Materials Chemistry and Physics 113 (2009) 6–9

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Materials science communication

Synthesis of monodisperse nanocrystals of high crystallinity magnetite through solvothermal process

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ARTICLE INFO

Article history:
Received 4 May 2008
Received in revised form 2 July 2008
Accepted 9 July 2008

Keywords:
Magnetic materials
X-ray diffraction
Crystallinity

ABSTRACT

A solvothermal process has been applied for the preparation of monodisperse magnetite by the decomposition of chelate iron alkoxide complexes with diethylene glycol. The magnetite nanocrystals have narrow size distribution and high crystallinity. The Fe_3O_4 products are characterized by X-ray diffraction and transmission electron microscopy, Mössbauer spectra and vibrating sample magnetometer (VSM). The nanoscale (∼50 nm) Fe_3O_4 powder obtained at 230 °C for 6 h possessed a saturation magnetization of 86.6 emu g^{-1}, a little lower than that of the correspondent bulk Fe_3O_4 (92 emu g^{-1}). It is suggested that the high-crystallized Fe_3O_4 nanocrystals formed under appropriate solvothermal conditions should be responsible for the increased saturation magnetization in the nanosized Fe_3O_4.

1. Introduction

The development of magnetic nanocrystals has been intensively pursued, for their fundamental scientific interests and many technological applications [1,5,2]. The synthesis of monodisperse nanocrystals is of key importance, because many novel properties and potential applications would emerge from monodisperse materials with small dimensions. For instance, monodisperse magnetic iron oxide nanocrystals are critical for the next-generation multi-terabit magnetic storage media [3,4]. Magnetic MFe_2O_4 nanoparticles, especially magnetite (Fe_3O_4) nanoparticles, have been used widely not only as ferrofluids in sealing, oscillation damping, and position sensing [5] but also as promising candidates for biomolecule tagging, imaging, sensing, and separation [6].

Generally, Fe_3O_4 nanoparticles can be prepared by co-precipitating ferrous and ferric ions in aqueous solution [7,8]. However, these straightforward reactions occur instantly on mixing and make it very difficult to control the course of crystallization. This makes the magnetic iron oxide nanoparticles to obtain relatively poor size uniformity and low crystallinity, which to some extent limit their use in many applications. Solvothermal process is one of the successful methods to grow crystals, in which grains formed have a better crystallinity than those from other methods. In our previous experiment, we successfully utilized this process to synthesize single crystalline Fe_3O_4 nanowires [9]. Recently, Alivisatos and co-workers reported a thermal decomposition approach to synthesize nearly monodisperse maghemite nanocrystals [10]. Sun et al. succeeded in preparing monodisperse magnetite nanocrystals by decomposition of [Fe(acetylacetonate)$_3$] in the presence of 1,2-hexadecanediol, oleic acid, and oleylamine [11]. Hyeon et al. reported maghemite nanocrystals synthesis through thermal decomposition of [$Fe(CO)_5$] [12]. However, the thermal decomposition of organometallic precursors are limited for industrial applications because of the (a) hazardous nature of precursors, (b) hazardous or complicated process, (c) high cost of the materials and (d) low product yield. We think that it is possible to solve those problems by passivating the surface of the nanocrystal by attaching capping ligands during synthesis process.

Here, instead of using toxic and expensive organometallic compounds, we intended to develop a new method for synthesis of the monodisperse Fe_3O_4 nanocrystals with a high product yield. To ensure the monodisperse nanoparticles state of the Fe_3O_4, their surface iron atoms would be complexed with capping ligands with diethylene glycol (DEG), because that the structure of its molecule is ideal for forming chelated complexes with metals, either neutral or anionic when its molecules are deprotonated. Our method is based on the hydrolysis of chelate metal alkoxide complexes using diethylene glycol and allows the preparation of nonaggregated monodisperse Fe_3O_4 nanocrystals with high crystallinity.

2. Experimental

The reagents and solvents: iron(III) chloride hexahydrate, diethylene glycol, sodium hydroxide, iron(II) chloride tetrahydrate from the Shanghai Reagent

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doi:10.1016/j.matchemphys.2008.07.080

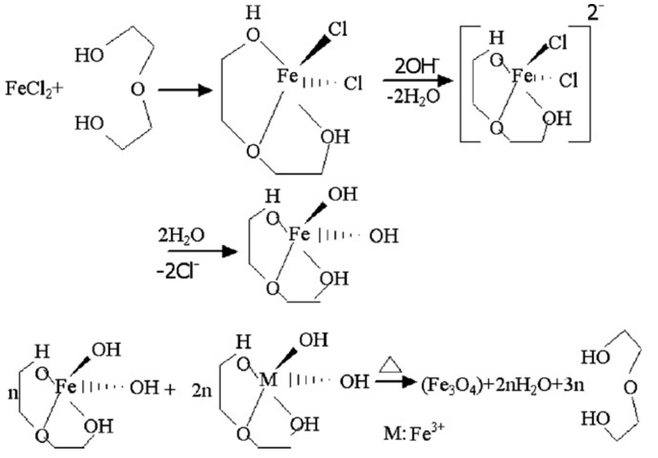

Fig. 1. Formation of metal chelated complexes and their decomposition yielding colloidal transition metal ferrites.

Company (PR China). Chemicals and solvents were used without further purification. 0.398 g $FeCl_2·4H_2O$ and 1.08 g $FeCl_3·6H_2O$ were dissolved in 80 g of diethylene glycol degassed with N_2 gas for half an hour. Separately, 0.64 g NaOH dissolved with 40 g of diethylene glycol degassed with N_2 gas was slowly added dropwise into the metal-ion solution mixture. The mixture was put into a Teflon-lined stainless autoclave. The autoclave was placed into an oven and kept at 230 °C for 6 h, then allowed to cool to room temperature. The magnetite nanocrystals were collected by centrifugation at 4000 rpm, and no size selective precipitation was applied to the sample. The product was washed with distilled water and ethanol several times to remove the excess of diethylene glycol that remained in the final products, and then dried in a vacuum oven at 50 °C for 4 h.

The samples were characterized by XRD using an X-ray diffractometer with high-intensity Cu Kα radiation (λ = 1.5418 Å), recorded at a scanning rate of 0.05° s^{-1} with the 2θ range from 20° to 80°. TEM images were taken with a Hitachi model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM) images were recorded on JEOL-2010 with an accelerating voltage of 200 kV. Their magnetic properties were measured on a Lake Shore 7410 vibrating sample magnetometer (VSM) at room temperature. ^{57}Fe Mössbauer spectra were performed at 300 K using conventional constant acceleration transmission spectrometer with a ^{57}Co (RH) source and a bath cryostat. The spectra were fitted by means of the Mösfit program, and an α-Fe foil was used as calibration sample.

3. Results and discussion

Fig. 1 shows the formation of iron metal chelated complexes and their decomposition yielding Fe_3O_4. We know that diethylene glycol can function as a complexing agent and a solvent for performing the synthesis, such as application of DEG as a solvent to synthesis of ZnO nanopowder [13]. The metal DEG complexes undergo nucleophilic substitution reactions when the temperature increases. This results in the beginning of condensation of mononuclear hydroxide reactive intermediates and eventually leads to precipitation of metal hydroxides or oxides. The crystal growth is slow enough to be monitored visually through adding a capping ligand that binds to the surface of growing nanoparticles and passivates it.

The crystalline structure of the samples shown in Fig. 2(A) was determined by powder XRD. The diffraction patterns and relative intensities of all diffraction peaks match well with those of JCPDS card (19-0629) of magnetite. The reflections characteristic of maghemite are not observed. The Mössbauer spectrum (Fig. 2B) consists of two hyperfine magnetic sextets, one for Fe^{3+} at tetrahedral sites and the other for the mixed valence $Fe^{2.5+}$ at octahedral sites. This result also indicates that the sample is not γ-Fe_2O_3 but Fe_3O_4 [14].

The average crystallite sizes of the powder have been estimated using several methods. The Debye–Scherrer formula [15] used from the reflection of (3 1 1) of the most intense peaks of X-ray diffraction pattern leads to ~50 nm. These values are in well agreement with those measured from the TEM and SEM. The TEM micrographs (Fig. 3A) of these nanocrystals demonstrate the high quality and monodispersity of the as-synthesized nanocrystals, with around 50 nm average size. The selected area electron diffraction pattern in Fig. 3B further supports the magnetite crystal structure. Electron diffraction measured from a large zone presents rings that can be indexed to the magnetite structure. The magnetite nanocrystals appear as cubic dots with narrow size distribution, even though no size selection was applied to the as-synthesized particles, which is what is commonly done by centrifugation to eliminate the larger particles that could not be stabilized by the solvent. High-resolution TEM image in Fig. 3C demonstrates that each magnetite nanoparticle is single crystal. It exhibits planes with interplanar distances of 0.48 nm that are characteristic of (1 1 1) spinel planes. No stacking faults are visible. These observations suggest that the nanoparticles are monocrystalline and quite monodisperse. An SEM image of the magnetic sample is shown in Fig. 3D. It shows that most of the magnetite nanoparticles possess uniform size.

The magnetic properties of the as-prepared magnetite nanoparticles were investigated with VSM at room temperature. Fig. 4 shows a typical magnetic hysteresis curves for the nanocrystals. The saturation magnetization of the cubic nanoparticles exhibits a high saturation magnetization (M_s) of ~86.6 emu g^{-1}, slightly below that of bulk Fe_3O_4 (92 emu g^{-1}) [16], but further higher than which of Fe_3O_4 nanoparticles by direct co-precipitation route

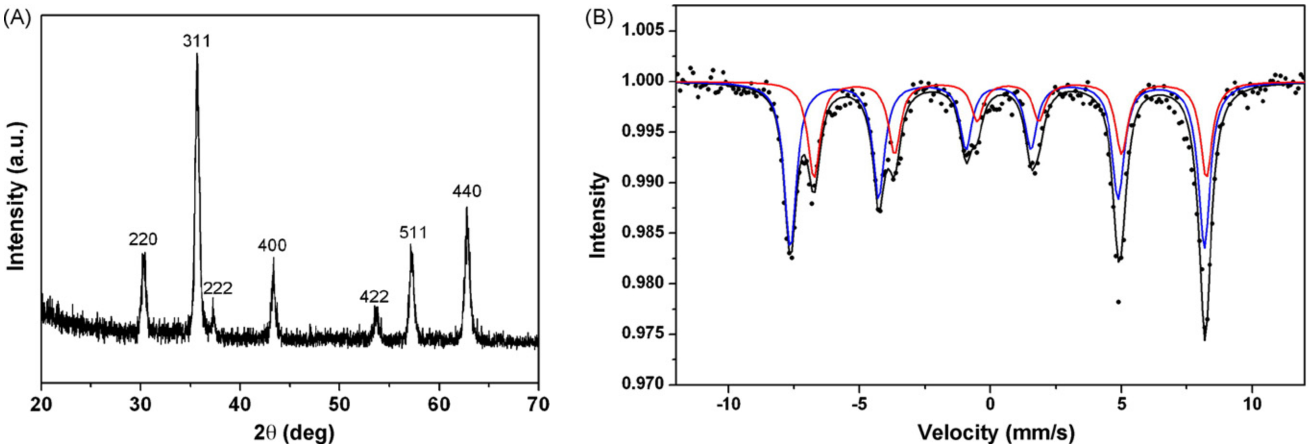

Fig. 2. Powder X-ray diffraction patterns (A) and Mössbauer spectra (B) of the Fe_3O_4 nanopowders.