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α-Fe nanoparticles produced by laser ablation: Optical and magnetic properties

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ABSTRACT

Nanoparticles with optical and magnetic responses are of great applicability in different fields. In this work, zero valent iron nanoparticles were prepared by laser ablation and stabilized in a surfactant solution to keep particles dispersed and protected in the solution. Optical and magnetic properties of nanoparticles were measured, by UV and Mössbauer spectroscopy. The results show the formation of nanoparticles of α-Fe (ferromagnetic). Our method of preparation, which uses a high H^+ concentration in the medium, diminishes the zero valent iron oxidation, producing iron nanoparticle with a core of α-Fe and a small shell probably composed of iron oxides.

1. Introduction

Magnetic nanoparticles (MNPs) have shown great potential in biomedical applications such as magnetic separation, magnetic resonance imaging (MRI), targeted drug delivery, and hyperthermia treatment of cancer. In particular, MNPs are excellent MRI contrast agents for cellular and molecular imaging. MNPs composed of Fe_3O_4 have been extensively investigated due to their excellent magnetic properties and biocompatibility.

Synthesis of metallic iron nanoparticles and their dispersion in various liquid media is of great interest in the field of nano-magnetic materials. Alpha iron (α-Fe) is a class of ferromagnetic material with high magnetic moment density (218 emu/g or 1713 emu/cc) and is magnetically soft. It has been reported to show superparamagnetic behavior for α-Fe nanoparticles in the size range below 20 nm [1,2], and its stable dispersions show high magnetic moment and are predicted to have important applications in bioseparation, biosensing, drug delivery and MRI contrast enhancement [3,4]. Procedures leading to monodisperse Fe nanoparticles are well documented [5]. The most common chemical methods used for the preparations include thermal decomposition of iron pentacarbonyl ($Fe(Co)_5$) [5–11], reductive decomposition of iron (II) bis(trimethylsilyl)amide ($Fe[NSi(CH_3)_3]_2$) [12] and reduction of iron (III) acetylacetonate ($Fe(acac)_3$) or other iron salts [13]. Although the size of the particles is well controlled, the syntheses reveal that the particles so prepared are extremely reactive and subject to easy oxidation, giving various iron oxide nanoparticles. As a result, the production of stable α-Fe nanoparticle dispersions, especially aqueous dispersions for potential biomedical applications is not easy to achieve via wet synthesis [1].

Recently, pulsed laser ablation of metal targets in liquid media has attracted great interest [14], because such laser ablation in liquid (LAL) can produce the extreme conditions of pressure and temperature to lead to formation of metastable nanostructures and hence novel properties. When a pulsed laser beam with enough energy irradiates on a metal target in a transparent liquid, a local plasma, at a super high temperature (about 6000 K) and high pressure (about 1 Gpa), will instantly be produced on the solid–liquid interface and quenched quickly after one pulse due to adiabatic expansion of the plasma and its interaction with the surrounding media. The whole process is finished in about 1 μs. So, the laser ablation of metal targets in liquid media can form some special nanostructures, which cannot be obtained by the conventional methods.

In the following work we present a laser ablation methodology for obtaining α-Fe nanoparticles. The nanoparticles were prepared and stabilized in a surfactant solution to keep particles dispersed and protected in the solution. Optical and magnetic properties of the nanoparticles were measured, by UV and Mössbauer spectroscopy. The results show the formation of nanoparticles of α-Fe (ferromagnetic), these surfactant-stabilized particles are protected from oxidation by surface passivation which maintains the magnetic state for periods longer than 1 month.

2. Materials and methods

2.1. Chemicals

Analytical grade ethanol and deionized water 18 mΩ were used as solvents. A 0.045 μM surfactant solution was prepared by dissolving the appropriate amount of sodium dodecyl sulfate (SDS) (ScharlauChemie, Barcelona, España) in a methanol–water

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mixture. All working solutions were filtered through a 0.45 μm Millipore filter. Iron (Fe) 99.5% from Sigma Aldrich.

2.2. Formation of iron nanoparticles and characterization

Iron nanoparticles (Fe Nps) were obtained by using the following method optimized in our laboratory: A pure iron plate (1.0 × 0.5 cm) was placed in a clean glass container filled with 3 mL of 0.045 M SDS aqueous solution. The plate surface was irradiated by the first harmonic of a Nd:YAG laser (wavelength 1064 nm, frequency 10 Hz, pulse duration 8 ns) for 15 min by using a power of about 145 mJ/pulse and a spot size about 0.43 mm in diameter on the target. The Fe Nps were characterized by measuring the size distribution using a homemade Dynamic Light Scattering Apparatus. The surface plasmon resonance of the Fe nanoparticles was determined by UV–Vis extinction spectrometry. The spectra of the solutions were recorded by using an UV–Vis spectrometer (Nicolet Evolution 300 from Thermo, WI, USA) in an optical quartz cell with a path length and volume of 10 mm and 0.7 mL, respectively.

2.3. Mössbauer spectroscopy

To identify the different phases of iron we used Mössbauer spectroscopy (MS) on the 14.4 keV transition of ^{57}Fe. The source is ^{57}Co in Rh and the spectrometer is a homemade combination of a driver, Multi-Channel Scaling system (MCS) and nuclear detection chain with a proportional counter, which was run in the triangular symmetric mode. The instrument was calibrated with α-Fe and the isomer shifts are given relative to it. The spectra were computer-fitted with lorentzian shapes for the lines and a limited number of free parameters (isomer shifts (IS), quadrupole splittings (QS), magnetic hyperfine field (HF) and relative area) for each sub-spectrum. The spectra were run at room temperature only, essentially due to the smallness of the samples, which implied a geometry where the source had to be very near to the absorber.

3. Results and discussion

Fe NPs were produced by laser irradiation on metal plate submerged in SDS. The formation of iron particles start by the fusion of the metal as a consequence of the laser energy absorption, then the solution vapors expand adiabatically at supersonic speed producing a high pressure and temperature plasma causing surface cracking, generating nano-scale particles and eventually iron clusters. Fe particles interact with water and dissolved oxygen in the medium to form a cluster composed by Fe (0), Fe_2O_3 and Fe_3O_4 species at the surface, according to the results published by Basu and Chakravorty [15] for the plasmon resonance spectra for oxides species using the Maxwell–Garnet model. Finally, the SDS is adsorbed on the nanoparticles surface forming stable micelles. The encapsulation on the NPs by SDS molecules prevents the agglomeration and hence its growth by effects of repulsive interaction, giving as a result a stable colloidal solution [19]. Experimentally, a color change of the solution from colorless to yellow indicates the formation of NPs. Figure 1 shows the size distribution of the NPs, a narrow size distribution is obtained with mean size of 17 nm ranging from 10 to 49 nm.

Figure 2 shows the optical extinction spectra of Fe NPs in acidic media. It was observed that spectra obtained at acidic pH media have a characteristic band at 330 nm corresponding to the surface plasmon signal due the presence of Fe(0) (α-Fe) at the Nps surface. At this pH all oxides and hydroxides are dissolved. The band broadening is inversely proportional to the radius of the particle for sizes smaller than 20 nm.
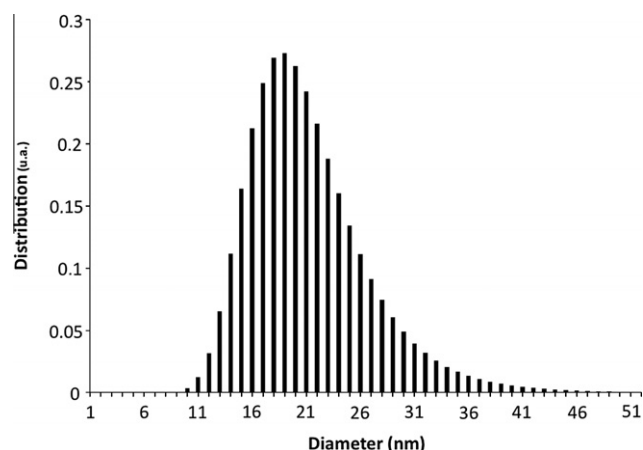

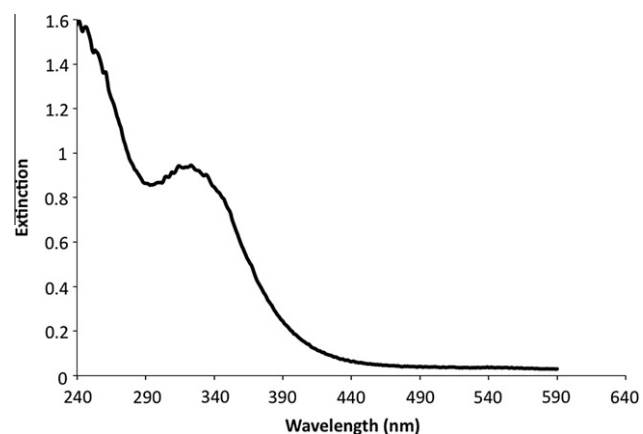**Figure 1.** Particle size distribution.

Figure 2. Fe nanoparticles spectra in acidic media.

Figure 3 presents the extinction spectra of the Fe Nps in pH 3 and 7 media. The plot clearly shows that at pH 7 the most stable species is the Fe^{+3} form of iron. The SPR characteristic band of zero valent Fe disappears and only a dispersion light response due to the presence of the nanoparticles in the media is observed.

Mössbauer spectra obtained at room temperature are shown in Figure 4. Spectrum (a) indicates the presence of α-Fe in a proportion of 41% (area%, six narrow lines fitted with a hyperfine field of 330 kG and an isomer shift 0.001 mm/s typical values of α-Fe) and an asymmetrical doublet whose parameters (IS = 0.37 mm/s and Qs = 0.85 mm/s) could be attributed to iron oxides nanoparticles in a superparamagnetic state as was reported by Bondera et al.
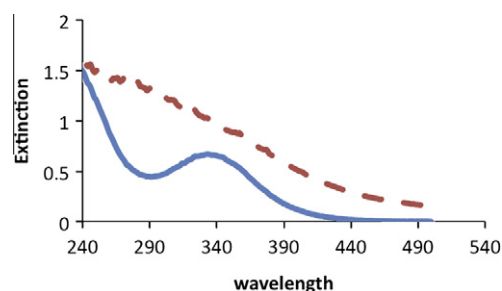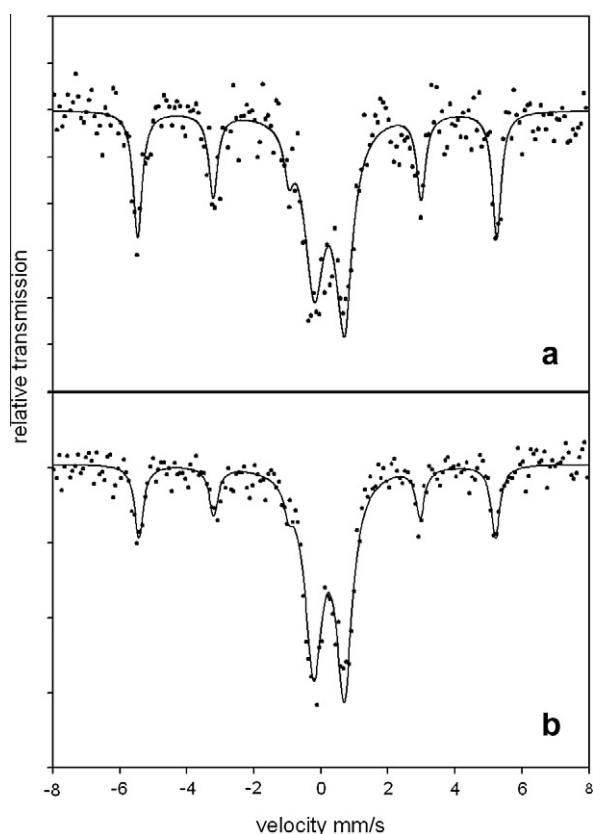

Figure 3. Fe nanoparticles SPR spectra at different pH. At pH < 3 (continued line) the predominant specie is zero-valent Fe at higher pH (dashed line) the predominant specie is Fe^{+3}.

Figure 4. Mossbaur spectra at room temperature and at different times for nanoparticles synthesized in acidic media (a) taken 1 month before (b).

[16,17]. Measurements made one month later (spectrum (b)) have shown a variation in proportions giving 30% for α-Fe and 70% for the oxides. This is the first time that the presence of metallic α-Fe after laser ablation has been experimentally demonstrated. In previous reports Liu et al. [18] synthesized iron nanoparticles by laser ablation with sizes between 5 and 45 nm with a predominant presence of iron oxides in the structure. This methodology, based in the nanoparticle production in a medium with high H^+ concen-tration, decreases the zero valent iron oxidation produces an iron nanoparticle with a core of α-Fe and a thin shell composed by superparamagnetic oxides.

4. Conclusions

An efficient methodology to obtain zero valence Fe nanoparticles using laser ablation was developed. Synthesized nanoparticles have shown optical and magnetic responses as well as a long term stability under the working conditions. The characterization of the nanoparticles prove that they are composed by a nucleus of zero valence iron surrounded by oxidized species which work like a protecting shield against oxidation.

Acknowlegment

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