO2} = 4.186·10^{-6} Å^{-2}). From form factor fit, we obtained the total particle size of $d_{particle}$ = 17.0(3) nm, where d_{FexOy} = 3.5(3) nm and $d_{\varepsilon-Fe3N}$ = 10.0 nm. The nuclear form factor was fixed for fit of scattering cross-sections with different incident beam polarization, and only magnetic scattering length densities of core and shell were fit parameters (**Figure 2 b)**). From the radial distribution of magnetic scattering length density (ρ_{mag}), we obtained that only the ε–Fe_3N core contributes to the magnetic scattering (ρ_{mag} = 1.4·10^{-6} Å^{-2} corresponding to the longitudinal magnetization of M_z = 962 kA/m) while Fe_xO_y shell does not contribute to the total magnetization of the sample.

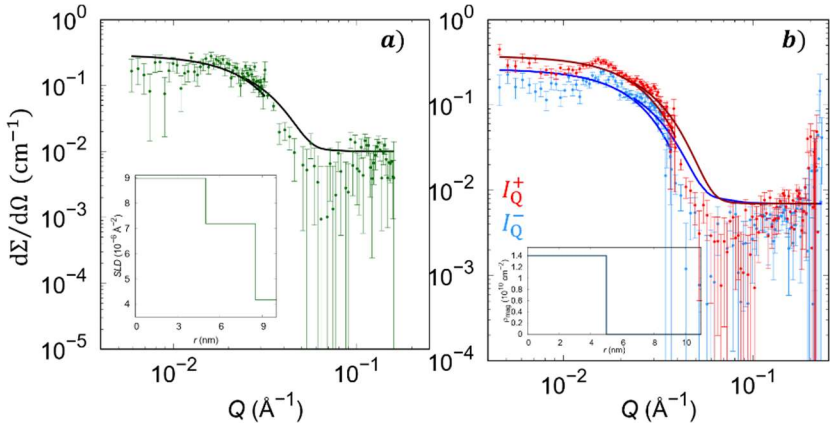

Figure 2 a) Pure nuclear scattering cross-section with core-shell-shell model with (black line). Insert: nuclear scattering length density profile. **b)** Two scattering cross-sections with different incident beam polarization (I_Q^-, I_Q^+) with core-shell-shell model fit (lines). Insert: radial distribution of magnetic scattering length density.

Further in-depth data evaluation is still ongoing.

Bibliography

[1] S. Mühlbauer *et al.*, Rev. Mod. Phys. **91**, 015004 (2019).