THE MAGNETIC BEHAVIOUR OF IRON OXIDE NANOPARTICLES PREPARED BY SELF ASSEMBLY ARRAY

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ABSTRACT

We have investigated the magnetic and structural properties of iron oxide nanoparticles prepared by two different self assembly nanotechnological approaches. Using a reverse micelle method we have prepared Fe_2O_3 nanoparticles coated by gold shell with average size of 8nm. Via a nanocasting pathway the iron oxide nanoparticles with size about 5 nm were loaded into pores of hexagonally ordered silica matrix with p6mm symmetry creating Fe_2O_3@SiO_2 nanocomposite. Magnetic measurements using SQUID magnetometer confirm in both samples the behaviour typical for a superparamagnetic system. The quantitative analysis of the real part of susceptibility χ' *due to the theoretical models confirms the existence of weak dipolar interactions between particles. Small size of iron oxide nanoparticles and their coating by Au shell or Si matrix, respectively, caused the existence magnetic moment originates in uncompensated surface spins of Fe^{3+}. Magnetic behaviour in both samples is mainly related to the surface effects (spin canting and different surface to volume spin ratio).*

Keywords: *Self-assembly system, Nanotechnology, Iron oxide nanoparticles, Magnetic susceptibility, SQUID magnetometry*

1. INTRODUCTION

Nanoparticles attract nowadays considerable research attention because they are expected to be useful as novel materials for applications in various devices such as memories, batteries, and displays showing enhanced properties [1]. Particularly the investigation in the fields of magnetic carriers of drugs and magnetic media are considered to be one of the most promising applications for nanoparticles technology. Recent progress in the electronics and information technologies resulted in the necessity to develop novel high-density storage devices and new techniques for ultrahigh density recording [2, 3]. The nano-magnetic materials of defined particle size are required for the application, which are chemically and mechanically resistant and without tendency to agglomeration.

Self-assembly process, by which molecular subunits spatially organize into well-defined supermolecular structures trough non-covalent interactions, is becoming a powerful synthesis approach for generating advanced materials such us nanoparticles, wires, rings, superlattices. One of promising method how to control the size and the shape of nanoparticles during synthesis is a reverse micelle method, where self-assembled surfactants are used. Recently we have used a reverse micelle method to prepare stable, perfectly spherical Fe@Au nanoparticles with interesting magnetic properties and superparamagnetic behaviour [4].

Another self assembly way how to prepare the magnetic nanoparticles and these densely packs into ordered structures with possibility to control their size and shape is to use the relatively new nanotechnology approach called "nanocasting" [5]. In this process, periodic porous silica materials are employed as a hard template, nanoscopic mould, where various metal or metal oxides can be incorporated creating magnetic nanocomposite with interesting magnetic properties and rigid structure.

The stability of electronic and high density data storage devices made of magnetic nanoparticles is limited by their superparamagnetic transition [2]. Therefore, here is strong interest to understand the magnetization processes in the superparamagnetic region. The current efforts are aimed at increasing the thermal energy barrier against the magnetic reversal in magnetic nanocomposite. For applicability of magnetic nanoparticles it is also important to know, how the inter-particles interaction affects the physical properties of magnetic nanoparticles system [6]. The nanoparticles samples may exhibit glassy dynamics due to strong dipolar inter-particle interaction [7], but weak or non-interacting nanoparticles systems were observed after embedding into isolated matrix [8].

In this work we present the interesting magnetic properties, such as superparamagnetism or exchange bias effect, caused by different distribution of surface and volume spins, of hematite (α-Fe_2O_3) nanoparticles.

2. EXPERIMENTAL METHODS

2.1. Preparation of nanoparticles and nanocomposite

Nanoparticles of iron oxide were prepared by two different nanotechnological approaches using a self assembled process.

i) As first, the nanoparticles of iron oxide were prepared by a reverse micelle method [10]. All micelle solutions were prepared using cetyltrimethylammonium bromide (CTAB) as the surfactant with octane as the oil phase. 1-butanol was used as co-surfactant, increasing the polarity of the surfactant and helping to stabilize the micelle solutions. The size of the nanoparticles is determined by the water to surfactant molar ratio. Here, the molar ratio of water to surfactant was ω =

$[H_2O/CTAB] = 8$.

ii) Another self assembly approach was used for preparation of magnetic nanocomposite build up from nanoparticles of iron oxide incorporated in the channel system of hexagonally ordered silica matrix. We have prepared a system via the nanocasting pathway. Tetraethoxysilane (TEOS) was used as silica source and poly-(ethylene glycol)-poly-(propylene glycol) -poly-(ethylene glycol) block copolymer Pluronic P123 as a templating agent [11]. Mesoporous silica matrix acts as a nanoscopic mould, which restricts the formation and growth of iron oxide species. The nanocomposite $Fe_2O_3@SiO_2$ we have synthesized by wet-impregnation of the porous matrix using precursor containing Fe^{2+} ions followed by the reduction of Fe^{2+} with $NaBH_4$. After reduction the sample was calcined in air at 500 ^oC [9].

2.2. Characterization

The microstructure and periodicity of the prepared nanoparticles and nanocomposite we have investigated using HRTEM micrographs 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. Long range ordering, symmetry and the phase analysis we investigated by a synchrotron related techniques SAXS and WAXS. The small angle X-ray scattering (SAXS) experiments were carried out at B1 Hasylab beamline (DESY Hamburg) with the beam energy 12 keV ($\lambda = 1.03$ Å). The wide-angle X-ray scattering was measured at BW5 Hasylab beamline (DESY Hamburg), at the wavelength $\lambda = 0.123980$ Å. 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 kOe). The same instrument was employed for *ac* susceptibility measurements carried out at frequencies 1-1000 Hz in a temperature region 2-300 K. The samples were encapsulated to a plastic sample holder. The diamagnetic contribution of plastic capsule and plastic sample holder is insignificant in comparison with high magnetic moment of the sample and no correction is necessary.

3. RESULTS

3.1. Structural properties of nanoparticles and nanocomposite

The microstructure and the morphology of the nanoparticles was determined using high resolution transmission electron microscopy (HRTEM). Representative micrograph of iron oxide nanoparticles coated by gold $Fe_2O_3@Au$ is presented in Fig. 1. The particles are isolated without aggregation, like spherical with average size of 8 nm.

As it is obvious from HRTEM micrographs on Fig. 2, the honey-comb structure of the silica matrix is retained after nanocasting of iron oxide nanoparticles ($Fe_2O_3@SiO_2$). The regular hexagonally ordered pore architecture of silica with pore size approximately 7nm is shown on micrographs taken with the beam direction longitudinal (Fig. 2a) and perpendicular (Fig. 2b) to the hexagonal axis.

The phase analysis of the samples by Wide Angle X-ray Scattering showed that iron oxide (α-Fe_2O_3, hematite) was present in the nanoparticles and in the nanocomposite [9].

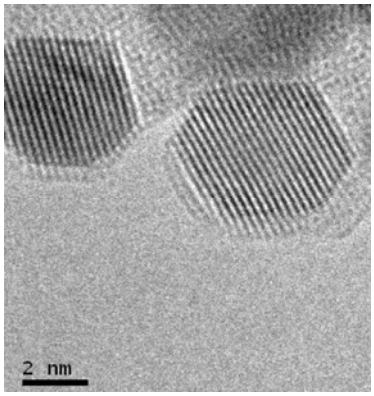

Fig. 1 HRTEM micrographs of isolated Fe_2O_3Au nanoparticles where the atomic planes are visible

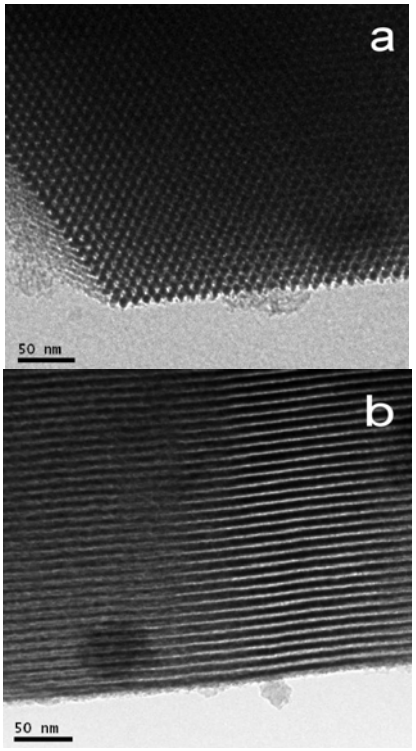

Fig. 2 HRTEM micrographs of $Fe_2O_3@SiO_2$ nanocomposite sample. (a) View along the hexagonal axis, (b) view perpendicular to the hexagonal axis [8]

Small angle X-ray scattering (SAXS) using synchrotron radiation confirmed that the host silica matrix retained its long-range order of *p6mm* symmetry and regular hexagonal pore architecture after incorporation of iron oxide particles.

3.2. Magnetic properties in *dc* magnetic field

The temperature and the field dependence of magnetization recorded in temperature range from 2 K to 300 K and in external *dc* magnetic field confirm the

superparamagnetic behaviour in both samples: Fe_2O_3@Au (see Fig. 3a) and Fe_2O_3@SiO_2 (see Fig. 3b).

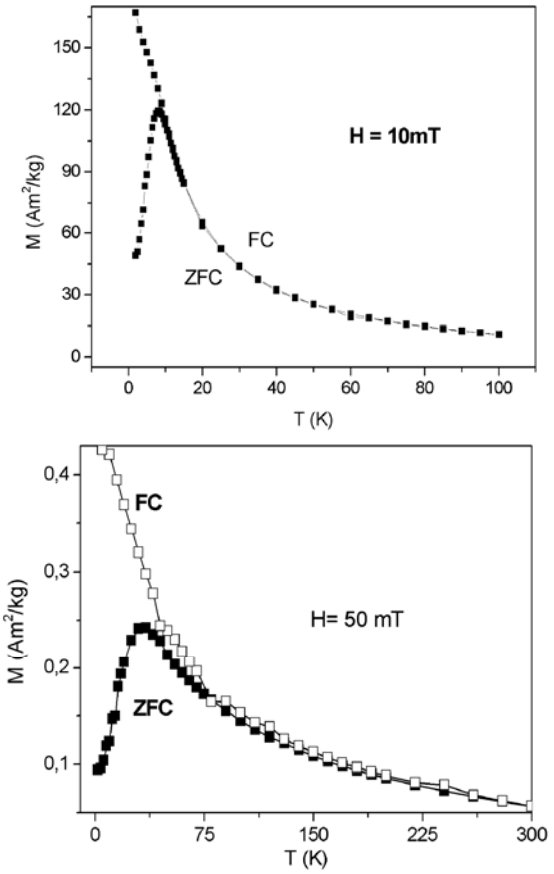

Fig. 3 Temperature dependence of magnetization in regimes ZFC (zero field cooled) and FC (field cooled) measured in a) nanoparticles of Fe_2O_3@Au [13], and b) nanocomposite of Fe_2O_3@SiO_2

The values of blocking temperature T_B about 10 K (for Fe_2O_3@Au) and 35 K (for Fe_2O_3@SiO_2) obtained from ZFC curve, and high irreversibility of ZFC and FC curves below blocking temperature T_B have shown, that above T_B moments of particles freely fluctuate in external magnetic field leads to superparamagnetism. On the contrary, below T_B the magnetic moments of each particle are blocked in the external field direction and reveal the coercivity. We have fitted our experimental data to Langevin formalism:

$$M = M_S \left(\coth\left(\frac{\mu H}{k_b T}\right) - \frac{k_b T}{\mu H} \right), \quad (1)$$

where: M_s is saturation magnetization, k_b is Boltzman constant and μ is the effective magnetic moment of each particle related $\mu = M_S(\pi d^3/6)$, where d is average size of particles. Through the fitting procedure we have obtain the value of effective magnetic moment of particles μ~150μ_B and μ~300μ_B for Fe_2O_3@Au and Fe_2O_3@SiO_2, respectively.

3.3. Magnetic properties in *ac* magnetic field

We have studied the magnetic properties of iron oxide nanoparticles (Fe_2O_3@Au) and nanocomposite (Fe_2O_3@SiO_2) in *ac* magnetic field. Data of *ac* susceptibility measured at frequencies in the range 1-1000 Hz exhibit the behaviour typical for blocking/freezing processes: i) the presence of a maximum (in real part of *ac* susceptibility $\chi'(T)$) at the temperature T_B, which shifts towards higher temperature with increasing frequency, and ii) the absorption component of *ac* susceptibility $\chi''(T)$ (imaginary part of *ac* susceptibility) exhibits a sudden onset near T_B [8]. The quantitative analysis of *ac* susceptibility data due to Arrhenius law and Vogel-Fulcher laws confirms the existence of a weak inter-particle interaction between nanoparticles of iron oxide in both samples prepared by different nanotechnological approach.

3.4. Influence of surface effect on magnetic behaviour

It is known, that perfectly compensated antiferromagnet does not show hysteresis (bulk hematite is known as typical antiferromagnet); while in our experimental results the values of coercivity about 250 mT at 2 K were observed. The unusual large coercivity could be explained by the fact that core spins are pinned by direct exchange interaction with the frozen spins at the surface layer. In this case the increasing of the coercivity would be observed only below the freezing/blocking temperature T_B of the disordered surface layer resulting to exchange interaction between surface spins [9, 12, 13]. For experimental verification of this assumption we have investigated the field dependences of magnetization (*M (H)* loops) in ZFC and FC regime at temperatures below T_B as well as we have estimated the exchange bias field E_B. Hysteresis curves under blocking temperatures for both samples exhibit a typical feature of exchange biased systems, namely, the shift of the FC hysteresis loop and enhancement of coercivity. This shift the hysteresis loop along the field axis defines directly the exchange bias field $H_{EB} = \left(H_{C+}^{FC} + H_{C-}^{FC}\right)/2$. The mechanism of exchange bias is explained by an existence of unidirectional anisotropy induced at exchange coupling interfaces with different spin orientation (e.g. ferro/antiferromagnetic). The observation of exchange anisotropy field H_{EB} = 150 mT in Fe_2O_3@Au nanoparticles and H_{EB} = 100 mT in Fe_2O_3@SiO_2 at 2 K is a clear indication of the existence of a magnetically disordered surface layer and confirms the magnetic interaction between surface spins.

4. CONCLUSIONS

In summary, we have prepared the iron oxide nanoparticles by a two different ways using self assembly pathways. After coating small nanoparticles by an isolated shell of Au and SiO_2 the interesting magnetic behaviour, such as superparamagnetism, or exchange bias effect were investigated. The results presented in this paper have shown that the magnetic behaviour in iron oxide nanoparticles is mainly related to the surface effects (spin canting and different surface to volume spin ratio).

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