One-pot size and shape controlled synthesis of DMSO capped iron oxide nanoparticles

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Abstract.   We report here the capping of iron oxide nanoparticles with dimethyl sulfoxide (DMSO) to make chloroform soluble iron oxide nanoparticles. Size and shape of the capped iron oxide nanoparticles are well controlled by simply varying the reaction parameters. The synthesized nanocrystallites were characterized by thermal analysis (TG–DTA), powder X-ray diffraction (XRD), transmission electron microscopy (TEM) for evaluating phase, structure and morphology. ^{1}H NMR spectra of the synthesized samples confirm DMSO, and the capping of DMSO on the ferrite samples. Shift of the S=O stretching frequency in Fourier transformed infrared (FTIR) spectra indicates that the bonding between DMSO and ferrite is through an oxygen moiety. The magnetic measurements of all the synthesized samples were investigated with a SQUID magnetometer which shows that the magnetic properties are strongly dependent on the size as well as shape of the iron oxide.

Keywords.   Iron oxide; thermal decomposition; TEM; VSM.

Magnetic nanoparticles are being intensively pursued not only for their fundamental scientific interest but also for their novel application capability. The unique and novel size dependent properties of magnetic oxides have initiated current worldwide intense research on magnetic nano-materials (Alivisatos 1996). Preparation and processing of magnetic nanoparticles have been widely studied because of their potential applications such as ferrofluids (Rosensweig 1985), data storage devices (Speliotis 1999), biomedicine like biomolecular separation (Perez *et al* 2003), magnetic resonance imaging (Oswald *et al* 1995), targeted drug delivery (Gupta *et al* 1988), DNA separation (Doyle *et al* 2002), a.c. magnetic field-assisted cancer therapy (Jordan *et al* 1999) etc. For all of these purposes, dispersions of magnetic nanoparticles in solvents are necessary. Dispersed ferrites also find applications as ferrofluids in position scanning, rotary shaft sealing, oscillation damping (Raj and Moskowitz 1990) etc.

Different synthetic chemical methods like co-precipitation (Kang *et al* 1996), hydrothermal (Komarneni *et al* 1998), radio frequency plasma treatment (Sreekumar and Sugunan 2002), reverse micelles (Tihay *et al* 2002) etc have been introduced in recent years to synthesize highly crystalline magnetic nanoparticles. But the major drawbacks of these synthetic procedures are the low dispersion in solvents and wide particle size distribution. To overcome these drawbacks, research is focussed on the colloidal chemistry route to synthesize surface modified nanoparticles with proper surface coating that drives the particles to solubilize in a specific solvent and also maintain a particular size. Thermal decomposition method has been frequently used to synthesize magnetic ferrites from different iron precursors such as Fe(*acac*)$_3$, Fe(CO)$_5$, FeC*up*$_3$*n* etc. Sun and Zeng (2002) succeeded in the synthesis of monodispersed magnetite nanoparticles using Fe(*acac*)$_3$ as the starting material. Hyeon and co-workers (2001) demonstrated that decomposition of Fe(CO)$_5$ followed by oxidation can also lead to high quality maghemite nanoparticles. Rockenberger *et al* (1999) reported the preparation of monodispersed maghemite by decomposition of FeC*up*$_3$ in the presence of octylamine and trioctylamine. All these methods yield nanoparticles that are highly dispersible in very nonpolar organic solvents like toluene, hexane, etc. Zhen *et al* (2004) synthesized water soluble magnetic nanocrystals but with larger particle size and agglomerations. The main aim of this study is to synthesize colloidal ferrite nanoparticles with proper surface coating having uniform particle size distribution and definite shape; this is because physical, chemical and magnetic properties, in particular, of these nanomaterials are strongly dependent on the size as well as shape of the particles. Here, we report the synthesis of well dispersed and highly crystalline γ-Fe$_2$O$_3$ nanoparticles using thermal decomposition of iron(III) acetylacetonate (Fe(*acac*)$_3$) in DMSO solvent. The synthesized materials have a very narrow particle size distribution with definite morphology depending on the reaction conditions. The nanoparticles are highly dispersible in chloroform.

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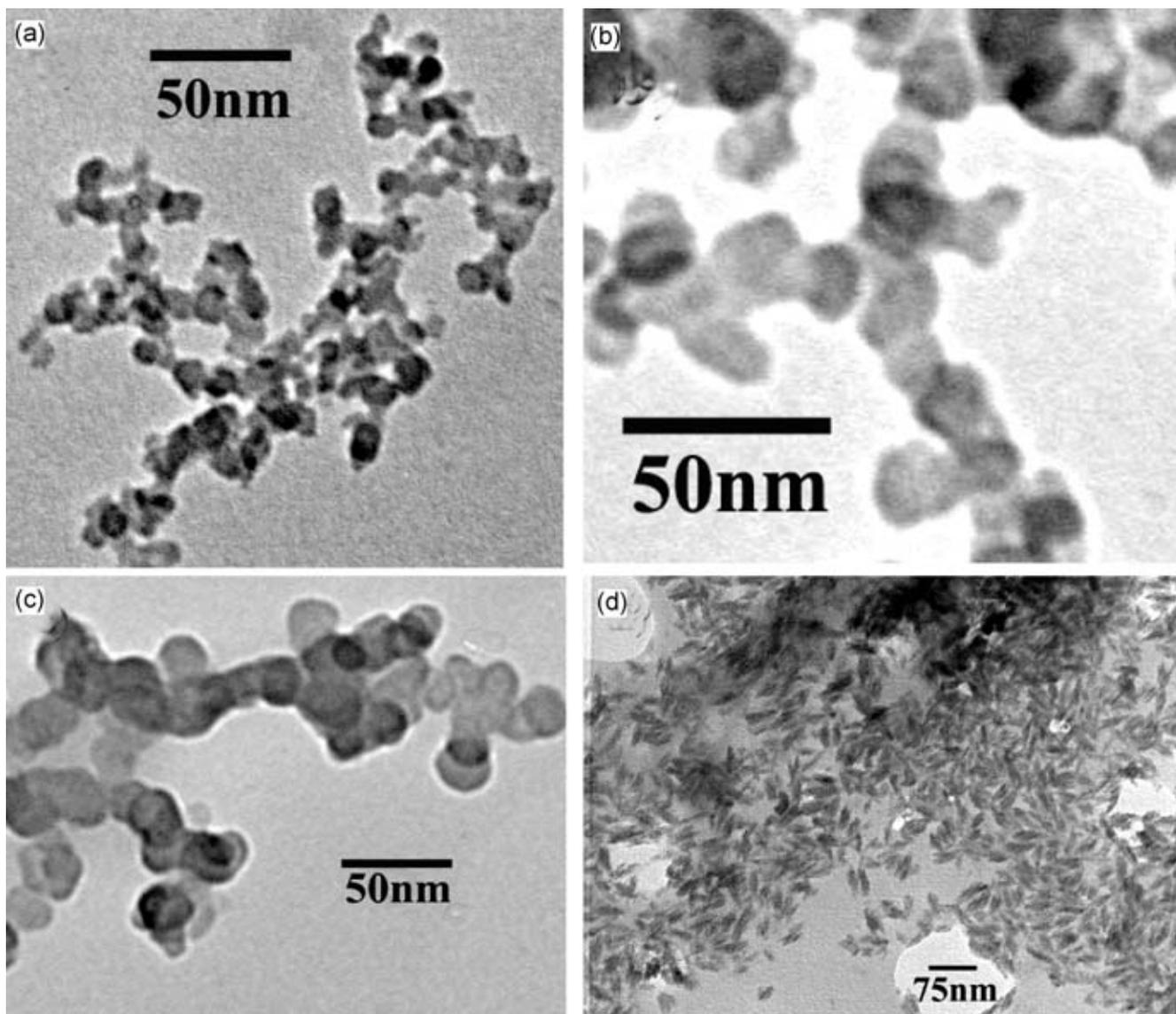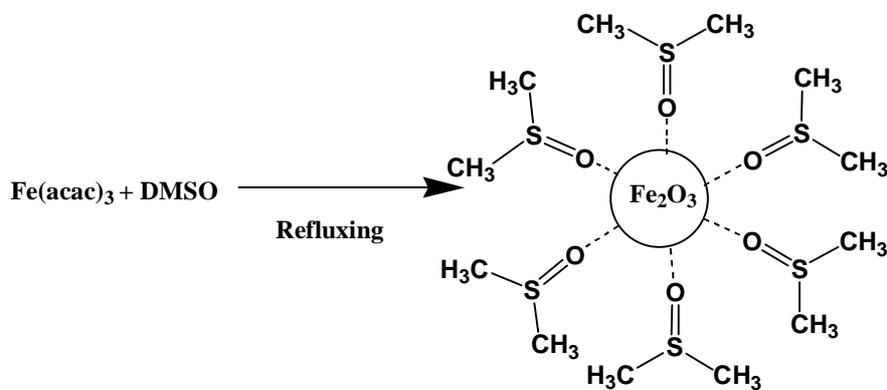(manorama@iict.res.in; manoramasv@yahoo.com)

Figure 1. Typical transmission electron micrographs of all the samples showing particle size distribution: (**a**) 1 h, (**b**) 12 h, (**c**) 18 h and (**d**) 24 h refluxed samples.

Scheme 1.

In a typical one-pot synthetic procedure, well dispersed iron oxide nanocomposites were prepared through thermal decomposition route as described in scheme 1. 1 mmol Fe(*acac*)$_3$ was dissolved in 20 ml DMSO and then re-fluxed for different durations resulting in black colour solution. The reaction mixture was then cooled to room temperature. To obtain dry powder, excess methanol was added to the mixture resulting in a dark brown precipitate.

The separated powder was washed several times with methanol, dried at room temperature and then stored under nitrogen atmosphere for further analysis and use. Particle size and shape are strongly dependent on the refluxing time. Different sized and specific shaped particles of well dispersed γ-Fe$_2$O$_3$ are obtained by varying the refluxing time.

The resulting precipitates are proved to be completely dispersible in chloroform. Both TEM and XRD are used to obtain structural information and morphology of the iron
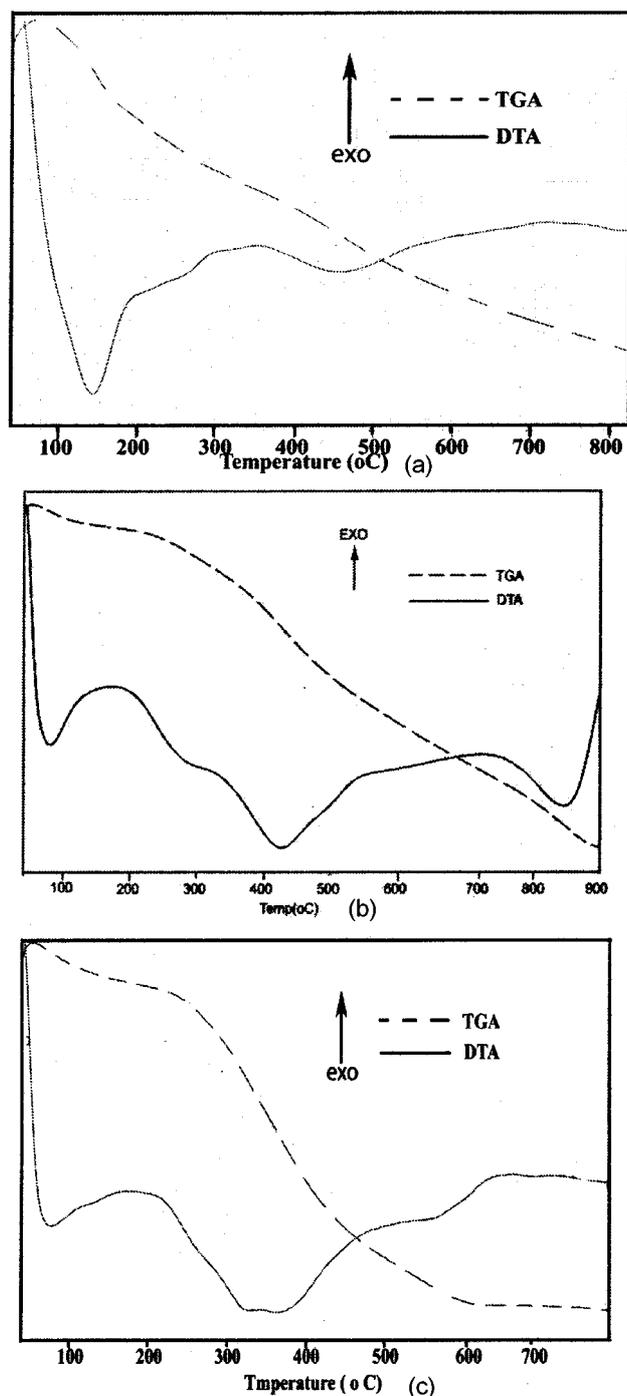

Figure 3. FTIR spectra of pure DMSO spindle iron oxides.

Figure 2. (a–c). TG–DTA thermograms of 1 h, 12 h, 24 h refluxed samples, respectively.
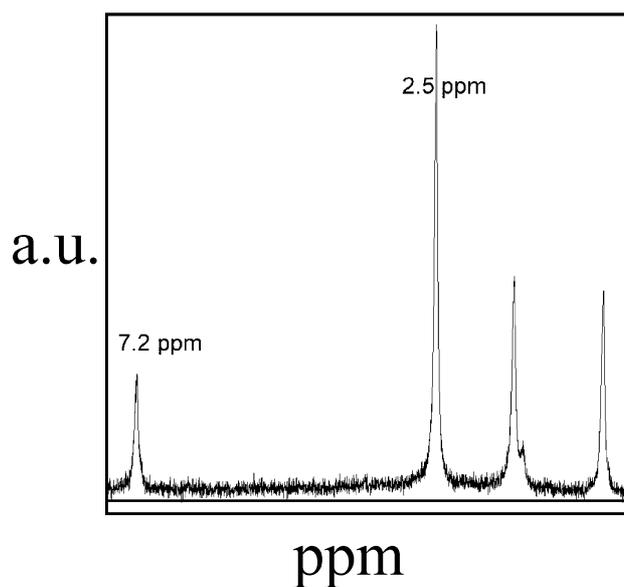

Figure 4. ^{1}H NMR spectra of spindle iron oxide in CDCl$_3$ solvent.

Table 1. Synthesis conditions, results from XRD, crystallite size and shape of the nanoparticles of DMSO capped iron oxides.

Sample code	Refluxed time (h)	Crystallite size (nm)[a]	Size (nm)[b]	Shape (nm)[c]
1	1	7	8	Spherical
2	12	–	12	Spherical
3	18	–	25	Spherical
4	24	15	50	Spindle

[a]Calculated from XRD; [b]from TEM; [c]observed from TEM.
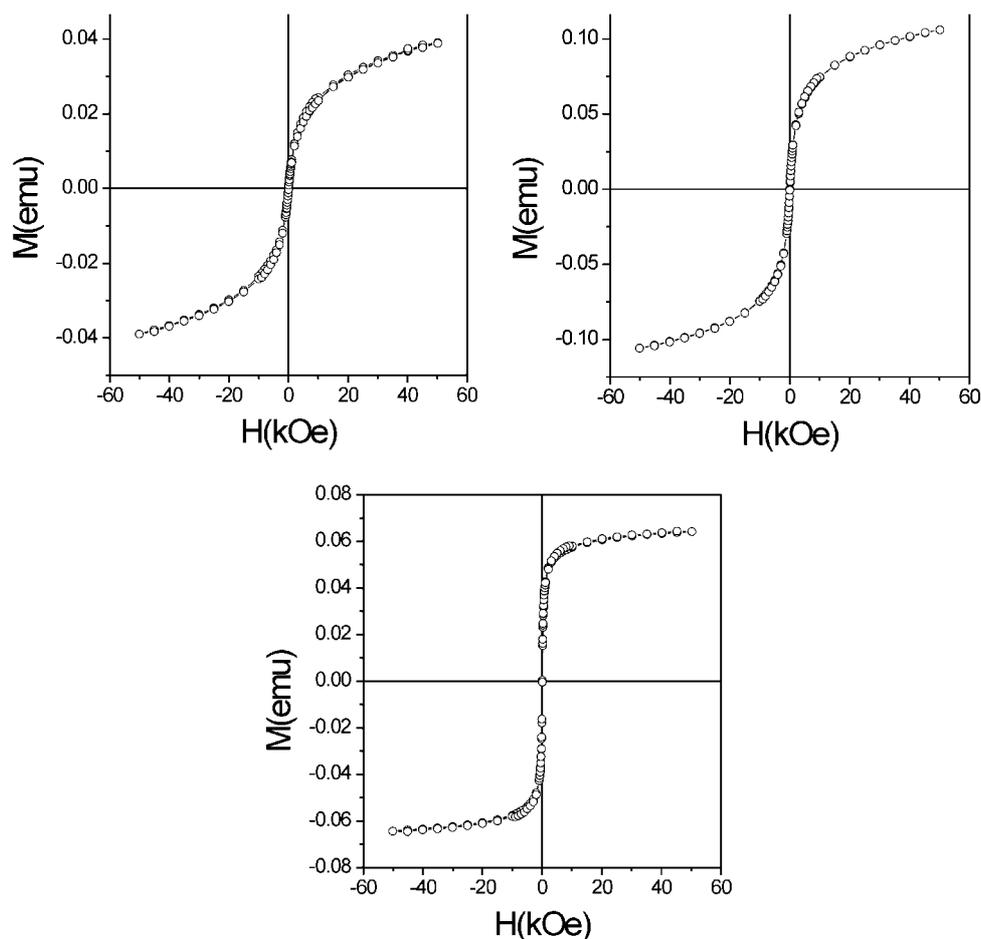
Figure 5. Room temperature (300 K) M–H data of 1 h, 12 h and 24 h refluxed samples.

oxide nanoparticles. Figures 1(a–d) are the TEM images of the nanoparticles obtained with different refluxing times. The samples refluxed for 1 h, 12 h, 18 h are spherical in shape having particle size around 8, 12, 25 nm, respectively whereas 50 nm sized spindle shaped ferrites are obtained after 24 h of refluxing. The X-ray diffraction pattern shows that the materials are highly crystalline γ-Fe_2O_3 nanoparticles. Crystallite size was estimated using Scherrer's formula (Klug and Alexander 1974) applied to line broadening of the major peaks in XRD pattern and presented in a tabular form (table 1). The FTIR spectra of spherical and spindle shaped samples are shown in figure 2. The FTIR measurements reveal that the vibrational band

of S=O shifts from $1020 \cdot 17$ cm^{-1} for pure DMSO to $1037 \cdot 15$ cm^{-1} for spindle shaped iron oxide nanocrystals. This indicates that the oxygen of DMSO coordinates with Fe on the surface of the ferrite nanoparticles. For further confirmation the as prepared samples are subjected to thermal analysis in N_2 atmosphere. The TG–DTA thermograms of 1 h, 12 h, 24 h refluxed samples are shown in figure 2. The TG traces show a continuous weight loss in the temperature range 200–600°C that may be due to loss of chemically adsorbed DMSO on the surface of the nanoparticles. In DTA analysis, the exothermic peak at around 190°C is associated with $0 \cdot 69\%$ weight loss and could be assigned to desorption of the adsorbed DMSO on the sur-

face of γ-Fe$_2$O$_3$. The endothermic peak at 450°C can be assigned to the phase change of maghemite to hematite.

As all DMSO capped iron oxide samples are readily soluble in chloroform, dried sample was taken in CDCl$_3$ solvent and ^{1}H NMR spectra was recorded (Aruntu *et al* 2004). The spectra (figure 4) show the characteristic peaks of 6 hydrogens belonging to two methyl groups of DMSO at 2·50 ppm. This provides supporting confirmation about the capping of DMSO on the ferrite nanoparticles.

The magnetic properties of the iron oxide magnetite nanoparticles were investigated with a SQUID Magnetometer. Figures 5a, b and c show the room-temperature magnetization of as-prepared γ-Fe$_2$O$_3$ nanocrystals. Both 8 and 12 nm magnetite nanocrystals exhibit the superparamagnetic characteristics and show no saturation in magnetization up to 60 kOe. The 50 nm sized spindle iron oxide has saturation magnetization at 25 kOe. The difference in saturation magnetization of our samples is mainly due to the differences in particle size and shape. In addition, the saturation magnetization of the present samples is lower than those of similarly sized nanoparticles prepared by other methods. It is probably caused by the surface spin canting effects since strong polar DMSO was used instead of oleic acid (Sun and Zeng 2002) or 2-pyrrolidone (Zhen *et al* 2004).

As seen from the M–H hysteresis curves, the coercivity observed in all the samples is about 15 Oe. Further, plausible explanation for the non-saturation of M_s in the coated samples can be attributed to the nature of the organic coating and shape of the particles, which is causing a difficulty in the domain motion and consequently in the alignment of spins along the field direction.

To the best of our knowledge, this is the first report on preliminary observations made on the iron oxide nanoparticles capped by DMSO. All the synthesized samples are soluble in chloroform. Well dispersed iron oxide nanoparticles of definite size and shape have been obtained by the synthetic route adopted. Further studies have shown that the synthesis is not limited to simple iron oxide nanoparticles but can be extended to various other types of ferrite nanoparticles as well. Detailed studies on size-controlled synthesis, size-dependent magnetic properties of various iron-based nanoparticles, and their potential applications are underway.

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