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Synthesis and characterization of iron, iron oxide and iron carbide nanostructures



Ron Snovski^a, Judith Grinblat^a, Moulay-Tahar Sougrati^b, Jean-Claude Jumas^b, Shlomo Margel^{a,*}

^a Institute of Nanotechnology & Advanced Materials, Department of Chemistry, Bar Ilan University, 52900 Ramat Gan, Israel

^b Institut Charles Gerhardt (UMR 5253 CNRS), Université Montpellier 2, CC 1502, Place E. Bataillon, 34095 Montpellier Cedex 5, France

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ABSTRACT

Magnetic iron oxide (Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$) and iron carbide (Fe_3C) nanoparticles of different geometrical shapes: cubes, spheres, rods and plates, have been prepared by thermal decomposition of a mixture containing the metal precursor $\text{Fe}(\text{CO})_5$ and the stabilizer polyvinylpyrrolidone (PVP) at 300 °C in a sealed cell under inert atmosphere. The thermal decomposition process was performed for 4 or 24 h at ([PVP]/[$\text{Fe}(\text{CO})_5$]) (w/v) ratio of 1:1 or 1:5. Elemental iron nanospheres embedded within a mixture of amorphous and graphitic carbon coating were obtained by hydrogen reduction of the prepared iron oxide and iron carbide nanoparticles at 450 °C. The formation of the graphitic carbon phase at such a low temperature is unique and probably obtained by catalysis of the elemental iron nanoparticles. Changing the annealing time period and the ([PVP]/[$\text{Fe}(\text{CO})_5$]) ratio allowed control of the composition, size, size distribution, crystallinity, geometrical shape and magnetic properties of the different magnetic nanoparticles.

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1. Introduction

Coated magnetic nanoparticles have numerous potential applications, particularly as recoverable catalysts [1,2] and in the biomedical sciences [3,4]. For example, functionalized magnetic nanoparticles have been employed for site-specific drug delivery [5,6]. The shape, size and size distribution of the magnetic materials are the key factors that determine their chemical and physical properties [7]. Thus, the development of size and shape-controlled magnetic materials has become very important for different uses. So far, the most widely used and studied magnetic material is iron oxide, in the form of magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$). The applications of these iron oxide particles rely upon the biodegradability and biocompatibility of the iron oxide phase [8,9]. Elemental iron on the other hand has a significantly higher magnetic moment than its oxides. Moreover, elemental iron is the most useful among the ferromagnetic elements; it has the highest magnetic moment at room temperature, and a Curie temperature which is high enough for the vast majority of practical applications. In addition, iron is a widespread

element, and therefore significantly cheaper than other ferromagnetic elements such as nickel and cobalt. However, Fe particles are easily oxidized leading to a significant reduction in their magnetic moment. In order to prevent this phenomenon, Fe particles should be protected by a protective layer, such as carbon, [10–13] silica [14,15] or alumina [16]. Recently, a few publications described the synthesis of Fe magnetic silica particles, by entrapment of iron nitrate within the mesopores of silica particles, followed by impregnation with ethylene glycol and then annealing at 450 °C [14].

An attractive alternative to elemental iron, offering both high magnetic saturation and chemical stability, is iron carbide (Fe_3C) [17]. As with many metal carbide materials, the synthesis of Fe_3C nanoparticles presents a considerable challenge. Many of the well-established routes to metal or metal oxide nanoparticles, such as microemulsion or coprecipitation synthesis, are unsuitable for metal carbide formation. The synthesis of phase-pure Fe_3C is particularly difficult, since the relatively high-temperature and reducing conditions characteristic of many carbide syntheses often result in the formation of metallic iron or mixed Fe and Fe_3C products [18,19]. While some routes, such as flame spray pyrolysis, [20] have been used to synthesize phase-pure Fe_3C ; most current methods involve multiple-step or high-energy procedures using hazardous or costly chemical precursors [21,22].

Magnetic nanoparticles tend to aggregate due to strong magnetic dipole–dipole and van der Waals attraction. Thus, the main

* Corresponding author. Tel.: +972 3 5318861; fax: +972 3 7384053.

E-mail addresses: ron.snovski@gmail.com (R. Snovski), grinby@mail.biu.ac.il (J. Grinblat), Moulay-Tahar.Sougrati@univ-montp2.fr (M.-T. Sougrati), jumas@univ-montp2.fr (J.-C. Jumas), shlomo.margel@mail.biu.ac.il (S. Margel).

challenge in the synthesis is to overcome these aggregation phenomena. This is usually done by coating the nanoparticles' surface with desired functional polymers or surfactants. The surfactant also plays a role in the nucleation process and in limiting particle growth. The functional groups belonging to the organic coating also allow the binding of biological molecules, such as proteins, oligonucleotides, etc., to the particle's surface for biomedical applications [23]. Iron and iron oxide nanoparticles are typically prepared by the decomposition of soluble iron precursors in solutions containing an appropriate stabilizer. The decomposition of the iron precursors is accomplished by means of processes such as sonochemistry, [24–27] thermal decomposition, [28,29] electrochemical [30] and laser decomposition [31]. Among the iron precursors, iron carbonyl compounds are the most useful ones, since they decompose and release CO molecules, which can easily be removed from the reaction mixture. Recently, several ways to prepare iron oxide and elemental iron nanoparticles using different iron precursors and surfactants have been reported [32–35].

The present manuscript describes a simple one-step route to synthesize iron oxide and iron carbide nanoparticles of different shapes. Elemental iron nanospheres embedded within graphitic carbon matrix are obtained by hydrogen reduction of the prepared iron oxide and iron carbide nanoparticles at 450 °C.

2. Materials and methods

2.1. Materials

The following analytical-grade chemicals were purchased from Aldrich (Israel) and were used without further purification: Fe(CO)₅ (>99%) and polyvinylpyrrolidone (PVP, MW 360,000). Water was purified by passing deionized water through the Elgastat Spectrum reverse osmosis system (Elga, High Wycombe, UK). The following gases were purchased from Israel Oxygen and Argon Factories Inc.: Ar and H₂, 99.999% purity.

2.2. Synthesis of uniform iron oxide and iron carbide nanoparticles of different shapes

200 mg of PVP were weighed into a letlock followed by the addition of 0.2 or 1.0 ml of Fe(CO)₅ (1:1 or 1:5 w/v ratio, respectively). The letlock was carefully flushed for 2 min by Ar (10 ml/min flow rate) and then sealed in order to prevent Fe(CO)₅ evaporation. The different mixtures were thermally decomposed in a pre-heated tube furnace at 300 °C for 4 or 24 h. The mixtures were then left to cool to room temperature.

2.3. Synthesis of uniform elemental iron nanoparticles embedded in carbon

Elemental iron nanospheres of 290.1 ± 247.1 nm size embedded in a mixture of amorphous and graphitic carbon were formed by reducing the iron oxide and iron carbide nanoparticles, prepared by thermal decomposition for 4 h of the mixture of PVP and Fe(CO)₅ at ([PVP]/[Fe(CO)₅]) ratio of 1:1 (w/v) with H₂ (20 ml/min flow rate) at 450 °C for 2.5 h. The H₂ reduction reaction was performed in a combustion boat containing the mentioned nanoparticles. The obtained carbon-coated nanospheres were then left to cool to room temperature.

2.4. Characterization of the different magnetic nanoparticles

High-resolution transmission electron microscope (HRTEM) images were obtained by employing a 200 kV, JEOL-2100 device with integrated digital scanning transmission electron microscope

(STEM) (annular dark and bright field detectors). Samples for HRTEM were prepared by placing a drop of the diluted sample on a 400-mesh carbon-coated copper grid. The particles' average size and size distribution of the electronic images were determined by measuring the diameter of approximately 200 particles with an image analysis software, AnalySIS Auto (Soft Imaging System GmbH, Germany). The sizes of the differently shaped nanoparticles were measured as follows: nanospheres were measured by diameter, nanocubes by the length of their diagonal and nanorods and nanoplates according to their width. Raman spectroscopy (HORIBA Jobin Yvon) measurements were carried out by using an Ar ion laser (power=10 mW and wavelength=632.8 nm). The exposure and data acquisition times were 20 and 2 s, respectively. C, H and O weight % of the various particles were measured using an elemental analysis instrument, model FlashEA1112 Instruments, Thermoquast. Fe weight % was calculated by subtracting the sum of the other elements from 100.

Powder X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer (model D8 Advance, Bruker AXS) with Cu K α radiation. Isothermal magnetization measurements at room temperature were performed in a commercial (Quantum Design) super-conducting quantum interference device (SQUID) magnetometer. The Mössbauer spectroscopy measurements were performed by putting the samples' powders (100 mg each) on a PMMA holder of 16 mm diameter without any binder. The powders could be recovered if necessary. ⁵⁷Fe Mössbauer spectra were then recorded in the constant acceleration mode and in transmission geometry on a standard Mössbauer spectrometer. A ⁵⁷Co(Rh) source with a nominal activity of 130 MBq was used. The source and the absorber were always kept at room temperature. The isomer shift is given with respect to α -Fe standard at room temperature. Data refinement has been performed using the Lorentzian lines. The thermal behavior of the particles was measured with a TC15 system equipped with TGA (thermal gravimetric analysis), model TG-50, from Mettler Toledo. C, H, N and O analyses of the various particles was performed using an elemental analysis instrument, model FlashEA1112 Instruments, Thermoquast.

3. Results and discussion

In this work, we use the term “nanospheres” for truly spherical particles, whereas the term “nanoparticles” is used for the particles that, while they are rounded in shape, are not perfectly spherical. The size and size distribution and the different geometrical shapes of the nanoparticles are summarized in Table 1. The different shapes are presented in Figs. 1–5. The sizes of the nanocubes and nanoparticles, obtained after thermal decomposition of a mixture of PVP and Fe(CO)₅ at ([PVP]/[Fe(CO)₅]) (w/v) ratio of 1:1 at 300 °C for 4 h under Ar atmosphere, are 54.5 ± 6.8 and 43.1 ± 13.0 nm, respectively. Following H₂ reduction of iron oxide, a change in shape to nanospheres and a significant increase in particle size to 290.1 ± 247.1 nm was observed. This increase in size probably occurred due to agglomeration. Thermal decomposition of a mixture of PVP and Fe(CO)₅ was also performed at a ratio of 1:5 for 24 h, also at 300 °C. The increase in Fe(CO)₅ relative concentration and duration of thermal decomposition resulted in formation of iron oxide nanoplates with a width of 120.0 ± 27.4 nm. Previous Fourier-transform infrared (FTIR) spectrometry studies have shown that PVP molecules may coordinate with metal ions to form stable metal–PVP complex molecules [36,37]. This complex formation may also explain the changes in the different geometrical shapes. Note that rather than obtaining a mixture of different shapes, each composite obtained in each experiment was produced with its own characteristic shape.

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