Experimental report

06/01/2024

Proposal: 5-42-578 **Council:** 4/2023

Title: Disentangling the core/shell nanoparticle magnetization and unraveling the pinning processes at the interface

Research area: Chemistry

This proposal is a new proposal

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Samples: FeO/Fe3O4
CoO/CoFe2O4
ZnO/CoFe2O4

Instrument	Requested days	Allocated days	From	To
D33	3	5	19/09/2023	21/09/2023
			28/11/2023	01/12/2023

Abstract:

Core/shell magnetic nanoparticle systems (NPs) exhibiting different magnetic orders and the structural mismatch between core and shell will be studied by employing half-polarized small-angle neutron scattering (SANSPOL). The main objective is to unravel the nature of the core/shell interface and magnetic morphology of these complex systems through analysis of the pure nuclear scattering and nuclear-magnetic interference term, respectively, and to investigate in detail the magnetic response of these systems with complex architecture for different structural mismatch and different magnetic order between phases. The results of our approach will ultimately uncover the entanglement between the macroscopic response (exchange-bias) and the core/shell structure (magnetic order and structural mismatch). Revealing the correlation of the magnetic order and structure with the exchange-bias coupling is highly important for the explanation of relaxation effects, technologically relevant for, e.g., magnetic hyperthermia and the magnetic microstructure.

Disentangling the core/shell nanoparticle magnetization and unraveling the pinning processes at the interface

Introduction

Magnetic nanoparticles (NPs) have been investigated for their numerous applications in different technological fields and biomedicine. Success in the design of systems to fulfil these applications require a fine tune in the magnetic properties of the NPs, which is directly related to the control of the composition and morphology of the system. In particular, the development of fabrication techniques of systems with complex architecture, such as core/shell or even onion-like multiphase NPs, gives new degrees of freedom to tune specific physical-chemical properties by combining materials with different compositions and magnetic characteristics and providing new perspectives for their potential applications. The complexity of these systems requires an exhaustive study of the stoichiometry, morphology, and crystallinity of each component of the core/shell NP, as well as the role played by surface effects and magnetic order of the phases combined with the coupling in the interfaces. However, the characterization with traditional and affordable techniques is challenging, for example, the magnetometry provides average information many times influenced by interparticle interactions, and chemical distribution within core/shell in high-resolution transmission microscopy can be affected by a high background from Fe and Co arising from microscope components. Therefore, a technique that reliably unveils the chemical and magnetization distribution within the core/shell NPs and unravels the interface's nature with spatial resolution is required. In this context, the halfpolarized small-angle neutron scattering (SANSPOL) technique is a unique and powerful tool to elucidate the nanoscale magnetization of each component with a spatial resolution allowing us to uncover the origin of the magnetic coupling at the interface in these complex nanostructured materials[1].

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 2.8 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). 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 averaging (with a total opening of 20◦) in the magnetic field direction (horizontal) at the saturating magnetic field (2.8 T). The nuclear SANS scattering cross-section with the obtained radial distribution of nuclear scattering density of the PO5 sample is presented in **Figure 1**. The data were best ascribed with spherical core-shell-surfactant (CSS) with oleic acid (OA) micelles form factor model. In the fit, nuclear scattering lengths densities of each component were fixed to the theoretical values ($\rho_{\text{FeO- core}} = 7.336 \cdot 10^{-6}$ Å^{-2}, $\rho_{\text{Fe3O4-shell}} = 7.008 \cdot 10^{-6}$ Å^{-2}, $\rho_{\text{OA-surfactant}} = 7.8 \cdot 10^{-8}$ Å^{-2}, $\rho_{\text{toluene- solvent}} = 5.660 \cdot 10^{-6}$ Å^{-2}). The nuclear size of whole core-shell nanoparticle of $r_{\text{particle}} = 7.53(4)$ nm and the shell thickness of $d_{\text{shell}} = 3.3(4)$ nm were obtained. Furthermore, the thickness of OA surfactant of $d_{\text{OA}} = 1.21(8)$ nm was extracted. From the obtained sizes of core-shell nanoparticles, the volume fractions of core and shell parts were calculated to be $\phi_{\text{FeO}} = 0.177$ and $\phi_{\text{Fe3O4}} = 0.823$, respectively.

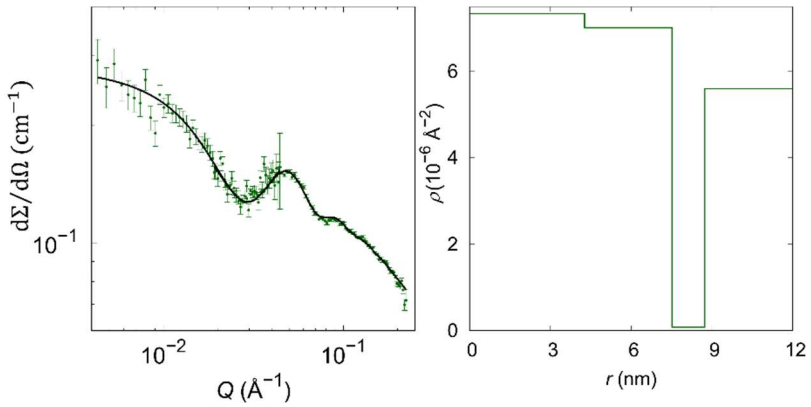

Figure 1: (left) Nuclear scattering cross-section (dark green points) with core-shell-surfactant and OA micelles form factor fit (black line) with (right) obtained radial distribution of nuclear scattering length density.

In the next step, the radial distribution of the magnetic scattering was obtained from fully radially averaged I_Q^+, I_Q^- scattering cross-sections. For the refinement, the CSS form factor model was applied, where all previously obtained nuclear parameters were fixed, and only magnetic scattering length densities of core ($\rho_{mag,core}$) and shell ($\rho_{mag,shell}$) were fit at different applied magnetic fields. Data with corresponding fits are shown in **Figure 2**.

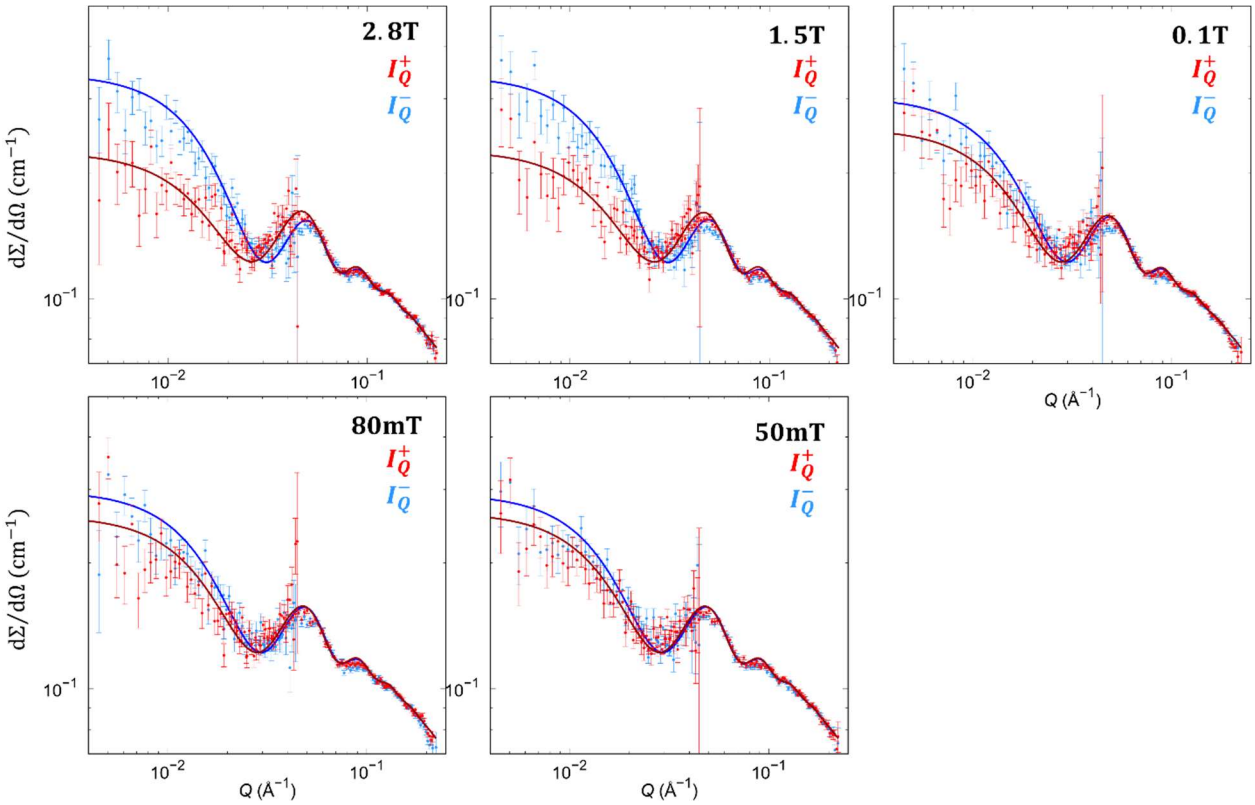

Figure 2: Measured SAXS data of all provided samples from D03 series with different form and structure factor fits.

Further data analysis on other core@shell nanoparticle systems is still ongoing.

Bibliography

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