Experimental report

06/01/2024

Proposal:	**5-32-937**	**Council:**	10/2022
Title:	Unveiling chemical and magnetic morphology of of core@shell nanoaprticles		
Research area:	Chemistry		

This proposal is a new proposal

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Samples:	CoFe2O4@Ag CoFe2O4@BaTiO3

Instrument	Requested days	Allocated days	From	To
D33	2	2	15/05/2023	17/05/2023

Abstract:

Magnetoplasmonic (MP) and magnetoelectric (ME) core/shell nanoparticles (CSNPs) are of high interest due to the enhanced potential application arising from the coupled properties between two different physical phenomena. However, confirming the CS structure and resolving the CS interface is challenging by the classical characterization methods as it requires unraveling their chemical and magnetic morphology with spatial resolution at the nm-length scale. This research aims to unveil chemical and magnetic CS morphology through SANSPOL experiments and examine the nature of the interface (diffusive or sharp) and the origin of the coupling in MP and ME CSNPs.

Unveiling chemical and magnetic morphology of of core@shell 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 Fe^{2+} 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].

Results

First, SANSPOL experiments were performed at the D33 instrument with one passivated sample of ε-Fe3N@FexOy nanoparticles dispersed in d8-toluene. Experiments were done using 5 Å neutron wavelength (with wavelength spread of $\Delta\lambda/\lambda$= 10 %). The incident neutron beam was polarized using a V-shaped polarizer, and the polarization of the neutron beam was changed with a radiofrequency spin flipper. Data were collected at 2 and 10.3 m detector distances with collimation of 2.8 and 10.3 m, respectively, to cover the complete momentum transfer of interest. The neutron beam was focused on the sample using an aperture of 5x5 mm, and at the sample position, the horizontal external magnetic field was applied from 0 – 2.0 T. The collected data were processed in the Grasp software, where data were corrected for the background scattering, blocked beam, and polarization efficiency of the V-shaped polarizer (0.941) and flipper (0.99). The scattering intensity was transformed to the absolute scale by measuring the intensity of the empty beam. The pure nuclear scattering cross-section was extracted by sector analysis (20° of total opening) of the sum of I(–) and I(+) scattering cross-sections along the applied magnetic field direction (horizontal, 0°) at the highest magnetic field when the nanoparticles are magnetically saturated. The multishell spherical, including the oleic acid micelles form factor model, was best to ascribe the measured data, where the core represents the ε-Fe3N, the shell the passivated oxide layer of FexOy, and the next shell of the oleic acid surfactant (**Figure 1**). In the fit, nuclear scattering lengths densities of each component were fixed to the theoretical values ($\rho_{\varepsilon\text{-Fe3N}} = 7.336\cdot10^{-6}$ Å^{-2}, $\rho_{\text{FexOy-shell}} = 7.008\cdot10^{-6}$ Å^{-2}, $\rho_{\text{OA-surfactant}} = 7.8\cdot10^{-8}$ Å^{-2}, $\rho_{\text{toluene-solvent}} = 5.660\cdot10^{-6}$ Å^{-2}). The nuclear size of whole core-shell nanoparticle of $r_{\text{particle}} = 83.0(1)$ Å and the shell thickness of $d_{\text{FexOy-shell}} = 32.5(1)$ Å were obtained. Furthermore, thickness of OA surfactant of $d_{\text{OA}} = 13.7(5)$ Å was extracted. From the obtained sizes of core-shell nanoparticles, the volume fractions of core and shell part were calculated to be ϕ(ε-Fe_3N) = 0.225(2) and ϕ(Fe_xO_y) = 0.775(7), respectively.

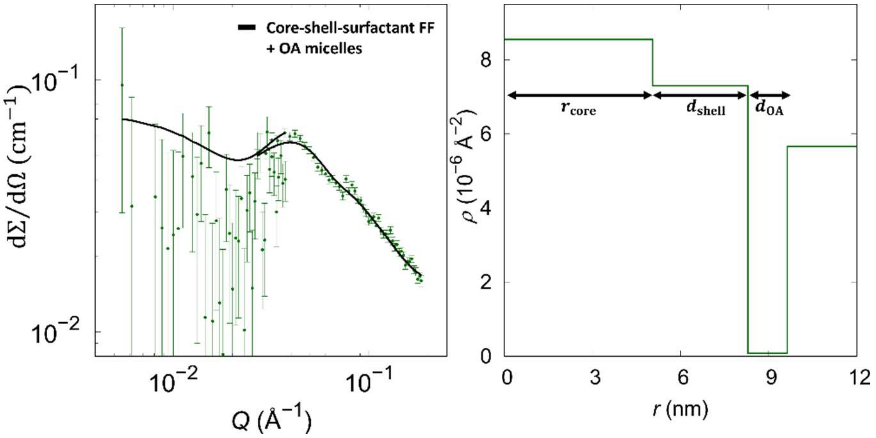

Figure 1: (left) Nuclear scattering cross-section (dark green points) with multishell and OA micelles form factor fit (black line) with (right) obtained radial distribution of nuclear scattering length density.

In the next step, the radial distribution of the magnetic scattering was obtained from fully radially averaged I_Q^+, I_Q^- scattering cross-sections. The magnetic morphology of nanoparticles was accessed from vertical sector integration (20° of total opening) of $I(-)$ and $I(+)$ scattering cross-sections. For the refinement, all previously obtained nuclear parameters were fixed, and only magnetic scattering length densities of core ($\rho_{\mathrm{mag,core}}$) and shell ($\rho_{\mathrm{mag,shell}}$) were fit at different applied magnetic fields. Data with corresponding fits are shown in **Figure 2**. From the obtained results (shown in **Figure 3**) it is evident that only the core has magnetic scattering. Looking closely at the magnetic field dependence of magnetization **Figure 3** right), the longitudinal magnetization ($M_z = \rho_{\mathrm{mag}}/b_H$, where $b_H = 2.91\cdot108$ A^{-1}m^{-1}) of the core follows Langevin-like behavior representing the core's superparamagnetic state. Using the known volume fractions of core and shell obtained from nuclear SANS fits, the total average volume weighted magnetization ($\langle M\rangle$) of core-shell nanoparticles was calculated. Further analysis of data with silica shell coating is ongoing.

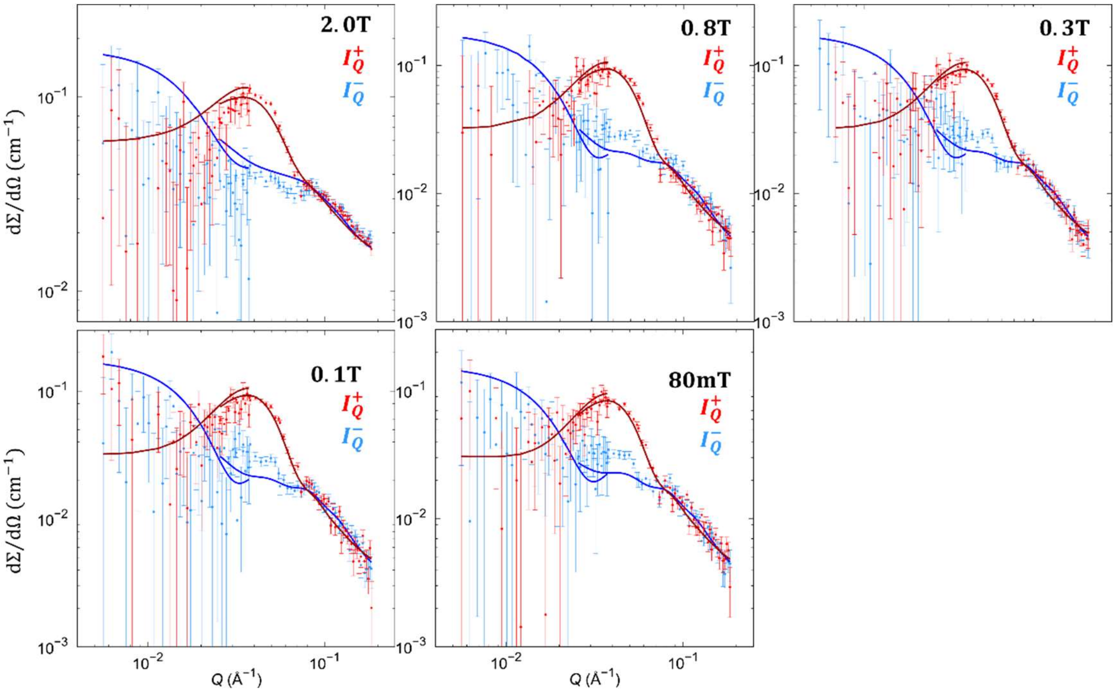

Figure 2: Field dependence of IQ+, IQ- scattering cross-sections of NHS4 sample with FF fit (lines).

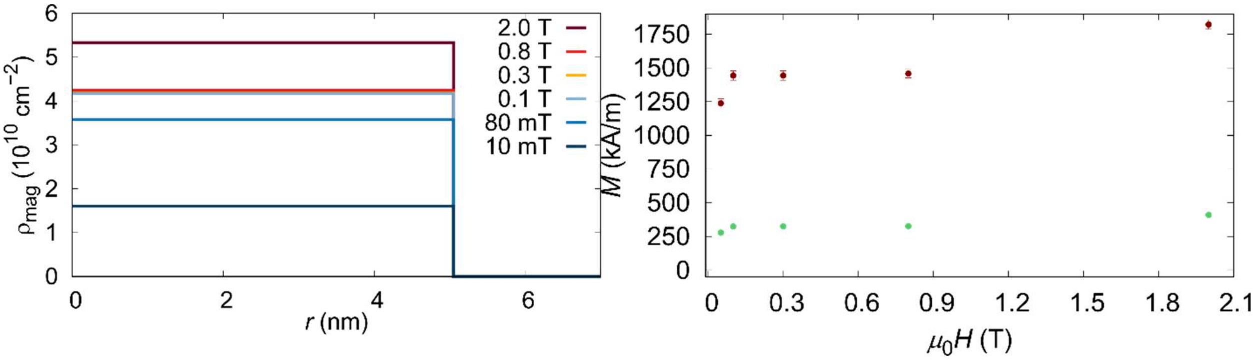

Figure 3: (left) Field dependence of radial distribution of magnetic scattering length density. **(right)** Field dependence of longitudinal (M_z - brown points) and averaged volume ($\langle M\rangle$ - green points) magnetization.

Bibliography

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