Materials Chemistry and Physics 222 (2019) 217–226

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Morphological metamorphosis of magnetic nanoparticles due to the presence of rare earth atoms in the spinel structure: From spheres to cubes

Kinnari Parekh[a,*], Daniel H.G. Espinosa[b], Dennys Reis[b], Cristiano L.P. de Oliveira[b], Wagner Wlysses[b], Antônio Martins Figueiredo Neto[b]

[a] Dr. K C Patel R & D Center, Charotar University of Science & Technology, Changa, 388421, Dist. Anand, Gujarat, India
[b] Institute of Physics, University of São Paulo, Rua do Matão 1371, 05508-090, São Paulo, SP, Brazil

HIGHLIGHTS

- Replacement of 5% Fe by Ho in magnetic nanoparticles changes shape from sphere to cubes.
- Magnetic parameters like T_B and K_{eff} are bigger with cubic than with spherical MNPs.
- Small-angle X-ray scattering (SAXS) confirms shape effect due to Ho substitution.
- SAXS pattern with and without magnetic fields shows non-aggregated particles.
- $Im\chi^{(3)}$ of nonlinear optical method is 30% higher for sphere than that of the cubes.

ARTICLE INFO

Keywords:
Magnetic colloid
Nanoparticle
Structure
Optics

ABSTRACT

We report the effect of replacement of 5% of the Fe atoms by Ho during the synthesis of magnetic nanoparticles (MNPs) in the original colloidal system composed of Mn, Zn, Fe, O. Without the presence of Ho the MNPs are spherical and, when the Ho is included in the synthesis they change the shape to cubes with rounded edges. Different experimental techniques were used for the structural characterization of both systems. The magnetic characterization of both colloids showed important differences between them on their magnetic response. The magnetic coupling parameter, the blocking temperature and the effective anisotropy constant are bigger in the colloid with cubic MNPs with respect to the one with spherical particles. The magnetization vs. the applied magnetic field (until 10 kOe) did not show saturation behavior in the colloid with cubic particles, differently from the colloid with spherical particles. This result could be explained taking into account the balance between the energy of the magnetic coupling of the field with the magnetic moment of the cubes, and the thermal energy. The result of Small-angle X-ray scattering (SAXS) pattern confirms the effect of shape due to the Ho substitution in MZ sample. SAXS pattern with and without the presence of external magnetic fields shows non-aggregated particles. The nonlinear optical characterization of the colloids revealed that the imaginary part of the third-order optical susceptibility of the spherical particles is about 30% bigger than that of the cubes.

1. Introduction

Magnetic colloids, also named ferrofluids, are suspensions of magnetic nanoparticles (MNPs) in a liquid carrier [1]. Due to the nanometric dimension of the particles (typically ~ 10 nm), they have just one magnetic domain. Different materials, mainly iron oxides, are employed to build up the MNPs (e.g., Fe_3O_4, γ-Fe_2O_3, $CoFe_2O_3$, $MnFe_2O_4$) and depending on the MNPs electrostatic characteristics, the liquid carrier can be polar (water) or nonpolar (oil). Such ferrofluids are widely used in technological devices for heat dispel and magnetic driven seals. However, the biomedical applications of this material seem to be the more promising nowadays. They have been employed as drug targeting [2] and in cancer treatment (hyperthermia) [3] due to the heat dissipation by the magnetic moment of the particle coupled to an external ac magnetic field.

More challenging applications of ferrofluids, mainly in optical devices, have been proposed recently [4–6]. Ferrofluids were incorporated into optical fibers to build microstructured optical fibers. In these optical applications, the knowledge of the nonlinear optical properties of the ferrofluid is essential to guarantee the desired

* Corresponding author.
E-mail address: kinnariparekh.rnd@charusat.ac.in (K. Parekh).

https://doi.org/10.1016/j.matchemphys.2018.10.020
Received 22 January 2018; Received in revised form 8 August 2018; Accepted 8 October 2018
Available online 09 October 2018
0254-0584/

performance of the device. In particular, the nonlinear optical absorption coefficient, β, which is related to the imaginary part of the third-order electric susceptibility $Im\chi^{(3)}$ of the nanoparticles present in the ferrofluid, must be known to design a particular device. Moreover, not only the value of the susceptibility, but also the anisotropy of this parameter along different directions of the crystalline structure of the particles will help in the designer of devices taking advantage of orient the nanoparticles by using an external magnetic field.

More recently, different shapes of nanoparticles have been synthesized [7–10], besides the usual spherical one, like cubes, stars and concave cubes. From the chemical point of view, the reaction time, temperature, surfactant concentration, solvent, precursor ratio and accelerating agent are the important parameters to achieve a particular nanoparticle shape. In particular the nanoparticle growth rate seems to be the key aspect of the process, and has been explored to tune the nanoparticle shape and size distribution function [10]. This possibility of control of the nanoparticles shape opened new branches for research, not only regarding improvements in existing technological applications, but also in the search of new phenomena involving the morphology of the particles.

An aspect that has not been addressed by researchers is the eventual control of the final shape of the nanoparticles by doping an original structure with rare-earth elements (REEs), keeping the overall synthesis process the same. These atoms are bigger than those present in the usual iron oxide materials. Its presence in the original crystalline structure could favor one particular nanoparticle shape with respect to another stabilized without the REE.

In the present work, we describe the synthesis of a ferrofluid made of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ (MZ) and $Mn_{0.5}Zn_{0.5}Fe_{1.9}Ho^{3+}_{0.1}O_4$ (MZH) to investigate the effect on the nanoparticles' shape of the Holmium doping in the original structure. The reason to choose this system is due to its high pyromagnetic coefficient, i.e., high value of rate of change of magnetization with change in temperature [11]. This makes the system interesting for several applications such as coolant in distribution transformer [12] and magnetic fluid hyperthermia [13], where the reduction in magnetization per degree increase in temperature either helps in faster heat transfer or killing of cancerous cell without damaging normal cells. In both the applications the cube shape particles with narrow distribution in size increases the efficiency of the system. With this motivation, we investigate the effect of change in morphology due to the REE substitution in MZ sample. To obtain narrow size distribution, the samples were prepared using metal salt reduction technique [14–16]. All the chemical processes are kept the same in both syntheses. Ferrofluids were characterized with different techniques viz; X-ray diffraction (XRD), magnetization, transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), linear and nonlinear optical absorption to determine its physico-chemical properties. Since the Small-angle X-ray scattering is very sensitive to the size, size distribution and the eventual formation of particles' aggregates with and without an external applied magnetic field, the study was performed for both the system. A nonlinear optical technique will be used to measure $Im\chi^{(3)}$ and the anisotropy of it in the particle's crystalline structure.

2. Materials and methods

2.1. Materials

$FeCl_3$ $6H_2O$, $HoCl_3$ $6H_2O$, $MnCl_2$ $4H_2O$, $ZnCl_2$, sodium oleate, ethanol, hexane and kerosene were purchased from Sigma- Aldrich. The chemicals were used as it received without any prior treatment.

2.2. Synthesis procedure

The metal-oleate complex was prepared by reacting metal chlorides and sodium oleate as reported by T. Hyeon et al. [16]. In a typical preparation, 10.26 g, (10 mM) of $FeCl_3$ $6H_2O$, 0.75876 g of $HoCl_3$ $6H_2O$, 1.9791 g of $MnCl_2$ $4H_2O$, 1.3628 g of $ZnCl_2$ and 36.5 g, (40 mM) of sodium oleate were dissolved in solvent composed of 80 mL ethanol, 60 mL distilled water and 140 mL of hexane. The resulting solution was heated to 70 °C and kept at that temperature for 4 h. On completion, the upper organic layer was removed and the iron-oleate complex was washed three times with 30 mL distilled water. After washing, the remaining amount of hexane was evaporated off resulting in iron-oleate complex in a waxy solid form. This metal-oleate complex is then mixed with 6 mM of oleic acid and 100 mL of 1-octadecene at room temperature. The reaction mixture was then heated to the reflux temperature with the heating rate of 3 °C/min and maintained the reflux temperature for 1 h. When the reaction temperature reached 300 °C, a severe reaction occurred and the initial transparent solution became turbid and brownish black. The resulting mixture after refluxing was cooled to room temperature and washed with ethanol. The nanoparticles can be separated by process of centrifugation and then dispersed in hexane or in kerosene. The same protocol was used to prepare the sample without REE.

2.3. X-ray diffraction

Rigaku model RU-200B powder X-ray diffractometer with Cu Kα source ($\lambda_{Cu\text{-}K\alpha} = 0.15414$ nm) was used to investigate the crystal structure of the sample. The instrument was operated at 40 kV, 40 mA and the X-ray diffraction (XRD) data were recorded in continuous scan mode, scattering angle 2θ from 25 to 75°, with steps of 0.02°.

2.4. Magnetization

Magnetic measurement of fluid samples was carried out using Quantum Design MPMS DC magnetometer as a function of the sample temperature.

2.5. Zero-field-cooled (ZFC) and field-cooled (FC) dc-magnetization

The low temperature measurements were carried out under zero-field-cooled condition by freezing the sample from 300 K to 5 K in the absence of magnetic field. This will freeze the easy axis of the particles randomly oriented. After cooling at 5K, the specific field of measurement was applied (10 Oe) and the data were recorded during warming up cycle. In field-cooled measurements, samples were first cooled from 300 K to 180 K (well below the melting point of the carrier) in the absence of magnetic field so as to hinder the rotational motion of the particles. At 180 K the small field (10 Oe) was switched on for further cooling from 180 K to 5 K. This field will align easy axis of some particles in the field direction. In this case also the measurements were carried out during the warm up cycle.

2.6. Transmission electron microscopy

The morphology, size and size distribution were investigated using transmission electron microscopy (TEM). Philips CM100 Biotwin was used to capture the TEM images of the samples. The fluid was diluted 100 times and then kept in an ultrasonic bath for half an hour. A drop of the obtained dispersion was deposited on a carbon-coated copper grid and the excess fluid was dripped and dried before examining the sample under the microscope.

2.7. Energy dispersive spectrometry

The MZ and MZH fluid were analyzed in a JEOL JSM-6460 LV SEM Scanning Electron Microscope, at working distance of 20 mm and a 20 kV accelerating voltage, equipped with an Energy Dispersive Spectrometry, EDS (NORAN System Six). A volume of 15 μL from MZ and MZH fluids were deposited on silicon ⟨100⟩ substrates and by spin coating operating at 500 rpm thin films were prepared [17]. These thin