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Magnetic nanoparticles and nanoparticle assemblies from metallorganic precursors

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Magnetic nanoparticles of γ -Fe₂O₃, Fe₂O₃/SiO₂ composite and magnetite (Fe₃O₄) have been prepared using novel metallorganic precursors Fe[NC(C₆H₄)C(NSiMe₃)₂]₂Cl, Fe₂[O₂Si(C₆H₅)₂]₃ and [Fe(OBu^t)₃Na(THF)]₂ by hydrolysis, sol-gel condensation and further ultrasound and thermal treatment of the samples. The nanoparticles have been investigated by X-ray powder diffraction, TEM, SEM and AFM.

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1. Introduction

Nanotechnology is an emerging technology of the 21st century. According to current analyst's prognoses the scaling era of integrated electronics will saturate around the year 2010. The most obvious way for future electronics to make things very much smaller than they are at present, is by inventing new types of electronic devices, circuits and magnetic storage media that have dimensions of the order of nanometers [1]. The approach that will use magnetic nanoparticles of the size of a single magnetic domain is very important for development of high-density magnetic recording materials [2]. Superparamagnetic nanoparticles also have very important biomedical applications (e.g. magnetic cell sorting, magnetocytolysis, drug-targeting experiments, gene transfection studies, magnetic fluid hyperthermia, etc.) [3–5].

Nanoparticles can usually be prepared either by dry processes (sputtering, CVD) or by liquid-based processes (sol-gel, or thermal and ultrasonic decomposition of readily decomposable metal compounds). Most of these processes lead to bulk materials that may or may not exhibit a nanostructure. Moreover, dry processes are quite expensive and energetically demanding and development of cheap and reliable liquid-based techniques for preparation of magnetic nanoparticles (e.g. Fe₂O₃ and Fe₃O₄) is very important. Recently, it has been shown that metallorganic precursors, e.g. Fe(CO)₅, can be successfully applied for the preparation of Fe₂O₃ and Fe₃O₄ nanoparticles by sonochemical methods [6, 7].

Here we report the preparation of magnetic nanoparticles of γ -Fe₂O₃, Fe₂O₃/SiO₂ (passivated nanoparticles) and magnetite (Fe₃O₄) using novel metallorganic precursors by combinations of sol-gel, ultrasonic and thermal treatment.

2. Experimental details

2.1. Preparation of precursors

The new metallorganic precursors Fe[NC(C₆H₄)C(NSiMe₃)₂]₂Cl, Fe₂[O₂Si(C₆H₅)₂]₃ and Fe(OBu^t)₂(THF)₂ (THF is tetrahydrofuran) have been prepared using standard argon-vacuum and Schlenk techniques.

Fe[NC(C₆H₄)C(NSiMe₃)₂]₂Cl was synthesized by reaction of 1 equivalent of FeCl₃ and 2 equivalents of Li[NC(C₆H₄)C(NSiMe₃)₂] in diethyl ether.

Fe₂[O₂Si(C₆H₅)₂]₃ was prepared from 1 equivalent of Fe(OBu^t)₃ and 1.5 equivalents of (C₆H₅)₂Si(OH)₂ in diethyl ether.

Fe(OBu^t)₂(THF)₂ was obtained by reaction of 1 equivalent of FeBr₂ with 2 equivalents of NaOBu^t in THF.

2.2. Sol-gel process and preparation of nanoparticles

0.12 g (0.18 mmol) of Fe[NC(C₆H₄)C(NSiMe₃)₂]₂Cl was dissolved in 40 ml of THF. The mixture was then treated with an excess (20 ml) of distilled water giving a brown suspension. The obtained mixture was then ultrasonically (Ultrawave U 100, 30 kHz, 130 W) irradiated at ambient temperature for 1 h. The dark precipitate was filtered, washed several times with distilled water and acetone and then dried at 300 °C for 30 min to yield a dark brown powder of γ -Fe₂O₃.

0.14 g (0.2 mmol) of Fe₂(OSiPh₂)₃ was dissolved in 45 ml of THF. The mixture was treated analogously to that in the previous experiment to yield a light brown powder of Fe₂O₃/SiO₂ composite.

0.17 g (0.49 mmol) of Fe(OBu^t)₂(THF)₂ was dissolved in 45 ml of THF. The mixture was treated analogously to that in the previous experiment to yield a black powder of Fe₃O₄.

2.3. Characterization of nanoparticles

X-ray powder diffraction (XRD) was carried out using a Siemens D-500 X-ray diffractometer. X-ray patterns from powder samples were taken in reflection mode.

The scanning electron microscopy (SEM) images of the samples were obtained using an Hitachi S-4300

scanning electron microscope, which was operated at 5.0 kV.

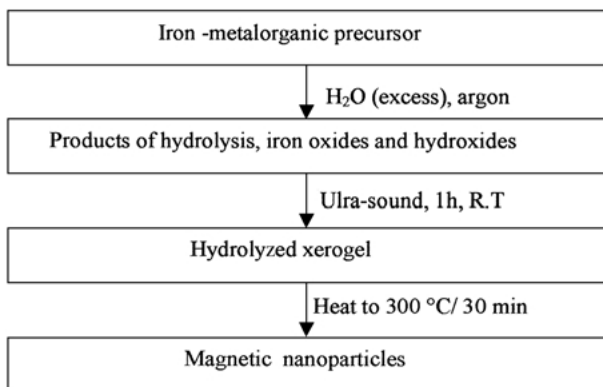
The transmission electron microscopy (TEM) images were taken on an Hitachi H-7000. The TEM was operated at a beam voltage of 100 kV. Samples for TEM were prepared by deposition and drying of a drop of the powder dispersed in ethanol onto a formvar-coated 400 mesh copper grid.

Atomic force microscopy (AFM) images were taken on a METRIS-2000 Atomic Force Microscope (Burleigh Instruments) with the METRIS-310 Personal AFM head. The samples for AFM were prepared on a glass substrate by evaporation and thermal treatment (100–150 °C) of hydrolyzed xerogel films from ultrasonically dispersed solutions.

3. Results and discussion

Novel metallorganic precursors have been preliminary prepared and characterized by elemental analysis, FTIR and ¹H NMR spectroscopy [8]. These novel precursors were chosen for this study for several reasons. We suggest that bulky ligands around the iron center could enable us to prepare nanoparticles with controlled size, uniformity and distribution. Derived from the ligands, organic products of sol-gel process might also help to stabilize the nanoparticles and their aggregates in solution to develop new types of magnetic fluids. Fe₂[O₂Si(C₆H₅)₂]₃ was chosen as a single-source precursor for preparation of Fe₂O₃-SiO₂ nanocomposites which, as reported earlier, demonstrate very interesting properties and magnetic behavior [9–12].

Hydrolysis of Fe[NC(C₆H₄)C(NSiMe₃)₂]₂Cl or Fe₂[O₂Si(C₆H₅)₂]₃ with distilled water in THF under argon followed by ultrasound and further thermal treatment gave γ-Fe₂O₃ or Fe₂O₃/SiO₂ composite, respectively. Similar operations with the Fe (II)-complex Fe(OBu')₂(THF)₂ led to the formation of magnetite (Fe₃O₄). The detailed structure and chemistry of the synthesis of precursors is beyond the scope of this paper and will be communicated as a separate publication [8]. The flow diagram for the processes is presented in Scheme 1. Reflections of the XRD patterns shown *d*-spacing values and relative intensities of the peaks with some line-broadening coincident exactly with JCPDS data of Fe₂O₃/SiO₂, γ-Fe₂O₃ and magnetite (Fe₃O₄), respectively.

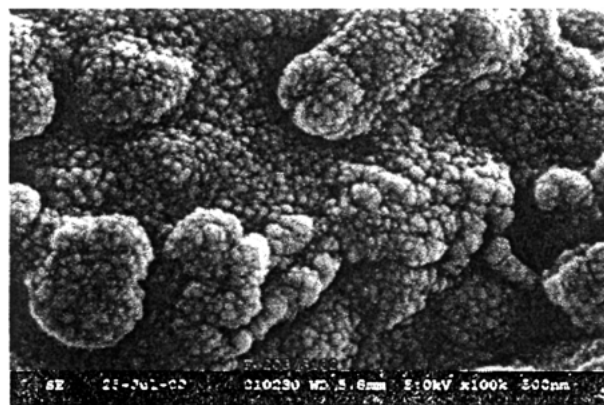


Scheme 1 Flow diagram for sol-gel preparation of iron oxides nanoparticles.

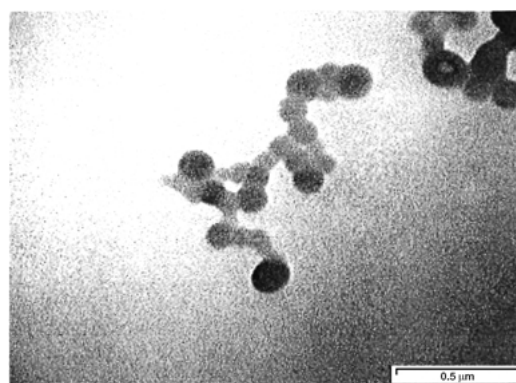
The samples have been investigated by TEM, SEM and AFM.

An SEM image of the Fe₂O₃/SiO₂ sample at ×10⁶ magnification has shown different shapes and sizes of nanoparticle aggregates (Fig. 1a). The nanostructures tend to form rather homogeneous aggregates with spherically packed structure. The TEM image (Fig. 1b) of the sample demonstrated that Fe₂O₃/SiO₂ nanoparticles adopt a quite regular spherical form and vary in size from 65 to 165 nm having an average diameter around 90–100 nm. A 3D AFM image of Fe₂O₃/SiO₂ (Fig. 1c) has shown low-dimensional assemblies of nanoparticles, which consist of parallel chains between 10 and 30 nm in breadth.

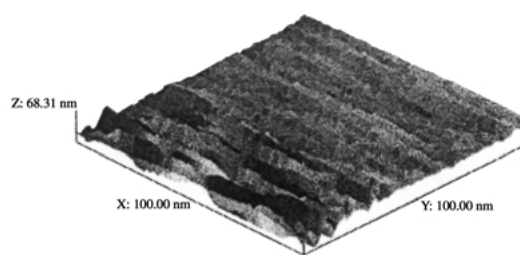
SEM observation of γ-Fe₂O₃ powder revealed a pattern with a very dense plain morphology, which consists of rather homogeneous grains of very narrow size distribution (Fig. 2a). The surface is very smooth with a few cracks. According to the TEM image, which is presented in Fig. 2b, the size of γ-Fe₂O₃ particles is in the range from 50 to 110 nm with an average diameter



a)

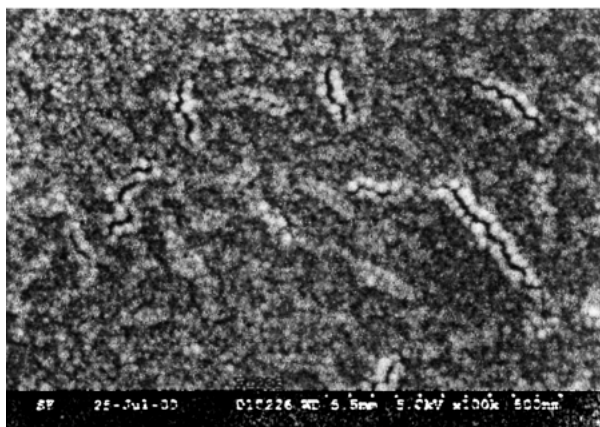


b)

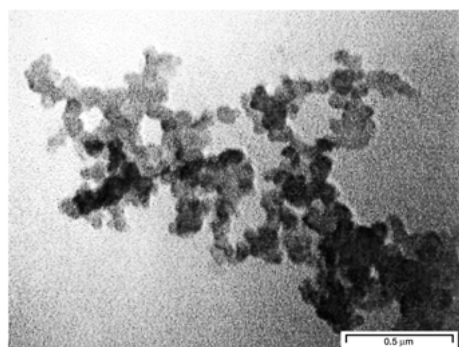


c)

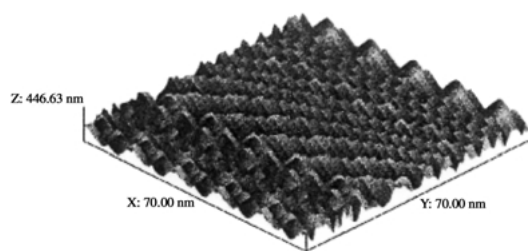
Figure 1 (a) SEM, (b) TEM and (c) AFM images of Fe₂O₃/SiO₂.



a)



b)



c)

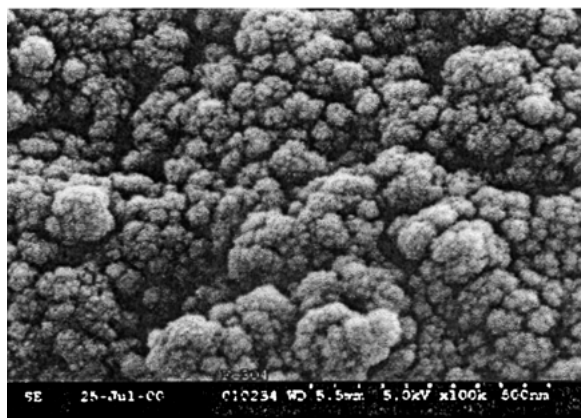
Figure 2 (a) SEM, (b) TEM and (c) AFM images of γ -Fe₂O₃.

around 75–80 nm. AFM microscopy of the sample deposited on a glass substrate has shown that γ -Fe₂O₃ layers contain several sets of parallel arrays of about 15 nm breadth with different orientation for each set giving zigzag (wood-grain) structures (Fig. 2c).

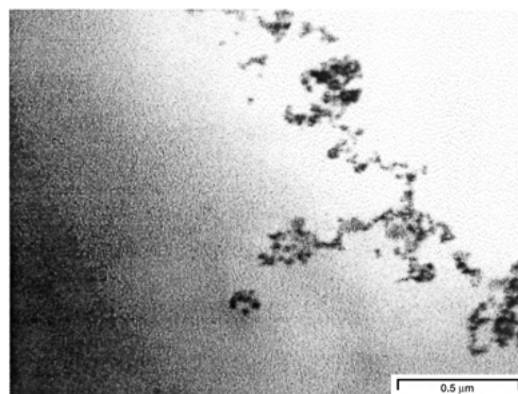
An SEM image of the Fe₃O₄ sample at $\times 10^5$ (Fig. 3a) shows rather large aggregates of small nanoparticles, which are randomly packed together. TEM images (Fig. 3b) show a good dispersion of nanoparticles, which have a very narrow size distribution and an average diameter ~ 15 nm. AFM scanning of Fe₃O₄ deposited on a glass substrate demonstrated narrow arrays of 8–10 nm breadth oriented mostly parallel to each other (Fig. 3c).

In all cases AFM has shown that data sizes of nanoparticles deposited on a glass substrate are smaller than those observed by TEM. This may be due to the difference in drying conditions and thermal treatment of the gel during the sample preparation procedures for TEM and AFM.

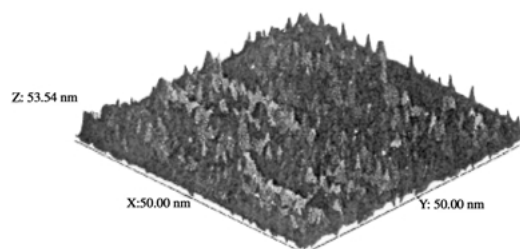
In general, TEM images of the samples demonstrated that particles are self-assembled into grain boundaries of mostly cyclic shapes. That is probably due to the



a)



b)



c)

Figure 3 (a) SEM, (b) TEM and (c) AFM images of Fe₃O₄.

magnetic interaction between the nanoparticles behaving as magnetic dipoles. Surprisingly Fe₂O₃/SiO₂ nanoparticles adopt a quite regular spherical form in contrast to less expressed forms of γ -Fe₂O₃ and Fe₃O₄ particles. Particles of Fe₂O₃/SiO₂ γ -Fe₂O₃ and Fe₃O₄ are arranged in such a way as to give aggregates of spherically packed structures attributed to the magnetic interaction between the nanoparticles behaving as non-single domains. It appears that the bulky organic groups coordinated to the iron metal control the initial nucleation and growth process of the particles, which leads to formation of well-defined nanoparticles.

4. Conclusions

Thus, the results illustrate that magnetic nanoparticles of γ -Fe₂O₃, Fe₂O₃/SiO₂ and magnetite (Fe₃O₄) of different size can be quite readily produced by wet methods from metallorganic precursors. The technique seems to be very promising for the preparation of controlled size

nanoparticles and their aggregates. Results of SEM, TEM and AFM analysis have shown that there are prospects for preparation of patterned media arrays of nanoparticle assemblies for high-density information storage.

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