



Effect of nanoconfinement on the formation, structural transition and magnetic behavior of mesoporous copper ferrite



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ABSTRACT

Superparamagnetic, cubic single phase, ordered mesoporous copper ferrite is synthesized through confinement in nanocages of mesoporous silica. The heat generated during the reaction is conserved in the silica template pore channels, which allows the formation of copper ferrite at a relatively low processing temperature. The Jahn–Teller distortion is suppressed due to the effect of nanoconfinement and thus the high temperature phase of cubic copper ferrite is stabilized at room temperature. The particle size obtained from TEM, the crystallite size calculated from XRD and the magnetic domain size estimated from magnetization measurements are all in good agreement, manifesting the significant role of the confinement in the growth and fabrication of crystalline, single magnetic domain, nanoparticles with superparamagnetic behavior at room temperature.

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1. Introduction

The investigation of material behavior under nanoconfinement has been a topic of intense scientific scrutiny in recent years [1–4]. The synthesis of porous non-siliceous compositions by reactions within a hard template of an ordered porous silica or carbon matrix as a confining nanomold has been employed for metal or metal oxide species [5–10].

Copper ferrite (CuFe_2O_4) is known as a mixed spinel, with the general formula $[\text{Cu}_{1-\delta}\text{Fe}_\delta]_{\text{TET}}^{1\text{TET}}[\text{Cu}_\delta\text{Fe}_{2-\delta}]_{\text{OCT}}^{1\text{OCT}}\text{O}_4$ where δ is the inversion parameter. It exists in two crystallographic spinel structures: (i) the high temperature cubic phase ($c - \text{CuFe}_2\text{O}_4$) and (ii) the low temperature tetragonal phase ($t - \text{CuFe}_2\text{O}_4$). Jahn–Teller (J–T) distortion causes a structural transition from cubic to tetragonal phase at 400 °C [11–13], which is undesirable since the cubic structure possesses a larger magnetic moment than that of the tetragonal one, due to the presence of more cupric ions (Cu^{2+}) on tetrahedral sites in cubic structure [14,15]. Common strategies to suppress the J–T effect and stabilize cubic single phase in solid state ceramics are increasing either the calcination temperature to 1000 °C or the calcination time to 24 h followed by quenching

in liquid nitrogen [14–16]. Drawbacks associated with these approaches are the presence of residual strains in the system, long process times and high energy consumption.

Finite-size and surface effects, in addition to changes in the degree of inversion, cause nanoferrites to display novel magnetic behaviors. In magnetic mesoporous ferrites, confining d-electrons to the thin walls between pores creates abnormal magnetic properties [17]. Magnetic and porous nanoparticles have attracted more attention due to their potential therapeutic applications, e.g. exploiting their novel magnetic characteristics for diagnostics while utilizing the pores for therapeutic drug delivery [18–20].

To surmount the above mentioned issues regarding the formation and stabilization of cubic CuFe_2O_4 at RT, in the present work the effect of carrying out the reaction in the confined space of a mesoporous (MP) vinyl-functionalized silica matrix has been investigated. Moreover, magnetic features of MP CuFe_2O_4 obtained through the restricted growth of particles within MP silica nanocages is described in detail.

2. Material and methods

2.1. Chemicals

Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), Pluronic P123 ($M_w = 5800$, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$), triethoxyvinylsilane

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(TEVS), tetraethoxysilane (TEOS), hydrochloric acid (37%), sodium chloride (NaCl), sodium hydroxide (NaOH), ethanol (C₂H₅OH), and hexane (C₆H₁₄) were purchased from Aldrich. All chemicals were used as received, without further purification.

2.2. Samples preparation

2.2.1. Synthesis of the hard template – MP 20% vinyl silica with cubic Ia3d structure

The vinyl functionalized MP silica was obtained using the method proposed by Wang et al. [21]. In a typical synthesis, 5.68 g of Pluronic P123 and 14.4 g of NaCl were dissolved in 160 mL of 1.0 M HCl aqueous solution. After stirring at 35 °C for 6 h, a mixture of TEOS (42.56 mmol, 8.87 g) and TEVS (10.64 mmol, 2.02 g) was added slowly under stirring. After 4 h, the obtained suspension was aged at 100 °C for 24 h under static conditions in a polypropylene bottle. The product was filtered, washed with deionized water, ethanol, and acetone, and then dried at 80 °C overnight. Finally P123 was removed by treatment with 60 wt.% H₂SO₄.

2.2.2. Nanocasting synthesis of the MP CuFe₂O₄

Typically, 2.7 g of the nitrate salts of copper and iron in stoichiometric proportion were mixed together and melted in hexane (40 cc) at 60 °C. At this temperature the iron nitrate melts and the copper nitrate subsequently dissolves in the iron nitrate melt, forming a homogenous mixture. This step is crucial to obtain a single phase of the final product. Then, 1 g of the vinyl functionalized MP silica powder was added to the reaction chamber. The resulting mixture was stirred for 15 h under reflux at 65 °C. Hexane is an organic solvent poorly miscible with water (hydrophobic solvent, non-polar) while the nitrate precursors are hydrophilic (i.e. ionic salt which prefers polar/hydrophilic sites). So, this mismatch between their hydrophobic-hydrophilic (non-polar – polar) characters favors phase separation, which pushes the precursors into the pore channels of the silica matrix. Moreover, the presence of the vinyl group on the interior surface of the MP silica matrix enhances the impregnation process. The resulting material was recovered by filtration, dried in air at 80 °C and then calcined at 600 °C for 6 h. The MP silica template was removed using a 2 M NaOH aqueous solution at room temperature. The final sample, a brown powder, was recovered by centrifugation, washed with water several times and finally dried at 80 °C. Reproducibility was checked by repeating the synthesis over several batches. In order to show the effect of confinement, the same experiment was performed under identical conditions but in the absence of the MP silica template.

2.3. Characterization methods

Wide angle X-ray diffraction patterns (WXR) of the powders were obtained using a XPERTPRO powder diffractometer (PANalytical, Almelo, Netherlands) (Cu K α radiation, $\lambda = 1.5418$ Å) operating at 45 kV and 40 mA settings. Low angle XRD measurement (LXR) was done on the same mode. In addition, X-ray crystallographic studies were performed in the MAX II synchrotron facilities (Lund, Sweden) at beamline i711. The experimental setup consisted of a 4-circle diffractometer with kappa geometry and a radiation source of 1.8 T multipole wiggler. The beamline setup consisted of a single crystal monochromator, delivering a high photon flux with high energy resolution at the sample. A wavelength of 0.99 Å was used with the sample placed in 0.5 mm glass capillaries. All the images were recorded with the help of a large area CCD detector. 'Fit 2D' software was used to interpret the Synchrotron XRD data.

The thermal behavior of the samples was measured using differential scanning calorimeters (DSC Q2000, TA instrument). Fourier transform infrared spectra (FT-IR) were collected at room temperature.

A JEOL, JEM 2100F analytical transmission electron microscope equipped with a field emission gun (FEG) operating at an accelerating voltage of 200 kV was used for TEM analysis of samples and getting selective area electron diffraction (SAED) patterns. The sample was dispersed in ethanol and a drop was placed on copper grid coated with 5 nm carbon film.

Uptake of N₂ was measured at the temperature of boiling liquid nitrogen (–196 °C) using a Micromeritics ASAP2020 volumetric adsorption analyzer. Each sample was treated under dynamic vacuum at 150 °C for 10 h prior to experiments. Multipoint Brunauer–Emmett–Teller (BET) surface area (S_{BET}) was estimated between relative pressures (p/p_0) of 0.05 and 0.21. Total pore volume (V_{tot}) was calculated at $p/p_0 = 0.98$, and pore size distributions were qualitatively estimated using the Barrett–Joyner–Halenda (BJH) method.

Magnetic properties were characterized using a superconducting quantum interface device-vibrating sample magnetometer (SQUID-VSM), for variable temperature measurements ranging between 2 K and 350 K. Sample cooled down from 350 K to 2 K, either at zero magnetic field, zero-field-cooled (ZFC), or in the presence of magnetic field, field cooled (FC), and magnetization was measured. The samples were demagnetized at 350 K and then temperature was decreased for ZFC and FC characterizations.

Mössbauer spectroscopy was carried out in constant acceleration mode with a Co⁵⁷ (Rh) source. A Janis Cryostat was used to vary the sample temperature. All isomer shifts are quoted relative to the iron calibration at room temperature.

3. Results and discussion

3.1. Structural properties

XRD patterns of samples formed in the absence and presence of the MP silica template show considerable differences (Fig. 1). In the pattern for the sample made in the absence of the MP silica template (Fig. 1a), there is no evidence for the formation of copper ferrite. All peaks were indexed to those of copper oxide (CuO; JCPDS # 045-0937) and hematite (α -Fe₂O₃; JCPDS # 033-0664) while the pattern for the sample made in the presence of MP silica template (Fig. 1b), in the limit of the accuracy of XRD, confirms the formation of a single phase cubic copper ferrite (CuFe₂O₄;

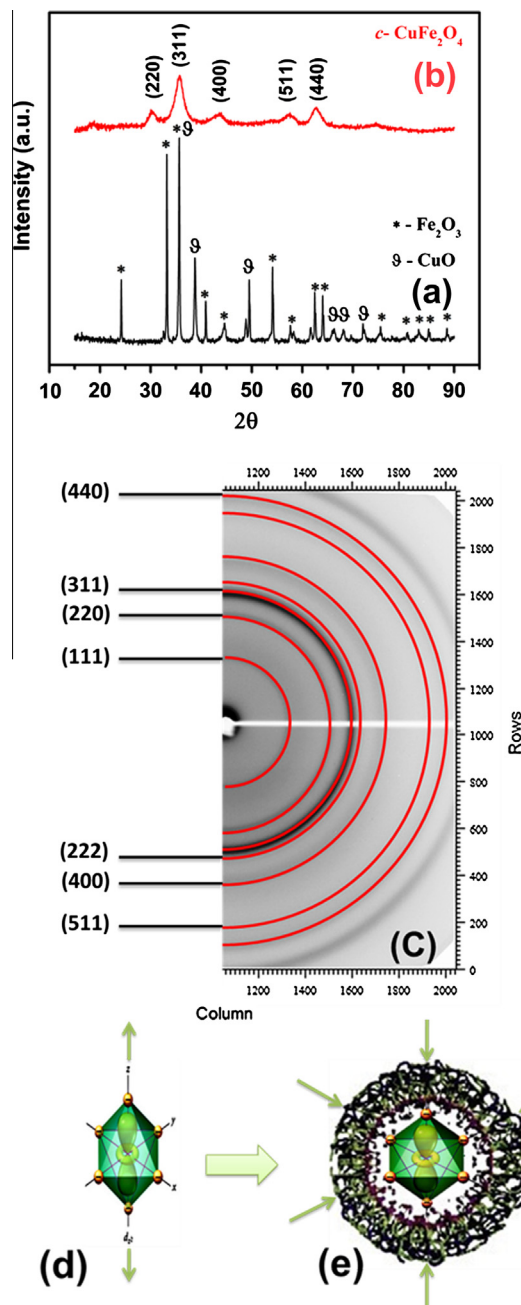


Fig. 1. Wide angle powder XRD patterns of ferrite samples synthesized in the absence (a) and presence (b) of the MP silica template. (c) Synchrotron XRD of MP CuFe₂O₄ indexed for *c* - CuFe₂O₄ (JCPDS # 01-077-0010). (d) Ligands overlap with orbital lobes, resulting in strong repulsion. (e) Simplified schematic presentation of Jahn–Teller distortion prevention in the confined space of MP silica.

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