Physica B 443 (2014) 1–5

Contents lists available at ScienceDirect

Physica B

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

Synthesis and magnetic characterizations of uniform iron oxide nanoparticles

FuYi Jiang [a,*], XiaoYi Li [a], Yuan Zhu [b,c], ZiKang Tang [b,c,**]

[a] *School of Environment and Materials Engineering, Yantai University, Yantai, Peoples Republic of China*
[b] *State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics and Engineering, Sun Yat-sen University, Guangzhou, Peoples Republic of China*
[c] *Department of Physics, The Hong Kong University of Science and Technology, Hong Kong, Peoples Republic of China*

ARTICLE INFO

Article history:
Received 19 January 2014
Received in revised form
3 March 2014
Accepted 3 March 2014
Available online 12 March 2014

Keywords:
Cubic nanoparticles
Iron oxide
Iron oleate
Thermal decomposition

ABSTRACT

Uniform iron oxide nanoparticles with a cubic shape were prepared by the decomposition of homemade iron oleate in 1-octadecene with the presence of oleic acid. The particle shape and size uniformity are sensitive to the quantity of oleic acid. XRD, HRTEM and SAED results indicated that the main phase content of as-prepared iron oxide nanoparticles is Fe_3O_4 with an inverse spinel structure. Magnetic measurements revealed that the as-prepared iron oxide nanoparticles display a ferromagnetic behavior with a blocking temperature of 295 K. At low temperatures the magnetic anisotropy of the aligned nanoparticles caused the appearance of a hysteresis loop.

1. Introduction

Nanoparticles exhibit unconventional or enhanced physicochemical properties, which are not encountered in the corresponding bulk materials. The properties of nanoparticles depend strongly on their dimension. For example, with size reduction, the structure of ferromagnetic particles changes from multi-domain to single-domain. A collection of such single-domain particles with further reduced size, freely dispersed, can exhibit superparamagnetism. Such magnetic nanoparticles have attracted considerable attention recently not only for fundamental research, but also for a broad range of applications, such as magnetic fluids [1], catalysis [2,3], ultra high-density magnetic storage media [4–6], biotechnology and biomedicine [7], magnetic resonance imaging [8–11], etc. Among these magnetic materials, iron oxides (Fe_2O_3 and Fe_3O_4) nanoparticles (IONPs) have been extensively investigated due to their excellent magnetic characteristics.

For the synthesis of nanoparticles, the key issue is the control of particle size, shape, uniformity, crystallinity and crystal structure. Iron oxides have a rich phase diagram with a variety of oxidation states, so it can be more complex for the controlled synthesis of IONPS with uniform shape, size and structure. To date, various chemical routes have been developed to prepare IONPs with good size control and narrow size distributions, such as through coprecipitation [12,13], hydrolysis of iron salt [14,15], decomposition of organic iron precursor [16–18], mechanical milling technique [19], microemulsion [20], hydrothermal and solvolthermal methods [21–24]. In particular, the preparation of IONPs with good uniformity in size and shape has been intensively pursued. The most successful route is through the high-temperature decomposition of organic iron precursors in organic solvents [25–28]. The narrow particle size distribution is due to the separation on the temperature scale in the nucleation and growth processes. By this method, IONPs coated by an organic monolayer can be obtained and dispersed in organic media. However, the size and shape of as-prepared IONPs are different from each other [28–30], the mechanism of forming different shape of IONPs is not fully understood, and controlling the shape and phase structure of IONPs still remains a challenge.

In this paper we report the preparation and characterization of mono-dispersed cubic IONPs with the same phase structure and with size uniformity, by decomposition of homemade iron oleate in high temperature organic solvent. The structure and magnetic properties of as-prepared IONPs are studied. We also discuss the effects of surfactant on the size and morphology of as-prepared IONPs.

---

[*] Corresponding author. Tel.: +86 535 670 6335; fax: +86 535 670 6038.
[**] Corresponding author at: State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics and Engineering, Sun Yat-sen University, Guangzhou, Peoples Republic of China. Tel.: +852 2358 7972; fax: +852 2358 1652.
E-mail addresses: fyjiang@ytu.edu.cn (F. Jiang), phzktang@ust.hk (Z. Tang).

http://dx.doi.org/10.1016/j.physb.2014.03.009
0921-4526

2. Experimental details

2.1. Synthesis of iron oleate

(1) 4.80 g sodium hydroxide (NaOH, ≥98%, Sigma-Aldrich) was dissolved in 30 ml de-ionized water (Milli-*Q*, 18.2 MΩ) under vigorous stirring to get a clear solution. 37.65 g oleic acid (90%, Sigma-Aldrich) and 50 ml ethanol was mixed in a Teflon container, and stirred for 10 min. Then the as-prepared NaOH solution was added dropwise under vigorous stirring. Because the solubility of result product sodium oleate is low under room temperature, in order to gain a well mixed solution, the Teflon container was put in a water bath and maintained a temperature of 353 K. The reaction duration is 2 h. In order to compensate the evaporation of ethanol, 10 ml ethanol was added every half hour. Then a uniform mixture contain sodium oleate was obtained.
(2) 6.48 g $FeCl_3$ (reagent grade, 97%, Sigma-Aldrich) was dissolved in 30 ml deioned water under vigorous stirring.
(3) The solution of $FeCl_3$ was added into the as-prepared mixture that contains sodium oleate slowly under vigorous stirring. After stir for 1 h, 140 ml *n*-hexane was added and stir for 10 min.
(4) The as-prepared mixture was transferred into a 500 ml three-necked flask that connected with a condenser tube, and heat up slowly to reflux. During this process, the low boiling point content evaporating and condensing constantly, this can made the reagent mixed well. The reaction product iron oleate was extracted into the organic layer of *n*-hexane continuously, which made the upper organic layer change to dark brown red. The reflux process continues for 2 h, and then cools down naturally.
(5) The mixture was transferred to a separating funnel so as to achieve separation of the upper organic layer from the mixture. 300 ml of de-ionized water was added to the separated upper organic layer, stirred by a glass rod and then left to settle down and separate. This process was repeated 6 times.
(6) The obtained organic layer was transferred into a glass container and put in an oven at a temperature of 353 K for 72 h to evaporate the low-boiling point content. The viscid dark brown red iron oleate was obtained.

2.2. Preparation of IONPs

IONPs were prepared by the decomposition of iron oleate in 1-octadecene in the presence of oleic acid. The effects of the amount of oleic acid on the as-prepared IONPs have been carefully monitored. A typical synthesis procedure is as follow: 2.068 g iron oleate and different amount of oleic acid (98%, Aldrich) was dissolved in 40 ml 1-octadecene (90%, Aldrich) in a 100 ml three-necked flask. The reaction mixture was heated to 373 K and maintained at this temperature for 2 h, and then degassed under vacuum for 10 min. After that, the mixture was heated to reflux with a heating rate of approximately 5 K min^{-1}, and reflux for 120 min, before cooling down. After cooling to room temperature, 40 ml of ethanol was added to the three-necked flask, stirred, and centrifuged at 10,000 rpm for 10 min. The precipitate was re-dispersed in *n*-hexane, with an equal amount of ethanol and centrifuged at 10,000 rpm for 10 min. The re-dispersion and centrifuge process was repeated 3 times.

2.3. Characterization of as-prepared IONPs

Samples for transmission electron microscopy (TEM, JEOL 2010F or JEOL 100CX) were prepared by dropping the *n*-hexane suspension onto a copper grid (400 mesh) coated with a carbon film. The phases of the products were characterized by X-ray powder diffraction (Philips PW1830) using Cu-$K\alpha$ radiation. The magnetic properties of as-prepared IONPs (powder sample) were studied using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-5s).

3. Results and discussion

3.1. The influence of the oleic acid

In order to study the effects of the amount of oleic acid on the morphology of as-prepared IONPs, we added different amount of oleic acid as the stabilizer. Fig. 1 shows the TEM images of IONPs synthesized using different quantities of oleic acid. Without the oleic acid, we obtained uniform particles with a size of ca. 15 nm, but most particles have a spherical shape (Fig. 1a). With 0.5 ml of oleic acid, we obtained monodisperse nanoparticles with a size of ca.15 nm. The particles have good size uniformity, and most of them have a cubic shape (Fig. 1b). When the oleic acid quantity was increased to 1 ml, the particles size distribution broadened, with the appearance of different shapes in the product (Fig. 1c). With the oleic acid quantity of 2 ml, most of the particles present a spherical shape (Fig. 1d), and the size and shape uniformity deteriorated. With the oleic acid quantity of 3 ml and 4 ml, the particle size distribution becomes very broad, with the appearance of some triangle and irregular particles in the product (Fig. 1e and f).

These results indicate that increasing the concentration of oleic acid can lead to larger particle size, together with a broad particle size distribution. The underlying reason is as follows. When a high oleic acid concentration is used, there can be an increase in the dissolution of as-formed iron oxide nuclei, and thereby the nucleation process becomes more difficult and only the large nuclei can survive the re-dissolution. As a result, the particle size increases with the increase of oleic acids concentration [29]. However, the thermal decomposition of iron oleate is very rapid under high temperatures and hence a high concentration of monomer will be present due to the lack of nucleation. When the super-saturation of the monomer is attained, the second nucleation occurs. As a consequence, the particle size distribution becomes very broad [30]. Another consideration for the broadening of the particle size distribution is the redistribution of monomers between particles with different sizes during the ripening process. Because the smaller particles have higher surface free energy, due to the Gibbs–Thomson effect, the monomers will move from smaller to larger particles. This process is usually denoted Ostwald ripening [31]. At a high oleic acid concentration, the inter-particle redistribution of monomers becomes easier, thereby leading to a broad particle size distribution (Fig. 1e and f).

The shape of crystalline nanopaticles is determined by the relative growth rate of the different facets. Various methods were used to adjust the relative growth rate of different facets to obtain nanocrystals with different shape [26,32–36]. For the cubic-structured Fe_3O_4, the {1 0 0} planes have the lowest surface free energy, so the cubical shape nanocrystals should be covered by the {1 0 0} facets [26,29]. HRTEM image shows that the cubic IONPs are single-crystalline, and the {2 2 0} fringes (spacing 0.2968 nm) run face-diagonally in the cube, indicating that the cube-like particles are terminated with {1 0 0} planes, with small {2 2 0} facets at the edge (Fig. 2a). In our experiment, the only varied synthesis parameter is the quantity of oleic acid, this means that with a proper oleic acid concentration, the {1 0 0} facets have the slowest growth rate.