



Magnetic nanocomposites of periodic mesoporous silica: The influence of the silica substrate dimensionality on the inter-particle magnetic interactions



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ABSTRACT

Magnetic nanocomposites consisting of iron oxide (hematite, α -Fe₂O₃) nanoparticles loaded into the pores of the periodically ordered mesoporous silica with hexagonal (SBA-15) or cubic (SBA-16) symmetry were investigated. The characterization of the samples was carried out by N₂ adsorption/desorption, Small-angle X-ray scattering (SAXS), High-energy X-ray diffraction (HE-XRD) and HRTEM measurements. The magnetic properties of the prepared nanocomposites were investigated by the SQUID magnetometry. It was shown, that in spite of its non-magnetic nature the silica matrix significantly influences the magnetism of the samples. The magnetic properties are strongly affected by the strength of inter-particle interactions and dimensionality of the porous matrix. Weak dipolar interactions between superparamagnetic (SPM) hematite nanoparticles were observed in the nanocomposite with hexagonally ordered silica channels (α -Fe₂O₃@SBA-15), while the strong interactions between hematite nanoparticles, suggesting the superspin glass behavior (SSG), were observed in the nanocomposite with silica matrix of cubic symmetry (α -Fe₂O₃@SBA-16).

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1. 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 or as contrast agents for MRI [1–3]. The use of the mesoporous silica to design functional composite materials follows from the properties of ordered mesoporous silica like high surface area, tuneable pore size and volume, high chemical and mechanical stability [4,5]. Among the silica based nanocomposites, the systems containing iron oxide nanoparticles embedded in porous silica matrix are particularly studied due to their unique magnetic properties [6–13]. Nanocomposite materials containing different iron oxides, like magnetite Fe₃O₄ [6], maghemite γ -Fe₂O₃ [7] or hematite α -Fe₂O₃ [8–11] were investigated up to date.

Ursachi et al. [8] studied hematite nanoparticles stabilized within MCM-41 mesoporous silica with hexagonal symmetry ($p6mm$). They reported the superparamagnetic nature of prepared

nanocomposite and they showed that the magnetization characteristics are influenced by the non-negligible interparticle interactions between hematite nanoparticles. Tadic et al. [10–12] studied the magnetic properties of crystalline iron oxide nanoparticles (hematite) prepared in a silica matrix synthesised by the sol–gel method. They reported very interesting magnetic properties of the prepared materials, like high saturation magnetization, low blocking temperature, superparamagnetic behavior above 30 K, and AC susceptibility behavior well described by the Néel–Arrhenius model for single domain non-interacting nanoparticles.

Several authors studied the influence of dimensionality and the textural properties of the porous supports on the physical properties of iron oxide nanoparticles. Tsoncheva et al. [14,15] found, that catalytic properties of composite materials containing iron oxide nanoparticles depend on the pore topology of the silica supports. Ballem et al. [16] showed that the size of the hematite nanoparticles can be controlled by the pore topology of mesoporous silica (SBA-15 or SBA-16). They reported that the nanoparticles synthesised using SBA-15 as a mold had a larger particle size and wider size distribution (10 nm) in comparison with the nanoparticles prepared using the SBA-16 as a mold (4 nm). However, they did not study the influence of dimensionality of mesoporous substrate on the magnetic properties of the nanocomposites [16]. Alam et al.

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[17] compared the structural and magnetic properties of different nanocomposite species build-up from iron oxide nanoparticles loaded into silica and carbon porous matrices. They found that the pore diameter of the supports controls the diameter of nanoparticles confined in the nano-channels of the supports whereas the structure of the silica template dictates the magnetic parameters of the immobilized iron oxide nanoparticles.

It can be seen, that although the several authors studied the interactions between the magnetic nanoparticles in the composite silica materials, no detailed study of the dynamics of the interparticle interactions and relaxation times has been published. However, such properties are crucial for fundamental research as well as potential technological application of magnetic nanocomposites [18]. For example, the inter-particle interactions between magnetic nanoparticles have a strong influence on the superparamagnetic relaxation [18–21]. The changes in the relaxation time can cause the spontaneous data erasure in recording devices (caused by thermal fluctuation). Moreover, interparticle interactions in composite systems are valuable for studying of different magnetic phenomena. Magnetic nanocomposites with an assembly of widely spaced (isolated) nanoparticles coupled by sufficiently weak inter-particle interactions may exhibit superparamagnetic behavior, while the strong interactions may result to a collective state of nanoparticles with similarities to atomic spin-glasses [19–22]. Such strongly interacting nanoparticles systems are often called as “superspin glasses” (SSG).

With aim to confirm the direct influence of silica matrix symmetry on the dynamic magnetic properties we have studied nanocomposites containing hematite nanoparticles (α -Fe₂O₃) loaded in the mesoporous silica matrix. Nanoparticles were loaded into SBA-15 silica with 2D organization of mesopores (hexagonal symmetry) and SBA-16 silica with 3D ordering of pores (cubic symmetry). We have focused on the measurements and analysis of AC complex magnetic susceptibility by SQUID magnetometry, because such measurements can help to better understand the dynamic properties of magnetic materials. In addition to magnetic measurements the nanocomposite samples were characterized by nitrogen adsorption/desorption, small angle X-ray scattering (SAXS), high-energy X-ray diffraction, and HRTEM measurements.

2. Experimental

2.1. Preparation of the SBA-15 and SBA-16 mesoporous matrix

SBA-15 silica was prepared using tetraethoxysilane (TEOS) as a silica source and poly-(ethyleneglycol)-poly-(propyleneglycol)-poly-(ethyleneglycol) block copolymer Pluronic P123 as a templating agent [23]. In a typical synthesis 4.0 g of Pluronic P123 were dissolved with stirring in a mixture of 30 g of water and 120 g of 2 M HCl at 35 °C and after the dissolution 8.5 g of TEOS was added. The resulting mixture was stirred at 35 °C for 20 h and subsequently aged at 80 °C for 24 h. The as-synthesised sample was recovered by filtration and freely dried. The organic template was removed by calcination in air at 500 °C for 7 h.

SBA-16 silica was synthesised using poly-(ethyleneoxide)-poly-(propyleneoxide)-poly-(ethyleneoxide) triblock copolymers (mixture of Pluronic F127 and P123) as supramolecular templates according to procedure reported by Kim et al. [24]. Synthesis was made in acidic conditions of 2 M HCl. The starting molar composition was 0.0016 Pluronic P-123: 0.0037 Pluronic F-127: 1.0 TEOS: 4.4 HCl: 144 H₂O. In the typical synthesis an aqueous solution of copolymers was prepared by dissolving 0.22 g of Pluronic P123 and 1.12 g of Pluronic F127 in 55.37 ml of distilled water acidified with 11.87 ml of 36% HCl. After complete dissolution of Pluronics at 308 K, 5 g TEOS was added and the mixture was stirred for 15 min. Then, the mixture was transferred into the oven heated to 373 K and kept at this temperature for 24 h under static conditions for precipitation of the product. The white solid precipitate was isolated by filtration, washed with ethanol and dried at 373 K. The product was calcined under air at 823 K to remove the copolymer templates.

2.2. Preparation of the magnetic nanocomposites

The hematite containing nanocomposite materials were prepared by filling of the pores of mesoporous matrix (SBA-15 or SBA-16) by the solution of Fe(NO₃)₃·9H₂O, followed by the thermal treatment and decomposition of the nitrate to the

iron oxide [25]. In the typical experiment the as-calcined SBA-15 or SBA-16 silica samples were treated at 200 °C for 3 h. Then 1 g of dehydrated samples SBA-15 or SBA-16, were wet-impregnated with 20 ml of 0.1 M solution of Fe(NO₃)₃ for 2 h at room temperature. After the impregnation the samples were dried at 323 K for 2 h. The dry material was heated by the rate 1 K/min up to the target temperature 773 K and kept isothermally at this temperature for 6 h. After the impregnation and calcination as-white SBA-15 and SBA-16 samples turned to orange-brown due to the decomposition of nitrate and formation of iron oxide particles. The prepared samples were denoted as α -Fe₂O₃@SBA-15 and α -Fe₂O₃@SBA-16, respectively.

2.3. Characterization

The textural properties of the parent mesoporous matrices and their nanocomposites were determined by the nitrogen adsorption/desorption experiments performed with a Quantachrome Gas Sorption System at 77 K. Prior to the experiments the samples were out-gassed at 423 K for 24 h. The specific surface area, S_{BET} , was estimated using Brunauer–Emmett–Teller (BET) equation in the relative pressure range (0.05–0.30). Pore volumes and pore size distribution were calculated using the NLDFT theory for cylindrical pores (SBA-15) or spherical pores (SBA-16). The t-plot method was used for the estimation of the micropore volume.

The high-energy X-ray diffraction (HE-PXRD) experiments were carried out at BW5 wiggler beamline of DORIS positron storage ring in DESY (Hamburg, Germany) using monochromatic synchrotron radiation with beam energy of 100 keV ($\lambda = 0.12398 \text{ \AA}$). The samples were measured at room temperature in the transmission mode. LaB₆ standard was used to calibrate the sample-to-detector distance. The background intensity was subtracted directly from XRD patterns, and the result was integrated to the Q -space ($Q = 4\pi \sin(\theta)/\lambda$) using the software package FIT2D [26].

The small angle X-ray scattering (SAXS) experiments were carried out at B1 HasyLab beamline (DESY, Hamburg) with the beam energy 12 keV ($\lambda = 1.03 \text{ \AA}$) using the PILATUS detector.

The HRTEM micrographs were taken with a JEOL JEM 3010 microscope. Copper grid coated with a holey carbon support film was used to prepare samples for the TEM observation.

The magnetic measurements were performed on a commercial SQUID-based magnetometer (Quantum Design MPMS 5XL) over a wide range of temperatures (2–300 K) and applied DC fields (up to 50,000 Oe). The inter-particle magnetic interactions were investigated from the magnetic measurements of DC magnetization and AC complex magnetic susceptibility and the experimental data were fitted by the Néel–Arrhenius law and Vogel–Fulcher law [27,28].

To determine of the quantity of the iron/iron oxide in the samples, the samples were dissolved in the hydrofluoric acid and the iron content was analyzed by atomic absorption spectroscopy (AAS). The determined content of iron corresponded to the 15 wt.% in the sample α -Fe₂O₃@SBA-15 and 12 wt.% in the sample α -Fe₂O₃@SBA-16.

3. Results and discussion

3.1. Structural properties of SBA-15 and SBA-16 matrix and their magnetic nanocomposites

Fig. 1a shows the SAXS patterns of pristine SBA-15 matrix (curve a) and that of the sample α -Fe₂O₃@SBA-15 (curve b). For the pristine SBA-15 material, three well-resolved diffraction peaks indexed as (10), (11), and (20) in the hexagonal $p6mm$ symmetry, were observed in the pattern. The respective d -spacing were 105, 60 and 53 Å. The unit cell parameter, calculated from the (10) diffraction peak using the equation $a = 2 \cdot d_{10}/\sqrt{3}$, was 121 Å. This value well agrees with the HRTEM results (see below). The SAXS pattern of the iron modified sample α -Fe₂O₃@SBA-15 (Fig. 1a, curve b) showed that the long-range order of the silica support was preserved upon impregnation and subsequent calcination of the sample during the preparation. The position of (10) diffraction peak in the SAXS pattern of the nanocomposite α -Fe₂O₃@SBA-15 is at the same q value as for the pristine SBA-15 sample. The diffraction peaks (11) and (20) diminished gradually in the composite sample (see Fig. 1a inset), which indicated the decrease in the electron density contrast between the silica walls and the mesopores due to the filling of the pores of the silica support by the iron oxide nanoparticles.

The SAXS patterns of the pristine SBA-16 and nanocomposite α -Fe₂O₃@SBA-16 are displayed in Fig. 1b as curves c and d, respectively. The SAXS pattern of the SBA-16 sample shows two peaks,

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