One step synthesis of highly crystalline and high coercive cobalt-ferrite nanocrystals

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Highly crystalline and almost monodisperse spinel cobalt-ferrite nanocrystals are synthesized in a one step process, which has very high coercivity at 10 K and exhibits superparamagnetic behaviour at 300 K.

Preparation and processing of fine magnetic particles have been the subject of extensive research over the last several decades due to their many technological applications including ferrofluids,[1] data storage[2,3] and medicine.[4,5] Most of these applications require particles of uniform size and shape distribution. In addition for any particular application the magnetic nanoparticles must possess specific properties. For example, data storage applications require particles with stable, switchable magnetic states to represent bits of information, states not affected by temperature fluctuations. In biomedical applications, the nanoparticles must exhibit superparamagnetic behavior at room temperature. In the synthesis of colloidal magnetic nanoparticles, there has been significant progress in the development of methods to produce colloidal Co,[6] FePt[7] and CoPt[8] nanoparticles, and more recently in the synthesis of colloidal magnetic oxide nanoparticles. Rockenburger *et al.* produced γ-Fe_2O_3 nanocrystals by pyrolysis of organometallic precursors.[9] Nanosized spinel ferrite particles currently receive considerable attention because of their interesting magnetic properties.[10–14] A variety of methods has been developed to prepare these nanoparticles, such as the sol–gel method,[15] hydrothermal method,[16] co-precipitation in normal or reverse micelles,[17] sonochemical reactions,[18] and ball milling.[19] However, in most cases, the nanoparticles obtained were severely aggregated with nonuniform shape, a serious disadvantage in their applications.[12,18,20–21] Moreover, in most of the cases the synthesized particles are poorly crystalline and calcinations at high temperature is needed to induce the highly crystalline structures.[22] Magnetic hardening occurs after heat treatment at a relatively high temperature, however, and a variety of artefacts are used to lower it.[23] High temperature annealing is technologically detrimental and induces coalescence and coarsening of the nanoparticles, broadening the size distribution. In this letter we describe a significant improvement of the process of Sun *et al.*[7] to produce highly crystalline cobalt-ferrite nanoparticles of uniform size that eliminate the need for calcination at high temperature.

The typical synthesis procedure is as follows. The reagents were obtained from Sigma-Aldrich and used without further purification. A mixture of 0.5 mmol of cobalt(II) acetylacetonate, 1 mmol of iron(III) acetylacetonate, and a 1.5 mmol of 1,2-hexadecanediol was added to a 100 mL round bottomed three-necked flask containing a PTFE coated magnetic stir bar. Dioctyl ether (30 mL) was then transferred into the flask and the contents stirred while purging with Ar for 20 min at room temperature. The flask was then heated to 100 °C and held at 100 °C for 15 min. During this hold, 1 mmol (0.34 mL) of oleylamine and 1 mmol (0.32 mL) of oleic acid were injected into the flask while continuing the Ar purge. After the 15 min hold, the mixture was maintained under an Ar blanket and heated to 295 °C at a rate of approximately 12 °C min^{-1}. During this reflux, air was introduced slowly for a very short duration (60 s) 2–3 times by stopping the argon flow. The flask was maintained at the refluxing temperature of 295 °C for 30 min. The heat source was then removed, and the reaction mixture was allowed to cool to room temperature under the Ar blanket. Afterwards, all handling was performed open to the atmosphere. Purification of the nanoparticles was accomplished as follows: first the materials from the flask were added to 40 mL of ethyl alcohol (EtOH) and the mixture centrifuged (6000 rpm for 15 min). The supernatant was discarded and the black precipitate redispersed in 25 mL of hexane and 5 mL of EtOH. Additional small amounts of oleylamine and oleic acid might be added to aid in redispersing the nanoparticles. This dispersion was centrifuged for 15 min at 6000 rpm. The supernatant was transferred to a new centrifuge tube, discarding any precipitate that separated. An additional 20 mL of EtOH was added to this dispersion and centrifuged again. The supernatant was discarded and the remaining dark brown precipitate redispersed in hexane and stored under refrigeration for characterization.

Transmission electron micrograph (TEM) and energy-dispersive X-ray analysis (EDX) were carried out on a Phillips-CM20 electron microscope. Fig. 1(a) shows a typical low-magnification TEM image of cobalt-ferrite nanoparticles deposited on a carbon coated copper grid immediately after the synthesis. A narrow particle size distribution around 10 nm shown in the inset of Fig. 1(a) is obtained. Fig. 1(b) shows the high-resolution TEM picture of the particles with a selected area diffraction pattern in the inset; this reveals lattice fringe patterns, demonstrating a highly crystalline structure, supported by the well-pronounced diffraction rings. The lattice parameter derived from the HRTEM image is around 8.4 Å, consistent with values for bulk cobalt-ferrite (8.39 Å). EDX analyses of these particles yields an iron/cobalt ratio equal to 2.03/1, consistent with a cobalt-ferrite composition.

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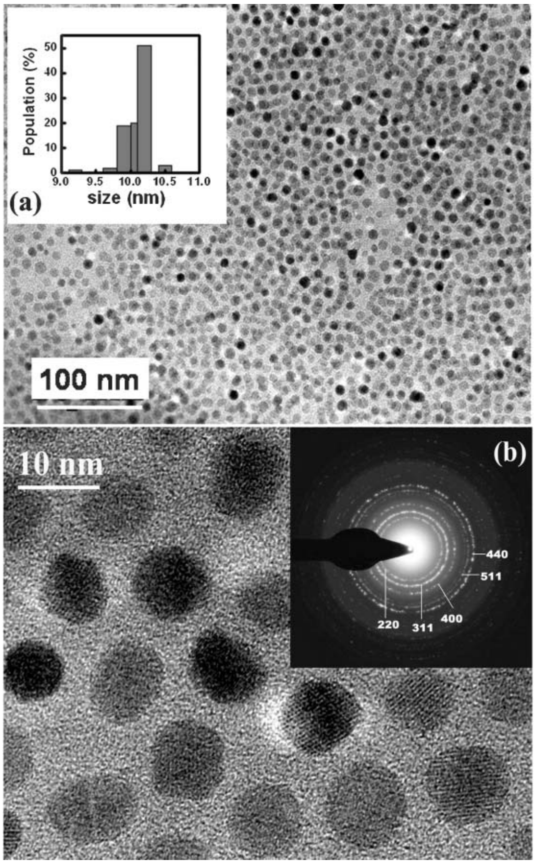

Fig. 1 (a) Low magnification TEM image of as synthesized cobalt-ferrite nanoparticles, inset is the size distribution of the nanoparticles. (b) High resolution TEM image of the as synthesized cobalt-ferrite nanoparticles, inset is the selected area electron diffraction pattern.

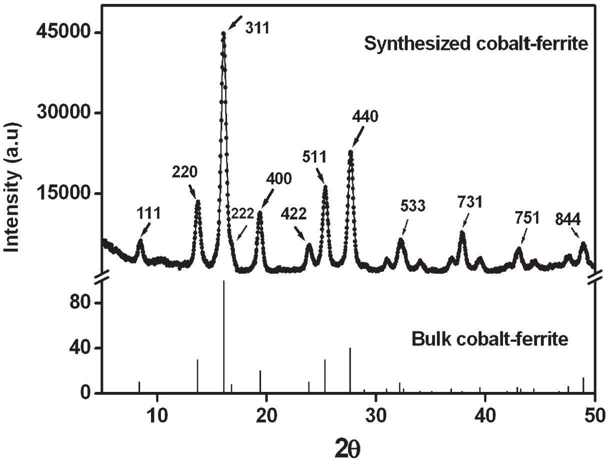

Fig. 2 X-Ray diffraction pattern of the as-synthesized nanoparticles.

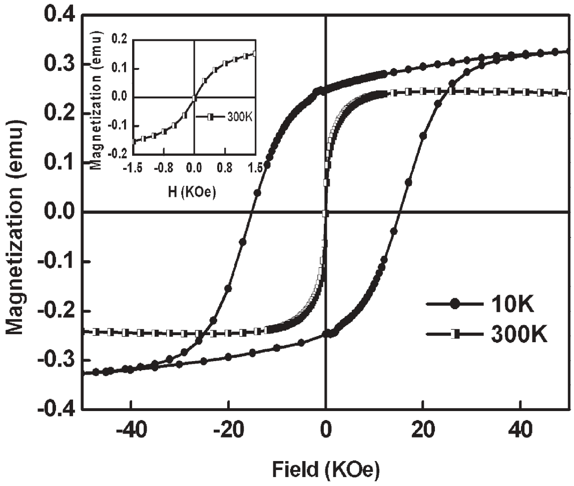

Fig. 3 Variation of magnetization with applied magnetic field for the cobalt-ferrite nanoparticles at temperatures 10 K and 300 K.

The crystalline structure of the samples was identified from the X-ray diffraction patterns taken on an INEL diffractometer using Mo-Kα radiation. The X-ray diffraction pattern of the as-synthesized nanoparticles is shown in Fig. 2, peak positions for the bulk cobalt-ferrite are shown at the bottom part of the graph. It is clear that the particles are highly crystalline and all the characteristic peaks for the spinel cobalt-ferrite phase are present and well resolved. The average crystallite size is calculated using several diffraction peaks from Scherer's formula[24]

$$d = 0.9\lambda/(\beta - \beta_1)\cos\theta$$

where d is the grain diameter, β is the half-intensity width of the relevant diffraction peak, β_1 represent the half-intensity width due to instrumental resolution, λ is the X-ray wavelength, and θ is the angle of the diffraction peak. The resulting average particle size is 11.2 nm which is reasonably consistent with that determined by TEM (10 nm).

The magnetic properties of the as-synthesized nanoparticles were measured with a superconducting quantum interference device (SQUID) magnetometer. Fig. 3 shows the hysteresis curve of the particles at 10 K and 300 K and the inset showing the low field region of the hysteresis curve at 300 K. These particles exhibit superparamagnetic behavior at room temperature because the coercivity is zero whereas at 10 K it reaches a value of 15.3 KOe, much larger than those of bulk cobalt-ferrite ($\sim$5 KOe at 5 K) and of iron oxide nanoparticles of similar size ($\sim$500 Oe at 10 K). This indicates that the incorporation of Co cations in the Fe–O matrix greatly enhances the magnetic anisotropy of the nanoparticles. The ratio of the remanent to saturation magnetizations M_r/M_s in Fig. 3 is 0.83, which is the exactly the same value as that reported for isolated particles with cubic anisotropy (0.83).

In conclusion, a significant modification of the technique of Sun *et al.* for synthesis of cobalt-ferrite nanocrystals produces high-quality uniform colloidal nanoparticles, with a remarkably high coercivity at low temperature. The synthesized particles are highly crystalline just after the synthesis without any further heat treatment. The procedure has considerable potential for application in magnetic devices and also in biology. Further investigations of the magnetic properties of these nanoparticles to fully realize the potential of this material are underway.

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