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Preparation of magnetic nanoparticles and their assemblies using a new Fe(II) alkoxide precursor

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Hydrolysis of the new metallorganic precursor $Fe(OBu^t)_2(THF)_2$ followed by ultrasound and thermal treatment yielded either nanoparticles of γ-Fe_2O_3 or Fe_3O_4, depending on the process conditions. The samples have been characterised by X-ray powder diffraction, TEM, SEM, Mössbauer spectroscopy and magnetization measurements. The maghemite nanoparticles (9 ± 2 nm) are superparamagnetic and form unique needle-like assemblies of nanoparticle arrays. The nanoparticles of Fe_3O_4 (19 ± 2 nm) form plate-like aggregates about 10 μm thick.

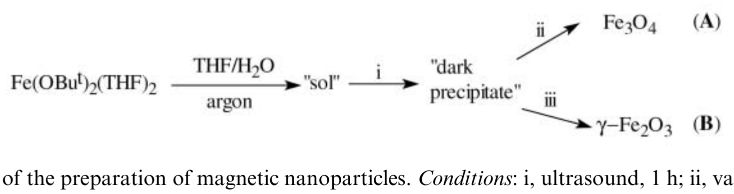
Magnetic nanoparticles, which approach the size of a single magnetic domain, have applications in magnetic storage.[1,2] In order to get higher storage densities future development in the area of magnetic storage media will rely on the ability to develop stable materials with particles a few nanometers in size.[3] Superparamagnetic single domain nanoparticles also have very important biomedical applications (*e.g.* magnetic cell sorting, magnetocytolysis, drug-targeting experiments, gene transfection studies, magnetic fluid hyperthermia, *etc.*).[4–6]

The development of reliable techniques for preparing arrays and assemblies of magnetic nanoparticles is of high scientific and technological importance. Despite the wide range of physical and chemical routes for the preparation of nanoparticles which have been developed over many years,[7] there is a great demand for precursors and for an effective technique to produce nanoparticles of magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3). Several new chemical routes for preparation of different magnetic nanoparticles and their arrays have been developed.[8] Using single-source precursors is one of the most attractive methods for the preparation of magnetic nanoparticles. A particularly interesting non-hydrolytic single-precursor approach for the preparation of metal oxides, including γ-Fe_2O_3 nanoparticles, from the corresponding metal cupferronates, was proposed by Alivisatos and coworkers.[9] Recently Gedanken and coworkers have also shown that Fe_3O_4 nanoparticles can be effectively prepared using a sonochemical method with commercially available metallorganic precursors such as $Fe(CO)_5$ and Fe(II) acetate.[10]

In this communication we report the preparation of nanoparticles of magnetite and maghemite (γ-Fe_2O_3) and their assemblies using a new metallorganic iron(II) alkoxide precursor $Fe(OBu^t)_2(THF)_2$ by modified sol–gel and ultrasonic techniques.

The precursor, $Fe(OBu^t)_2(THF)_2$ was prepared from $FeBr_2$ and $NaOBu^t$ in THF using standard argon–vacuum and Schlenk techniques.† A solution of $Fe(OBu^t)_2(THF)_2$ (1.1 g, 2 mmol) in THF (60 cm^3) was carefully hydrolysed with doubly distilled non-degassed water (30 cm^3) under argon (Scheme 1). The resultant mixture was then ultrasonically (30 kHz, 130 W) irradiated under argon at ambient temperature for 1 h. The dark precipitate was filtered off and washed several times with distilled water. The product was then divided into two equal parts. One part of the product was dried *in vacuo* for 3 h at room-temperature giving a black powder (**A**), while the other part was dried in air at 200 °C for 30 min giving a dark brown powder (**B**). Both products were characterised by X-ray powder diffraction (XRD). Reflections of the XRD patterns (2θ from 5 to 70°) for both samples showed *d* spacing values and relative intensities of the peaks coincident exactly with JCPDS data of magnetite (Fe_3O_4) for **A** and maghemite (γ-Fe_2O_3) for **B** with some line-broadening. The particle sizes were calculated using the Debye–Scherrer formula[11] (crystalline diameter $= 0.9\lambda/B \cos\theta$, where $\lambda =$ X-ray wavelength, $\theta =$ Bragg angle, $B =$ line broadening) giving a particle diameter of 19 ± 2 nm for Fe_3O_4 and 9 ± 2 nm for γ-Fe_2O_3 samples.

Fig. 1 presents the Mössbauer spectra of the two samples taken at room temperature. For the black powder (**A**) the spectrum shows combined magnetic and quadrupole splittings. A least square fit to the experimental data indicates that the lines are characteristic of non-stoichiometric magnetite, with a small line broadening due to a distribution of hyperfine magnetic fields caused by the different iron ion environments in the structure, and a small contribution of paramagnetic Fe^{3+}. For the brown powder (**B**) the room-temperature spectrum shows only quadrupole splitting. A fitting to these data suggests that the quadrupole doublet can be assigned to Fe^{3+} ions in superparamagnetic γ-Fe_2O_3 particles as indicated by the absence of any magnetic splitting.



Scheme 1 Schematic illustration of the preparation of magnetic nanoparticles. *Conditions*: i, ultrasound, 1 h; ii, vacuum, 3 h, *ca.* 20 °C; iii, heat, *ca.* 200 °C, in air, 30 min.

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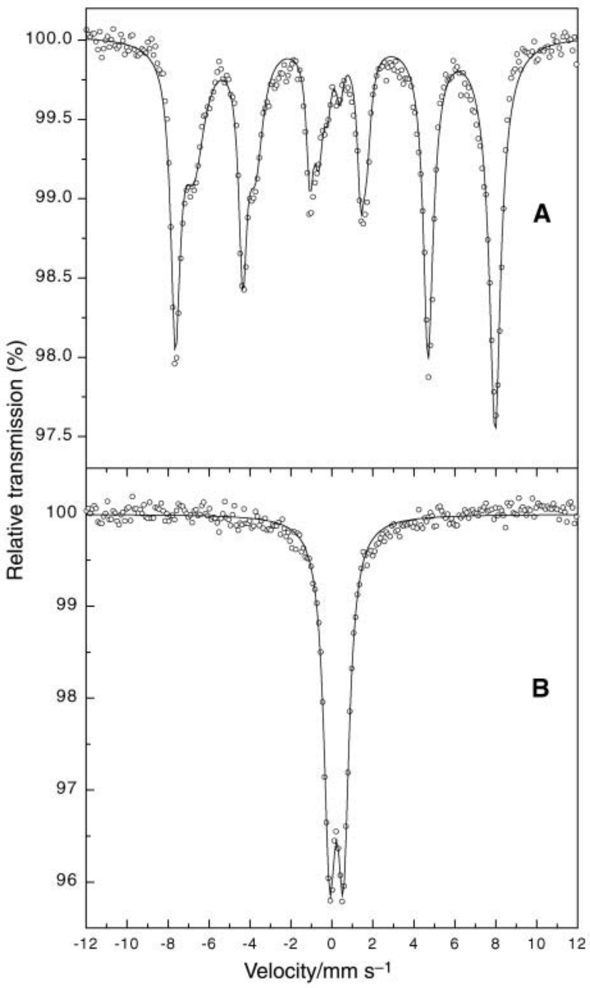

Fig. 1 Room-temperature Mössbauer spectra of Fe_3O_4 (**A**) and γ-Fe_2O_3 (**B**) nanoparticles.

Field emission scanning electron microscopy (FESEM) images of the powders demonstrated that the Fe_3O_4 sample (Fig. 2) consists of broken plates, which are about 100 µm in diameter and about 10 µm thick. Magnification of the broken edge and plate surface up to 150 000 × shows that each plate is an assembly of nano-sized particles. The estimated size of individual aggregates from FESEM is between 10–100 nm. By contrast the FESEM images of γ-Fe_2O_3 at 2000 × and 100 000 × magnification (Fig. 3) show a straw- or needle-like sample morphology with needle lengths of *ca.* 10 µm. The image at 100 000 × indicates that each straw or needle consists of three-dimensional self-assemblies of parallel arrays of nanoparticles. The average size of the each nanoparticle is *ca.* 10 nm.

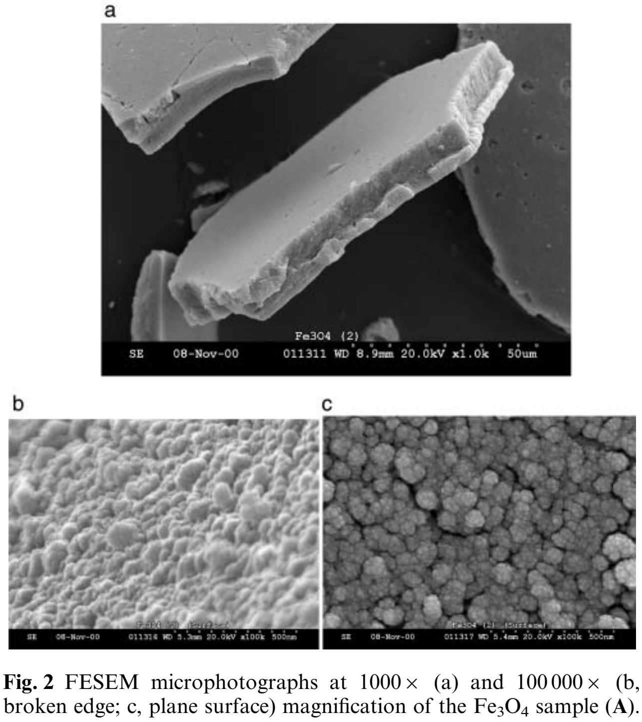

Fig. 2 FESEM microphotographs at 1000 × (a) and 100 000 × (b, broken edge; c, plane surface) magnification of the Fe_3O_4 sample (**A**).

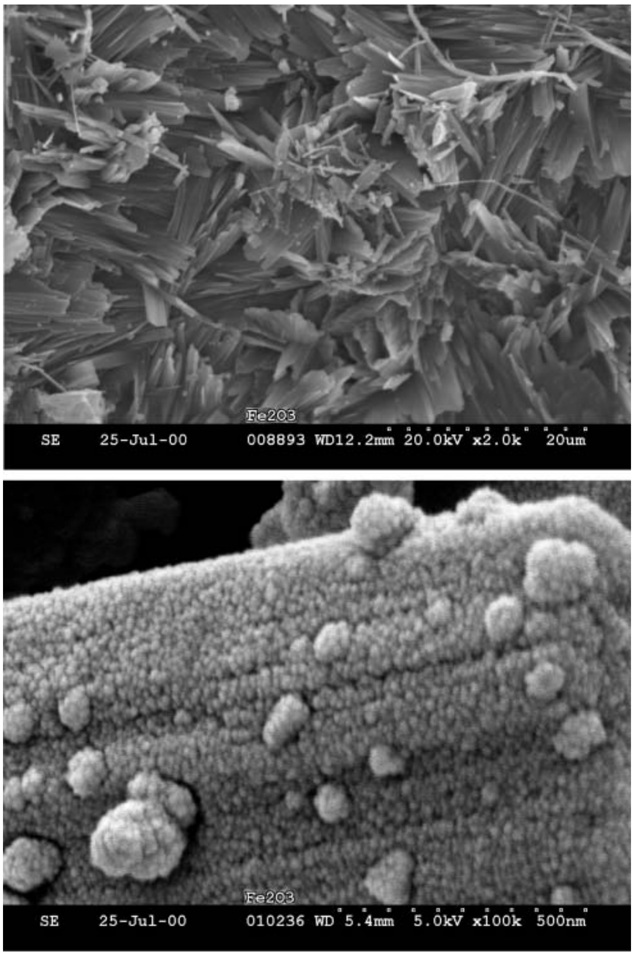

Fig. 3 FESEM microphotographs at 2000 × (top) and 100 000 × (bottom) magnification of the γ-Fe_2O_3 needles (**B**).

Samples for transmission electron microscopy (TEM) were prepared by deposition of a drop of very dilute colloidal solutions of Fe_3O_4 or γ-Fe_2O_3 in ethanol onto formvar coated 400 mesh copper grids. TEM images of the magnetite sample show a dispersion of nanoparticle aggregates with a size distribution between 10 and 60 nm. According to TEM images the nanoparticles of the maghemite sample have a quite narrow size distribution and an average diameter of 7–10 nm.

Fig. 4 shows the room-temperature magnetization of the Fe_3O_4 sample. The room-temperature spontaneous magnetization (σ) is 65 J T^{-1} kg^{-1} in a field of 1 T which is considerably less than the usual spontaneous saturation magnetisation (*ca.* 90 J T^{-1} kg^{-1}) of bulk Fe_3O_4.[12] The value of the coercivity is around 10 mT. A decreasing size of particles leads to a decrease in total magnetization due to the increased dispersion in the exchange integral.[13] On the other hand, the magnetization curve of the maghemite sample is typical of superparamagnetic behaviour showing a steep increase in magnetisation with increasing field. The magnetisation does not saturate even at 1 T magnetic field. Using the expression for the mass susceptibility of a paramagnet ($\chi = Nm^2/3k_B$, where N is the

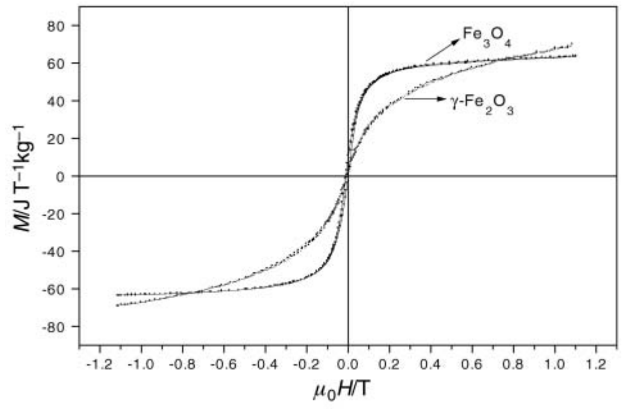

Fig. 4 Room-temperature magnetization curves of Fe_3O_4 and γ-Fe_2O_3 samples.

number of particles per kg and m is the particle moment (J T^{-1})), from the initial slope a particle diameter of 7 ± 1 nm is deduced. This size is quite consistent with XRD, FESEM and TEM results. The lack of saturation of magnetisation and the reduction in the room-temperature magnetisation may be attributed to the smaller particle size.

The mechanism of formation of magnetic nanoparticles obviously involves an oxidation of Fe(II) into Fe(III) by oxygen from the water during the hydrolysis and further ultrasonic treatment. Ultrasonically generated radical and peroxide species from water or THF also might contribute to the oxidation of Fe(II), as has been recently reported by Gedanken and coworkers.[9,10] We suggest that the formation of γ-Fe_2O_3 nanoparticles proceeds *via* precursor materials containing –Fe–(OH)–Fe– and –Fe–O–Fe– polymeric chains and that these then can be ultrasonically and thermally broken giving individual nano-sized aggregates. Plausibly even after the treatment, aggregates still continue to retain a chain-like orientation forming needle-like assemblies of nanoparticles as observed by FESEM.

In summary, the results illustrate that nanoparticles of magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) can be conveniently produced from an Fe(II) alkoxide derivative. The maghemite nanoparticles so prepared are superparamagnetic. Results of FESEM have shown that nanoparticles of Fe_3O_4 form plate-like aggregates of 100 μm diameter and about 10 μm thickness; γ-Fe_2O_3 consists of needle-like assemblies of nanoparticle arrays. This work presents new opportunities for the preparation of three-dimensional assemblies of magnetic nanoparticles for practical applications.

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Notes and references

†*Synthesis of* Fe(OBu^t)$_2$(THF)$_2$: NaOBu^t (0.68 g, 7.08 mmol) was added to $FeBr_2$ (0.76 g, 3.54 mmol) in THF (100 ml) at *ca.* 0 °C. The mixture was stirred for 24 h at ambient temperature, filtered and the filtrate then concentrated to *ca.* 30 ml *in vacuo*. Grey crystals of Fe(OBu^t)$_2$(THF)$_2$ (0.64 g, 53%) were gradually deposited at 4 °C. Further concentration of the remainder of the mother-liquor (*ca.* 15 ml) *in vacuo* and cooling to −22 °C afforded an additional crop of Fe(OBu^t)$_2$(THF)$_2$ (0.31 g, 78% in total).

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