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# Experimental Report

## SANS study of nanoporous materials for magnetic and biomedical applications

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### Introduction

The fabrication of nanocomposites containing metal or metal oxide nanoparticles loaded in mesoporous silica supports have received a considerable attention within the last years due to their high application potential in different fields such as development of magnetic sensors, efficient catalytic materials, drug delivery systems [1-4] or as contrast agents for MRI. Two different classes of MRI contrast agents are know: i) T1 contrast agents reducing proton relaxation time and providing positive contrast (bright signal) and ii) T2 contrast agents are shortening the proton transverse relaxation time thereby they are causing negative contrast (dark signal) [2]. Positive contrast agents (T1) are typically of paramagnetic nature e.g. gadolinium complexes (containing $Gd^{3+}$ ions), while superparamagnetic materials, mainly based on iron oxide nanoparticles (containing $Fe^{3+}$ ions), are negative contrast agents (T2). To be effective, MRI contrast agents must have a strong effect on longitudinal and transverse relaxation rate of water proton. To design the contrast agent two parameters are usually considered, increasing the rotational correlation time by increasing molecular weight and size or increasing the number of coordinated waters. Modified mesoporous silica could be excellent medium how to prepare MRI contrast agents. Due to porous structure of the silica, water can freely move in and out of the matrix and simultaneously, it can be carrier of metal nanoparticles.

In our work we prepared and compared nanocomposite consisting of $Gd_2O_3$ and $Fe_2O_3$ nanoparticles with size of 7 nm, embedded in the hexagonal mesoporous silica matrix SBA-15 with perfectly ordered pores of p6mm symmetry. The HRTEM, XDR and SANS study were used to confirm the loading of $Fe^{3+}$ and $Gd^{3+}$ nanoparticles with different concentration into the mesoporous system.

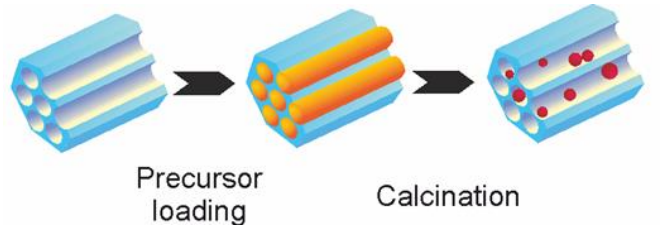
### Experimental

Nanocomposite samples consisting of $Fe_2O_3$ and $Gd_2O_3$ nanoparticles encapsulated into silica matrix (SBA-15) with 2D organization of mesopores (hexagonal symmetry) were prepared by nanocasting method and previously studied [4-9]. At first, a blank mesoporous silica matrix SBA-15 was synthesized by conventional procedure using triblock copolymer Pluronic P123 ((EO)20(PO)70(EO)20)) and tetraethylortosilicate (Si(OC2H5)4, TEOS) in acidic conditions (HCl). Subsequently, the blank matrices were used as a hard template and they were modified by

iron and gadolinium oxides via wet-impregnation. X-ray powder diffraction was used for phase analysis of nanoparticles inside porous matrices. Diffraction measurements were carried out by synchrotron radiation with energy 60 kV and wavelength λ = 0.0207 nm on accelerator PETRA III in DESY, Hamburg. SANS measurements were performed at the IBR-2 pulsed reactor, Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research (Dubna, Russia). A YuMO spectrometer was used, which has two ring detectors of scattered intensity covering the scattering vectors q dynamical range 0.005−0.7 $Å^{-1}$ due to a two-detector system. The powdered samples were putted in Alumina cells and the scattering from empty cell was measured and subtracted from scattering of the samples.

**Results and discussions**

The fabrication procedure is schematically illustrated in Scheme 1. Blank mesoporous SBA-15 silica was synthesized using poly-(ethylene oxide)-poly-(propylene oxide)-poly-(ethylene oxide) triblock copolymers as supramolecular templates. Subsequently, two different metal ions ($Fe^{3+}$ or $Gd^{3+}$ ) and four different nanoparticles concentrations (denotes as 0.01M, 0.1M, 0.5M and 4M) were used to prepared $Fe_2O_3$@SBA-15 and $Gd_2O_3$@SBA-15 nanocomposites.




**Schema 1**. Schema of fabrication procedure.

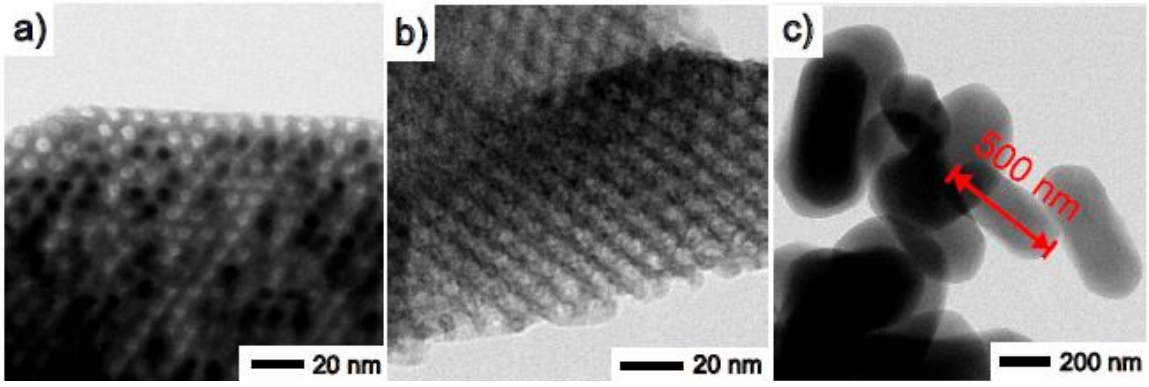



**Figure 1**: TEM micrographs: a) $Fe_2O_3$@SBA-15 (cross-section); b) $Gd_2O_3$@SBA-15 (cross-section); c) blank silica particles.

TEM micrographs (Fig. 1) of composites revealed retained hexagonal symmetry of porous matrices after loading and crystallization of $Fe_2O_3$ and $Gd_2O_3$ and nanoparticles. The size of embedded particles inside silica matrix was controlled by the pore size and was approximately of 7 nm.

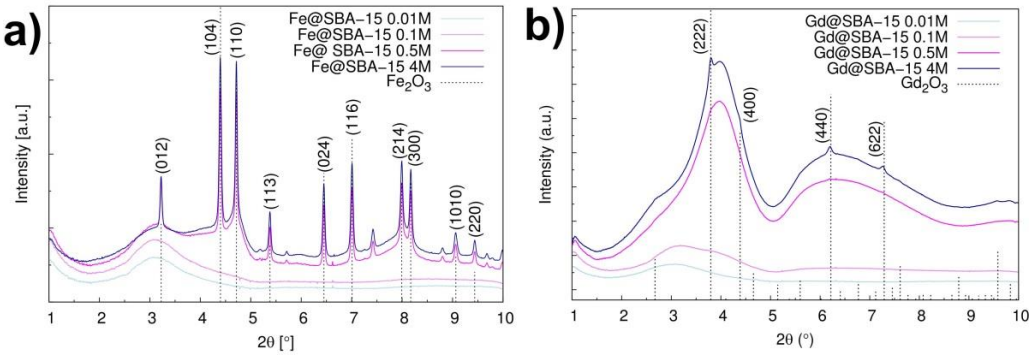



**Figure 2:** Diffraction pattern of studied samples a) $Fe_2O_3$@SBA-15, b)$Gd_2O_3$@SBA-15. The solid lines represent the peak positions of the hematite (reference JCPDS No. 86-0550) and gadolinium oxide (reference JCPDS No. 43–1014).

The diffraction patterns of the nanocomposites are demonstrated on Fig. 2. All samples modified with iron (Fig.2a) and gadolinium (Fig.2b) precursors exhibited one broad peak at 2θ = 3.09° assigned to mesoporous silica matrix. Samples with higher concentration (0.5M a 4 M) of $Fe^{3+}$ ions, see Fig. 2a, and $Gd^{3+}$ ions, see Fig. 2b, show reflections for α-$Fe_2O_3$ (hematite) (space group R-3c (No. 167), JCPDS No. 86-0550) and for $Gd_2O_3$ (space group Ia-3 (No. 206), JCPDS No. 43-1014), respectively.

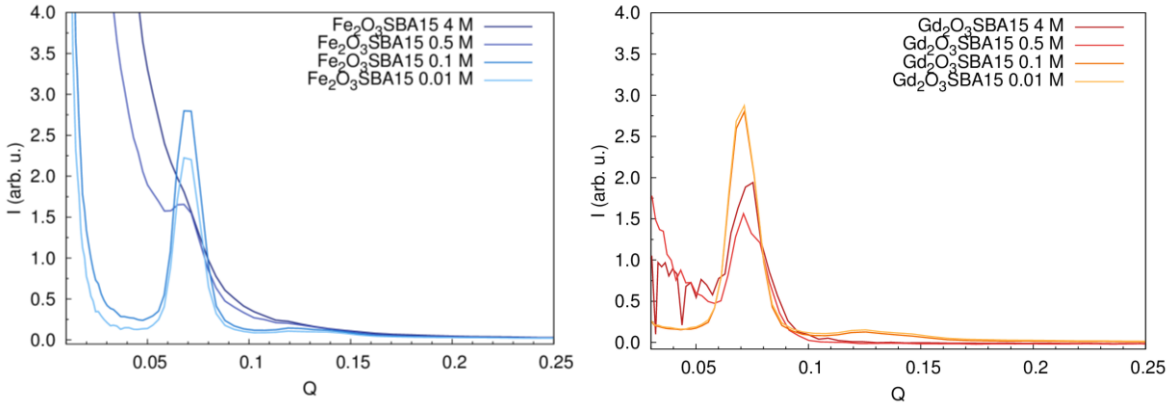



Figure 3: SANS profile of studied samples a) $Fe_2O_3$@SBA-15, b)$Gd_2O_3$@SBA-15.

The SANS pattern of the iron modified sample $Fe_2O_3$@SBA-15 (Fig. 3a) showed that the long-range order of the silica support was preserved upon impregnation and subsequent calcination of the sample during the preparation. The peaks of the modified samples with four different concentrations of nanoparticles and different ions ($Fe^{3+}$ and $Gd^{3+}$) have the same q value which indicates no change of the structural arrangement during the modification.

Empiric model of examined composite systems scattering curves is currently being developed. It takes into account structure factor of hollow mesoporous silica matrix based on previous works [9-11] including diffuse scattering. Model has been extended by additional term considering scattering from isolated spherical objects with size distribution simulating nanoparticles randomly dispersed within the pores of matrix. We report the example of fit of

proposed model to experimental data obtained for the $Gd_2O_3$@SBA15 0.01M sample, where we assume the contribution of scattering signal originating from nanoparticles is minor, (Fig. 4, red curve). Fit parameters have been set according to the structural studies of examined systems reported elsewhere [10], pore center-to-center distance 10.2 nm, pore radius 3.8 nm. For the comparison, we also plot model scattering curve with enhanced signal originating from spheres of radius 3 nm (Gauss distribution, standard deviation 0.5 nm), (Fig. 4, blue curve). As we can see, model fits experimental data for the matrix with low particle concentration quite well, corroborating the presence of hexagonal matrix (the presence of significant maximum at q = 0.072 $A^{-1}$ and two minor maxima in the range of q = 0.1-0.15 $A^{-1}$)

The trend of progressive filling the pores by nanoparticles can be simulated roughly by increasing the term corresponding to form factor of spherical objects. The q = 0.072 peak is becoming less apparent and successively disappears in cases of samples with the highest concentration of nanoparticles, samples $Fe^{3+}$ in Fig.3 and Fig. 4. This shows on effective introduction of $Fe_2O_3$ nanoparticles to the porous system. Similar effect, even though not so pronounced, can be observed in the samples containing $Gd_2O_3$ nanoparticles.

Since this study can be regarded as pioneering work devoted to investigation of such kind of nanocomposites by SANS, more profound analysis of the systems is inevitable. Further SANS measurements by means of contrast matching method would be feasible in order to gain more information about the systems, enabling the consideration of the significance of particular terms contribution to overall signal resulting in proper tailoring of developed model.

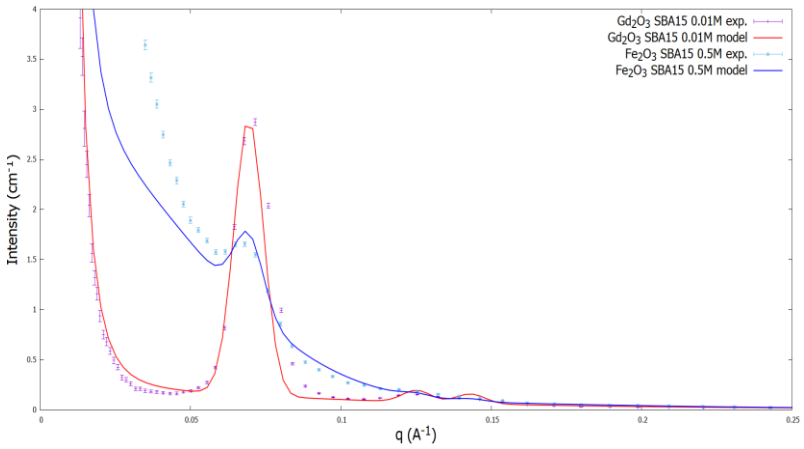



**Figure 4:** The comparison of experimental data with models designed for scattering of hexagonal matrix containing nanoparticles with low concentration $Gd_2O_3$@SBA-15 0.01M (resembling hollow matrix), red curve, and high concentration $Fe_2O_3$@SBA-15 0.5M, blue curve.

## Conclusions

We have prepared $Fe_2O_3$ and $Gd_2O_3$ nanoparticles with the same concentration embedded into channels of mesoporous silica matrix SBA-15. SANS study confirm the presence of iron and gadolinium oxides allocated within the silica pores and the fact that the long-range order of the silica support was preserved upon impregnation and subsequent calcination of the sample during

the preparation. Moreover, matrix serves not only as nanoreactor for size and growth control of nanoparticles but also serves as medium to increase number of bonded water molecules.

**References**

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