



Characterization of tetraethylene glycol passivated iron nanoparticles



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ARTICLE INFO

Article history:

Received 3 June 2014

Received in revised form 1 July 2014

Accepted 24 July 2014

Available online 1 August 2014

Keywords:

Iron@iron oxide

Core@shell

Magnetic nanoparticle

Metallic iron

Nanoparticles

Polyol

ABSTRACT

The present study describes the synthesis and characterization of iron@iron oxide nanoparticles produced by passivation of metallic iron in tetraethylene glycol media. Structural and chemical characterizations were performed using transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Mössbauer spectroscopy. Pomegranate-like core@shell nanoparticulate material in the size range of 90–120 nm was obtained. According to quantitative phase analysis using Rietveld structure refinement the synthesized iron oxide was identified as magnetite (Fe₃O₄) whereas the iron to magnetite mass fractions was found to be 47:53. These findings are in good agreement with the data obtained from Mössbauer and thermal gravimetric analysis (TGA). The XPS data revealed the presence of a surface organic layer with higher hydrocarbon content, possibly due to the tetraethylene glycol thermal degradation correlated with iron oxidation. The room-temperature (300 K) saturation magnetization measured for the as-synthesized iron and for the iron–iron oxide were 145 emu g⁻¹ and 131 emu g⁻¹, respectively. The measured saturation magnetizations are in good agreement with data obtained from TEM, XRD and Mössbauer spectroscopy.

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1. Introduction

Metallic iron nanoparticles are of great interest in several technological applications including data storage [1], magnetic fluids [2], biotechnology and biomedicine [3,4], environmental remediation [5], and catalysis [6], due to their magnetic, chemical, and electronic properties [7]. The main concern related to metallic iron nanoparticles is their instability towards oxidation in ambient atmosphere. In the presence of moisture the oxidation process can lead to a mixture of iron oxides and iron oxyhydroxides and in dried conditions the oxidation reaction can be vigorous and highly exothermic due to the pyrophoric behaviour of metallic iron nanoparticles [8,9]. To overcome this drawback, several strategies of surface protection have been developed, including encapsulation with carbon [10], noble metals such as gold [11], silver [12] and palladium [5], and oxides such as Fe₃O₄ [13], Al₂O₃ [14], and SiO₂ [15]. All these strategies result in magnetic nanoparticles with a core@shell structure, in which the shell serves as a

protective layer. In particular, coating with Fe₃O₄ layers is of great interest, for a magnetic coating on top of a magnetic nanoparticle usually influences on the end magnetic properties [16]. The ferromagnetic behaviour of the coating metal oxide results in a smaller reduction of the saturation magnetization in the final core@shell nanoparticles while compared with the magnetic dilution effect generated by using paramagnetic or diamagnetic shell materials [10,15,17].

Production of metallic iron nanoparticles and passivation via surface oxidation resulting in an iron oxide coating layer has been investigated by a number of authors through different synthetic routes. Typical approaches are the evaporation of iron to form nanoparticles followed by later oxidation in the presence of oxygen [18,19], flame spray pyrolysis [20,21] and solution based methods such as thermal decomposition of iron coordination compounds in high boiling solvents [3,13,22,23], solvothermal [24,25], and polyol synthesis [26]. By controlling the structure and composition of the iron oxide coating layer, the magnetic properties of the resulting core@shell particles can be tailored through tuning the dimensions of the core and shell, which selectively controls the magnetic properties of core@shell nanoparticles for the desired applications [16].

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In this study, the passivation of iron nanoparticles with an iron oxide coating layer of well-defined composition is described. Our main objective is to obtain a synthetic route to produce a highly crystalline iron oxide coating layer to protect the iron cores more efficiently, since the non-crystalline iron oxide could not protect the metallic iron core from deep oxidation [13]. For this purpose, we performed the passivation of pre-synthesized metallic iron nanoparticles by heating the sample at reflux temperatures in di-, tri- and tetraethylene glycol media leading to the formation of a crystalline Fe_3O_4 oxide layer, thus resulting in nanoparticles with magnetic properties between iron and iron oxide. This approach provides new insights for tailoring metal@metal-oxide core@shell structured nanocomposites.

2. Materials and methods

2.1. Materials

All chemicals were used as received. Sodium borohydride (96%, Fluka), tetraethylene glycol (TTEG) (99%, Alfa Aesar). Iron (II) chloride tetrahydrate (98%, ReagentPlus®), triethylene glycol (TEG, 99%, ReagentPlus®), diethylene glycol (DEG, 99%, ReagentPlus®), poly(ethylene glycol) (PEG) (MW 4600, Aldrich), triglyme (99%, ReagentPlus®) were acquired from Sigma–Aldrich Brazil.

2.2. Methods

2.2.1. Synthesis of passivated iron nanoparticles

The metallic iron nanoparticles were synthesized by reduction of iron (II) ions with sodium borohydride. In typical procedure, 4 mmol (0.811 g) of iron (II) chloride and 1 g of PEG were dissolved in 40 mL of oxygen-free water and added to a 250 mL three-neck round-bottom flask. The system was sparged with Ar gas for 30 min. Then, a freshly dispersion of 12 mmol (0.473 g) of sodium borohydride in 3 mL of triglyme was injected into the mixture. A black solid formed instantly with vigorous gas evolution. After 20 min the solid was separated by magnetic decantation and washed with oxygen free acetone three times.

For the passivation step, the pre-synthesized metallic iron nanoparticles were dispersed in 20 mL of oxygen-free TTEG and added to a 125 mL three-neck round-bottom flask. The system was thoroughly sparged with Ar gas and the mixture was heated with a heating rate of $10^\circ\text{C min}^{-1}$ up to 310°C for 30 min. After cooling at room temperature the nanoparticles were precipitated with acetone and, with the aid of a permanent magnet, washed with oxygen-free ethanol:water 50:50 several times and twice with oxygen-free acetone, dried in vacuum, and stored in Ar atmosphere. The same procedure was conducted using TEG and DEG as solvents for comparison.

In order to verify the role of the reaction media in the formation of the iron oxide phase, the as-synthesized metallic iron sample was dried in vacuum and then submitted to a thermal treatment at 500°C in Ar atmosphere. The obtained powders were stored in Ar atmosphere for further analysis.

2.2.2. Characterization

XRD diffractograms of the powder samples were recorded using a Siemens D5005 system equipped with Cu ($K\alpha_1$ and $K\alpha_2$) radiation source and with a graphite monochromator, operating at 40 kV in the 2θ range between 20° and 90° in a fixed-time mode with 0.02° step size. The Rietveld structure refinement of the samples was performed using the GSAS software with the EXPGUI interface [27,28]. The profiles were fitted using the Thompson–Cox–Hastings pseudo-Voigt profile function and the background was fitted using the Chebyshev polynomial [27]. The as-synthesized metallic iron sample was protected with mineral oil before analysis. The size and

morphology of the nanoparticles were initially investigated using the JEOL model JSM-7500F scanning electron microscope (SEM), operated at an accelerating voltage of 2 kV. The samples were dispersed in isopropyl alcohol by using an ultrasonic probe and dropped in Si wafers. Transmission electron microscopy (TEM) was performed to assess the structural information of the passivated nanoparticles. Low-magnification and high-resolution transmission electron microscopy images (HR-TEM) were obtained using the JEOL 3010 TEM-HR operating at 300 kV. Fast Fourier Transforms (FFT) of TEM images were obtained using the Digital Micrograph (Gatan) software to obtain the lattice d-spacing. For TEM analysis the sample dispersed in isopropyl alcohol was deposited on a copper grid covered with an amorphous carbon film and left to dry in Ar-atmosphere. Iron concentrations were determined by using inductively coupled plasma atomic emission spectroscopy (ICP-AES) after removing the magnetic nanoparticles out from the reaction media (supernatant) by centrifugation at 10,000 rpm. Thermogravimetric analysis (TGA) was carried out in the SDT 2690 DTA-TGA system from TA Instruments, running from room temperature up to 1000°C , using air flow at $50\text{ cm}^3\text{ min}^{-1}$ and setting the heating rate at $10^\circ\text{C min}^{-1}$. The X-ray photoelectron spectroscopy (XPS) analysis was carried out using the UNI-SPECS UHV instrument using Mg $K\alpha$ line ($h\nu = 1253.6\text{ eV}$) at a pressure of less than 10^{-7} Pa. The inelastic background of the C (1s), O (1s) and Fe (2p) spectra was subtracted using Shirley's method. The deconvoluted spectral components were obtained using the Gaussian–Lorentzian profile and the binding energies for core level spectra were corrected using the hydrocarbon component of adventitious carbon fixed at 285.0 eV. Mössbauer spectroscopy measurements were performed at room temperature (300 K) and at 77 K, using transmission geometry of a computer controlled Wissel spectrometer with a triangular mode and using a $^{57}\text{Co/Rh}$ source. The system velocity was calibrated with a thin natural iron foil whereas the spectra were least-squared fitted to a combination of Lorentzian-like lines. Magnetization measurements (field- and temperature-dependent) were performed using the commercial Physical Property Measurement System (PPMS) model 6000 platform with the vibrating sample magnetometer (VMS) module from Quantum Design. The hysteresis loops (M – H curves) ($-20,000$ – H – $20,000$ Oe) were at temperatures $T = 5$ and 300 K .

3. Results and discussion

3.1. Morphological and structural characterization

Metallic iron nanosized particles were first synthesized by chemical reduction with sodium borohydride in aqueous media and then submitted to a passivation process in tetraethylene glycol at 310°C . The passivation step promoted the formation of a ferrimagnetic oxide layer of well-defined composition on top of the iron surface. Fig. 1 shows field emission scanning electron microscopy (FESEM) images of the as-synthesized metallic Fe and passivated $\text{Fe@Fe}_3\text{O}_4$ -TTEG nanosized particles. Most of the synthesized nanosized particles presented quasi-spherical morphology while revealing wider size dispersity. Furthermore, in both samples, the nanosized particles assume chain-like ordering due to strong particle–particle magnetic interaction. The particle size distribution histograms were fitted to a log-normal function (Fig. 1c and f), whereas the mean particle size (distribution width) were estimated at about 95 nm (0.45) and 127 nm (0.45) for the as-synthesized metallic Fe and passivated $\text{Fe@Fe}_3\text{O}_4$ -TTEG samples, respectively. The observed increase in the mean particle diameter seems to be related to particle ageing, such as digestive ripening, which is governed by iron hydrolysis and precipitation as oxide, associated to the passivation step [29]. This assumption is

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