Synthesis and Characterization of Air-Stable Iron Nanocrystalline Particles Based on a Single-Step Swelling Process of Uniform Polystyrene Template Microspheres

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Polystyrene template microspheres of narrow size distribution were prepared by dispersion polymerization of styrene in a mixture of ethanol and 2-methoxy ethanol. These template particles dispersed in aqueous solution have been used for entrapping $Fe(CO)_5$, by a single-step swelling process of methylene chloride emulsion droplets containing $Fe(CO)_5$, within these particles. The influence of different swelling parameters, such as the volume ratio $[CH_2Cl_2/[Fe(CO)_5]$, on the size and size distribution of the swollen template particles was elucidated. Air-stable Fe/Fe_3C nanocrystalline particles have been prepared by thermal decomposition of the $Fe(CO)_5$ swollen template particles at 600 °C in an inert atmosphere. Characterization of these air-stable Fe/Fe_3C nanocrystalline particles has been accomplished by light microscopy, TEM, XRD, TGA, XPS, elemental analysis, and magnetic susceptibility measurements. These nanocrystalline particles have a core−shell structure where a coating of Fe_3C and carbon protects the core body-centered cubic Fe from oxidation.

Introduction

There is much interest among the academic and industrial scientific community in coated magnetic nanoparticles due to their broad range of potential applications (e.g., magnetic recording,[1] magnetic sensors,[2] toners,[3] imaging reagents,[4] and magnetic carriers), particularly for biomedical applications.[5−7] The magnetic behavior of these systems has been found to be particularly dependent on their crystalline character and on their size and size distribution. Coated iron nanoparticles are of special interest since iron has the highest magnetic moment among the ferromagnetic transition metals and is easily oxidized. Air-stable iron particles have been prepared by different methods (e.g., carbon arc, flowing gas plasma, laser-induced pyrolysis, mechanosynthesis, thermal carbonization, and ultrasound).[8−16] The present paper describes a new method to prepare air-stable iron nanocrystalline nanoparticles, based on a single-step swelling of polystyrene (PS) template microspheres with $Fe(CO)_5$, followed by thermal decomposition of the swollen template particles in an inert atmosphere.

Ugelstad and co-workers invented a useful multistep swelling method of uniform template particles with various acrylate monomers and initiators for the production of different uniform-sized particles of controlled desired properties.[17−18] This basic swelling process was then significantly elaborated by Cheng et al.[19] and Hosoya and co-workers.[20−23] The first step of the multistep swelling method is associated with the activation of template uniform particles (usually PS) formed by either emulsion or dispersion polymerization processes. The activation of the template particles is accomplished by swelling the particles dispersed in aqueous phase with emulsion droplets of a swelling solvent (e.g., dibutyl phthalate, methylene chloride, toluene, or 1-chlorodecane).[20,26−27] The first swelling step stimulates the

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swelling of the template particles in the subsequent steps. When the activation swelling step is completed, the second swelling step takes place by introducing the slightly enlarged template particles to monomers, initiator, and porogens. This can be done in one step or through sequential addition of each component. The initiator can be added in the first swelling step or in the second one. Polymerization of the monomers within the uniformly swollen particles can then be induced by increasing the temperature. An alternative swelling method was invented by Okubo et al. and was named "the dynamic swelling method".[24−25] According to this method, uniform PS template particles can be swollen enormously, while maintaining their uniformity, by slow, continuous, dropwise addition of water into an ethanol/water medium containing the template particles and hydrophobic monomer/s and initiator (e.g., styrene and benzoyl peroxide [BP]). Polymerization can then be performed, as previously described, by increasing the temperature. According to the dynamic swelling method, there is no need to use a swelling solvent, and the process can be performed in a one-step procedure. A new method for preparing particles of narrow size distribution and controlled properties (i.e., surface area) based on a single-step swelling process of template uniform microspheres was recently published by Margel et al.[26−28] According to this process, the swelling of the template particles with the initiator and monomer/s via a swelling solvent is accomplished in a single step, in contrast to the multiswelling steps where the swelling with these reagents is accomplished in two or more steps. The present article is different from the previous ones in that the single-step swelling process was used for entrapping $Fe(CO)_5$ rather than acrylate monomers within the template PS microspheres. The $Fe(CO)_5$ swollen particles were then used for the formation of air-stable Fe nanocrystalline particles by thermal decomposition of the swollen template particles at 600 °C in an inert atmosphere.

Experimental Procedures

Materials. The following analytical-grade chemicals were purchased from Aldrich and were used without further purification: $Fe(CO)_5$ (>99%), BP (98%), sodium dodecyl sulfate (SDS), poly(vinylpyrrolidone) (PVP, mw 360 000), ethanol (HPLC), 2-methoxy ethanol (HPLC), and methylene chloride (HPLC). Styrene (Aldrich 99%) was passed through activated alumina (ICN) to remove inhibitors before use. Water was purified by passing deionized water through Elgastat Spectrum reverse osmosis system (Elga Ltd., High Wycombe, UK).

Synthesis of PS Template Microspheres. PS template microspheres of narrow size distribution were prepared according to a procedure similar to that described in the literature.[22−23] Briefly, these microspheres were synthesized in a three-neck round-bottomed flask equipped with a condenser and immersed in a constant temperature silicone oil bath at a preset temperature. In a typical experiment, PS microspheres with an average diameter of 2.4 ± 0.2 μm were formed by introducing into the reaction flask (1 L) a solution containing PVP (3.75 g, 1.5% w/v of total solution) dissolved in a mixture of ethanol (150 mL) and 2-methoxy ethanol (62.5 mL). The temperature of the mechanically stirred solution (200 rpm) was then preset to 73 °C. Nitrogen was bubbled through the solution for ca. 15 min to exclude air, and then a blanket of nitrogen was maintained over the solution during the polymerization period. A deairated solution containing the initiator BP (1.5 g, 0.6% w/v of total solution) and styrene (37.5 mL, 16% w/v of total solution) was then added to the reaction flask. The polymerization reaction continued for 24 h and was then stopped by cooling to room temperature. The microspheres formed were washed by extensive centrifugation cycles with ethanol and then with water. The particles were then dried by lyophilization.

Single-Step Swelling of PS Template Microspheres with $Fe(CO)_5$. In a typical experiment, PS template microspheres of 2.4 ± 0.2 μm were swollen with a mixture of methylene chloride (1.3 mL) and $Fe(CO)_5$ (0.3 mL) up to 4.9 ± 0.3 μm, by adding to a 20 mL vial, 10 mL of SDS aqueous solution [1.5% (w/v)] and 1.6 mL of the swelling solvent [e.g., a mixture of methylene chloride and $Fe(CO)_5$]. Emulsion droplets of the swelling solvent were then formed by sonication (Sonics and materials, model VCX-750, Ti-horn 20 kHz) of the former mixture at 4 °C for 30 s. A total of 3.5 mL of an aqueous suspension of the PS template microspheres (7% w/v) was then added to the stirred methylene chloride emulsion. After the swelling was completed, and the mixture did not contain any small emulsion droplets of the swelling solvent, as verified by optical microscopy, the diameter of the swollen microspheres was measured. PS swollen microspheres of various diameters were prepared by changing various parameters of the swelling process (e.g., volume and type [methylene chloride, $Fe(CO)_5$, and mixtures of different volume ratios between methylene chloride and $Fe(CO)_5$] of the swelling solvents).

Hemispherical particles were formed by evaporating the methylene chloride from the swollen template particles containing a volume ratio of [methylene chloride]/[$Fe(CO)_5$] < 1. This was performed by purging nitrogen at room temperature for 3 h through the shaken open vial containing the swollen particle aqueous mixture.

Formation of Air-Stable Fe Nanoparticles. The swollen PS particles containing $Fe(CO)_5$, after removal of methylene chloride, were washed from excess reagents by several centrifugation cycles with water and then water-dried by nitrogen flow for several hours. Air-stable Fe nanoparticles were then formed by heating the water-dried $Fe(CO)_5$ swollen PS particles in a quartz tube at 600 °C under flowing Ar gas for 3 h.

Characterization of the Particles. Optical microscope pictures were obtained with an Olympus microscope, model BX51. The particles' average size and size distribution were determined by measuring the diameters of more than 100 particles on optical micrographs with the image analysis software AnalySIS Auto (Soft Imaging System GmbH, Germany). Low-resolution TEM pictures were obtained with a JEOL-JEM100SX electron microscope with a 80−100 kV accelerating voltage. High-resolution TEM (HRTEM) images were obtained by employing a JEOL-3010 device with a 300 kV accelerating voltage. Samples for TEM and HRTEM were prepared by placing a drop of the diluted sample on a 400-mesh carbon-coated copper grid. Fourier transform infrared (FTIR) analysis was performed with a Bomem FTIR spectrophotometer, model MB100, Hartman and Braun. The analysis was performed with 13 mm KBr pellets that contained 2 mg of the detected material and 198 mg of KBr. The pellets were scanned over 200 scans at 4 cm^{-1} resolution. Elemental analysis of the various particles was performed using an elemental analysis instrument, model EA1110, CE Instruments, Thermoquast. Surface elemental analysis was

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obtained by X-ray photoelectron spectroscopy (XPS), model AXIS-HS, Kratos Analytical, England, using Al Kα lines, at 10^{-9} Torr, with a take-off angle of 90°. The reported values of both XPS and elemental analysis are an average of measurements performed on at least three samples of each of the tested particles and have a maximum error of about 10 and 2%, respectively. Powder X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer (model D8 Advance, Bruker AXS) with Cu Kα radiation. Thermogravimetric analysis (TGA) was performed with a TC15 system equipped with TGA, model TG-50, Mettler Toledo. The analysis was performed with approximately 10 mg of dried samples in a dynamic nitrogen atmosphere (200 mL/min) with a heating rate of 10 °C/min.

Magnetic measurements were performed on a sample of Fe−FeC that was introduced into a plastic capsule. Measurements at room temperature were performed using an Oxford Instrument vibrating sample magnetometer (VSM). Magnetization was measured as a function of the external field being swept up and down ($-16\,000$ Oe $< H_{\text{applied}} <$ 16 000 Oe, in steps of 200 Oe).

Results and Discussion

Figure 1 shows light microscope pictures that allow one to compare the swelling ability of the template PS particles by methylene chloride and $Fe(CO)_5$. The PS microspheres before swelling have a size and size distribution of 2.4 ± 0.2 μm (Figure 1A). As a consequence of their swelling with 2 mL of methylene chloride, their size distribution was retained, while their diameter increased from 2.4 ± 0.2 to 5.3 ± 0.3 μm, ca. 220% increase in the average diameter (Figure 1B). On the other hand, a similar swelling process, substituting the 2 mL of methylene chloride for 2 mL of $Fe(CO)_5$ (Figure 1C), resulted in nonuniform swelling of the template particles (i.e., the size and size distribution changed from 2.4 ± 0.2 to 7 ± 5.0 μm). Approximately 74% of the template particles was hardly swollen by $Fe(CO)_5$, while ca. 26% of these particles was swollen by $Fe(CO)_5$ to a larger extent than by methylene chloride (e.g., the maximal average diameter of the swollen particles by 2.0 mL of methylene chloride or $Fe(CO)_5$ was 5.3 and 7.0 μm, respectively). These results may indicate that methylene chloride is a good swelling solvent for PS particles, while $Fe(CO)_5$ is rather poor. Since the goal of these studies was to fill the swollen PS particles with $Fe(CO)_5$ while retaining their narrow size distribution, trials to use mixtures of methylene chloride and $Fe(CO)_5$ as a swelling solvent, followed by evaporation of methylene chloride from the swollen particles, have been performed. Figure 2 demonstrates the influence of different volumes of the swelling solvents on the diameter and size distribution of the template PS particles. For each volume, five types of swelling solvents have been tested: methylene chloride and $Fe(CO)_5$ alone and three mixtures of these solvents: [methylene chloride]/[$Fe(CO)_5$] = 3:1, 1:1, and 1:3 (v/v). Figure 2 illustrates that increasing the volume of all types of the swelling solvents resulted, as expected, in an increased average diameter of the swollen particles. For example, in the absence of methylene chloride, and in the presence of 1, 2, 3, and 4 mL of methylene chloride, the diameter of the swollen particles increased from 2.4 ± 0.2 μm to 4.7 ± 0.2, 5.3 ± 0.2, 5.5 ± 0.2, and 6.7 ± 0.3 μm, respectively. A further increase in the volume of methylene chloride significantly damaged the uniformity of the swollen particles. The addition of 7 mL of methylene chloride resulted in the dissolution of the PS particles by methylene chloride dispersed in the aqueous phase. Figure 2 also shows that increasing the volume ratio [$Fe(CO)_5$]/[methylene chloride] resulted in a significant increase in the size distribution of the swollen particles. For example, in the absence and in the presence of 3 mL of the different swelling solvents: methylene chloride alone, [$Fe(CO)_5$]/[methylene chloride] = 1:3 and 3:1, and $Fe(CO)_5$ alone, the size distribution of the swollen particles increased from 2.4 ± 0.2 μm to 5.5 ± 0.2, 6.4 ± 0.4, 7.4 ± 6.8, and 10.6 ± 7 μm, respectively. Kinetics studies of the swelling of the PS template microspheres by

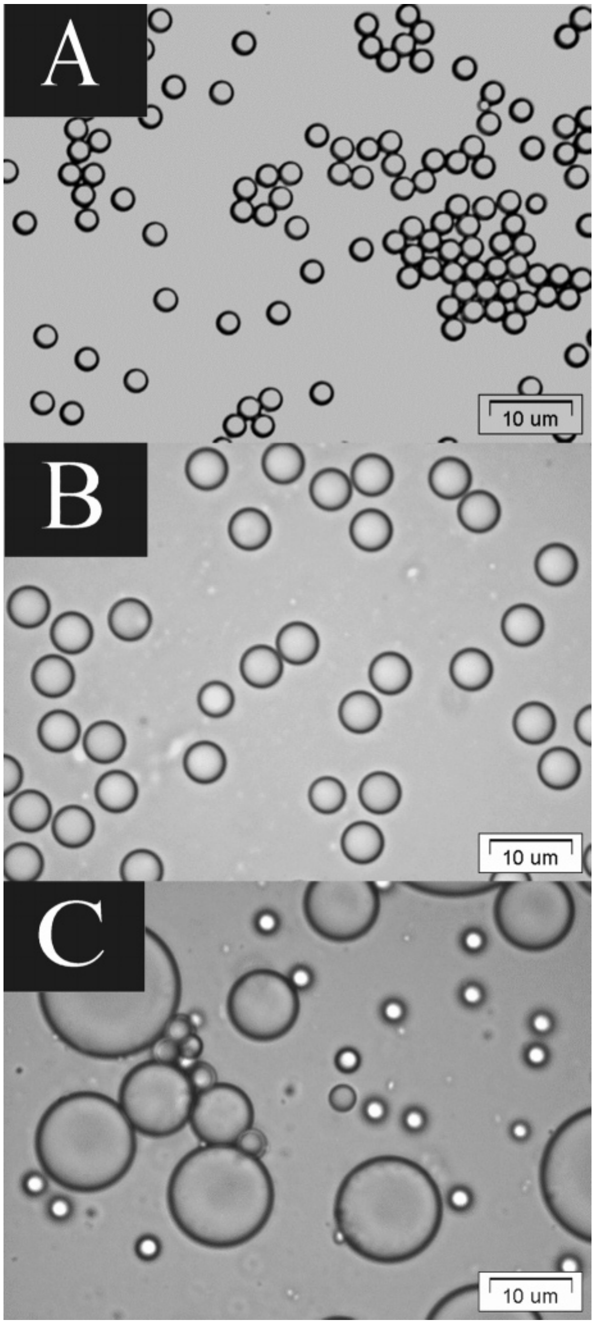

Figure 1. Light microscopy pictures of PS template microspheres before (A) and after swelling with 2 mL of methylene chloride (B) or $Fe(CO)_5$ (C). The swelling process was accomplished according to the experimental part with 2 mL each of the swelling solvents, omitting the methylene chloride evaporation step.

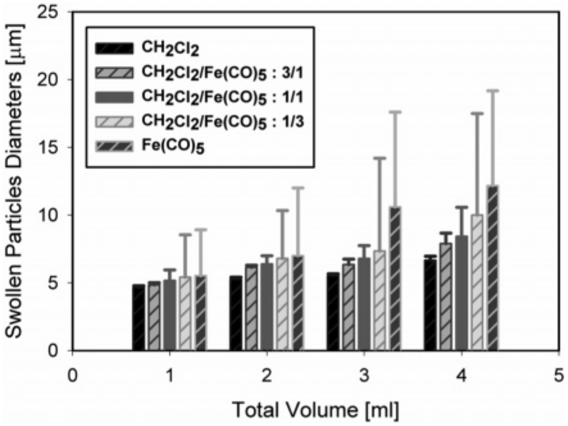

Figure 2. Influence of the swelling solvents volume on the diameter and size distribution of the template PS particles. Five types of swelling solvents have been tested: methylene chloride and $Fe(CO)_5$ alone and three mixtures of these solvents: [methylene chloride]/[$Fe(CO)_5$] = 3:1, 1:1, and 1:3 (v/v). The swelling process was accomplished according to the experimental part with 1, 2, 3, and 4 mL each of the swelling solvents, omitting the methylene chloride evaporation step.

2 mL of the different swelling solvents indicated that under the experimental conditions, the swelling process is completed within ca. 20 min. It should also be noted, as shown in Figure 2, that the increase in the diameter (and volume) of the swollen particles was not linearly proportional to the volume of the added swelling solvent. For example, the addition of 1.0 or 4.0 mL of methylene chloride led to an increase in the average diameter of the template particles of 195 and 278%, respectively. The first 1 mL of methylene chloride increased the diameter of the PS particles significantly more than the additional 3 mL. This nonlinear behavior is probably due to the packing arrangement of the PS chains within the template particles. The degree of entanglement of these chains determines the size (and volume) of the particles. The swelling solvents swell the template particles by penetrating within the PS chains of the particles, decreasing their degree of entanglement, and thereby increasing the counter length of the PS polymeric chains. As a consequence, the particles are less compact and their size and volume increase according to their swelling degree.

Methylene chloride was evaporated from the PS swollen particles containing both methylene chloride and $Fe(CO)_5$ by purging nitrogen through the shaken open vial containing the swollen particle aqueous mixture. Figure 3 shows light microscope pictures of the PS template microspheres (A) swollen with different volumes of $Fe(CO)_5$: 0.3 mL (B), 0.9 mL (C), and 1.2 mL (D). The swelling process was accomplished with 1.6 mL of swelling solvents composed of different mixtures of methylene chloride and $Fe(CO)_5$), followed by the evaporation of methylene chloride from the swollen particles. Figure 3 demonstrates, as expected, an increase in the diameter of the PS swollen particles with an increasing volume of the encapsulated $Fe(CO)_5$. Figure 3 also indicates that PS particles with biphase hemispherical morphology consist of PS and $Fe(CO)_5$ phases. This figure clearly demonstrates the relative increase in the $Fe(CO)_5$ phase with an increasing volume of the encapsulated $Fe(CO)_5$. This biphase hemispherical shape is similar to that recently reported for PS/poly(butyl methacrylate) composite

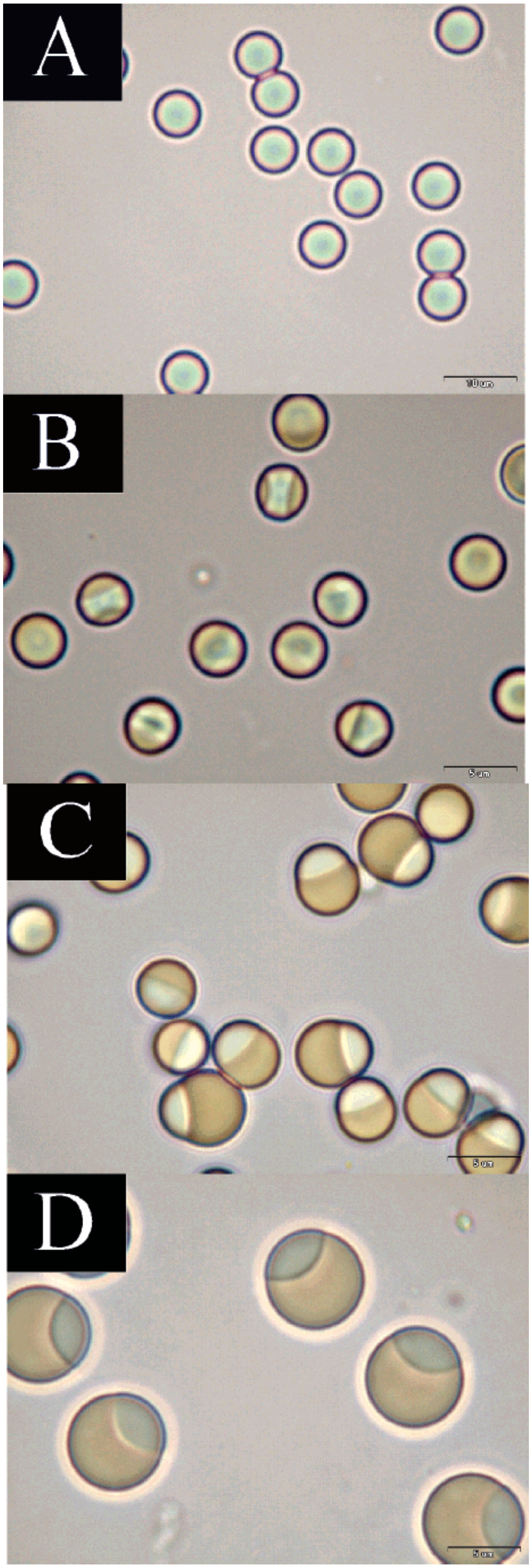

Figure 3. Light microscope pictures of the PS template microspheres (A) swollen with different volumes of $Fe(CO)_5$: 0.3 mL (B), 0.9 mL (C), and 1.2 mL (D). The swelling process was accomplished according to the experimental part with 1.6 mL of the swelling solvents (different mixtures of methylene chloride and $Fe(CO)_5$), followed by evaporation of methylene chloride from the swollen particles.

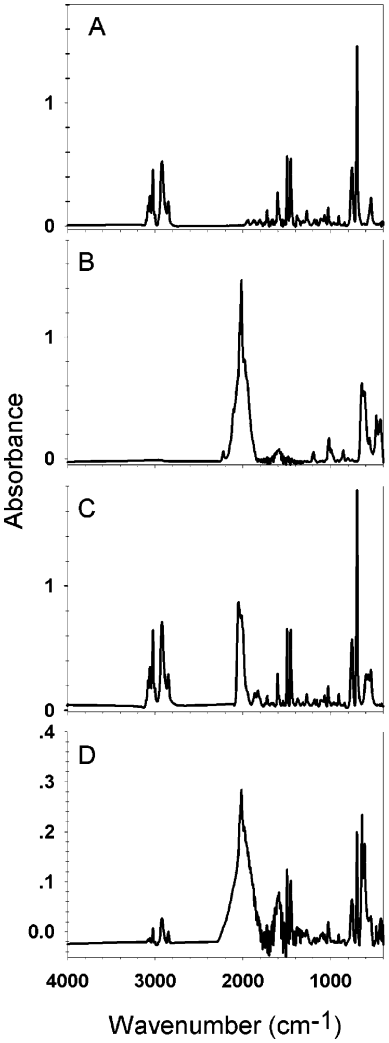

Figure 4. FTIR spectra of the template PS microspheres (A), $Fe(CO)_5$ (B), and swollen PS template microspheres containing 0.3 mL (C) and 0.9 mL (D) of $Fe(CO)_5$.

particles.[28] It should, however, be noted that biphase hemispherical particles were also observed by light microscopy when the swelling of the PS template particles was accomplished with mixtures of methylene chloride and $Fe(CO)_5$, where the volume ratio of [methylene chloride]/[$Fe(CO)_5$] < 1.0. On the other hand, when this volume ratio > 1.0, single-phase spherical particles were observed, and transition to biphase hemispherical particles was observed only after evaporation of the methylene chloride from the swollen particles. Methylene chloride is an excellent swelling solvent for PS particles, while $Fe(CO)_5$ is a poor one. Therefore, the swelling ability of mixtures of methylene chloride and $Fe(CO)_5$ decreases as the volume ratio between these two solvents decreases. We assume that during the swelling process, methylene chloride carries $Fe(CO)_5$ into the PS particles. However, upon removal, or decreasing the relative concentration of methylene chloride, the $Fe(CO)_5$ phase separates from the PS phase.

Figure 4 depicts the FTIR spectra of the PS template microspheres (A), $Fe(CO)_5$ (B), and swollen PS template particles containing two different volumes of $Fe(CO)_5$: 0.3 mL (C) and 0.9 mL (D). Figure 4A reveals a typical IR spectrum of PS: 1492 and 3000−3100 cm^{-1} correspond to the aromatic CH stretching bands, 2849 and 2922 cm^{-1} correspond to the CH_2 stretching bands, and 700 cm^{-1} corresponds to the vibrational band of C−C. Figure 4B reveals an IR spectrum of $Fe(CO)_5$: 2100 cm^{-1} corresponds to the CO stretching band and 550 cm^{-1} corresponds to Fe−C stretching band. Figure 4C shows the IR spectrum of the swollen PS particles containing 0.3 mL of $Fe(CO)_5$. As expected, this spectrum is composed of peaks belonging both to PS (700, 1492, and 3000 cm^{-1}, etc.) and to $Fe(CO)_5$ (2100 and 550 cm^{-1}, etc.). The presence of 3 times more of $Fe(CO)_5$ within the swollen PS particles is illustrated in Figure 4D by the significantly increased absorbance peaks of the CO groups at 2100 cm^{-1} and Fe−C at 550 cm^{-1}.

Air-stable Fe nanoparticles were formed by heating the dried $Fe(CO)_5$ swollen PS particles in a quartz tube at 600 °C under Ar atmosphere, according to the experimental conditions. Typical microscopy pictures of the Fe/C composite particles are shown in Figure 5.

A light microscopy image of the Fe/C composite particles is shown in Figure 5A, indicating some chains of particles, presumably oriented in a magnetic field. When prepared and fixed for electron microscopy, particles can be seen in their true size range as shown in Figure 5B,C. A low-resolution TEM image is presented in Figure 5B. It can be assumed that iron nanoparticles formed from $Fe(CO)_5$ are included in carbon formed from the PS matrix (the bright region is carbon and the dark region is iron). The high-resolution TEM image, depicted in Figure 5C, provides further evidence for the identification of the product as Fe coated by carbon. The image illustrates the perfect arrangement of the atomic layers of bcc Fe, the Fe_3C (111) plane, and the carbon shell with a thickness about 4 nm. The d spacing of bcc Fe and the Fe_3C (111) plane are very close: 0.287 and 0.302 nm, respectively. Figure 5C demonstrates d spacing of 0.292−0.294 nm in the inner core of the particle and 0.298−0.3 nm in the outer part of the core (close to the carbon shell). Because of the close values of the d spacing of bcc Fe and the Fe_3C (111) plane, it is quite difficult to distinguish between these two phases. Figure 5 shows that the formed Fe/C composite particles possess broad size distribution ranging approximately from 10 to 600 nm. These results are quite disappointing since before burning off, the $Fe(CO)_5$ swollen particles had very narrow size distribution (approximately 5%). We assume that the main reason for this significant change in size distribution and shape is the noncrosslinked character of the PS template particles, which probably melted during the heating process, before the pyrolysis.

The X-ray diffraction (XRD) for the Fe/C particles is shown in Figure 6. The pattern was dominated by bcc Fe as shown by $2\theta = 44.8$ and $2\theta = 65.2$. The smaller peaks between $2\theta = 43$ to $2\theta = 46$ match Fe_3C.

The magnetization curve presented in Figure 7 shows that the Fe/C particle exhibits ferromagnetic behavior. Saturation magnetization is (M_S) = 75 emu g^{-1}, remanent magnetization is (M_R) = 13.5 emu g^{-1}, and coercivity is (H_C) = 250 Oe.

XPS is a common tool for studying the elemental surface composition (except for hydrogen) of the Fe/C composite particles.[29−30] The sampling depth of XPS is limited by the effective mean free path of electrons escaping from the

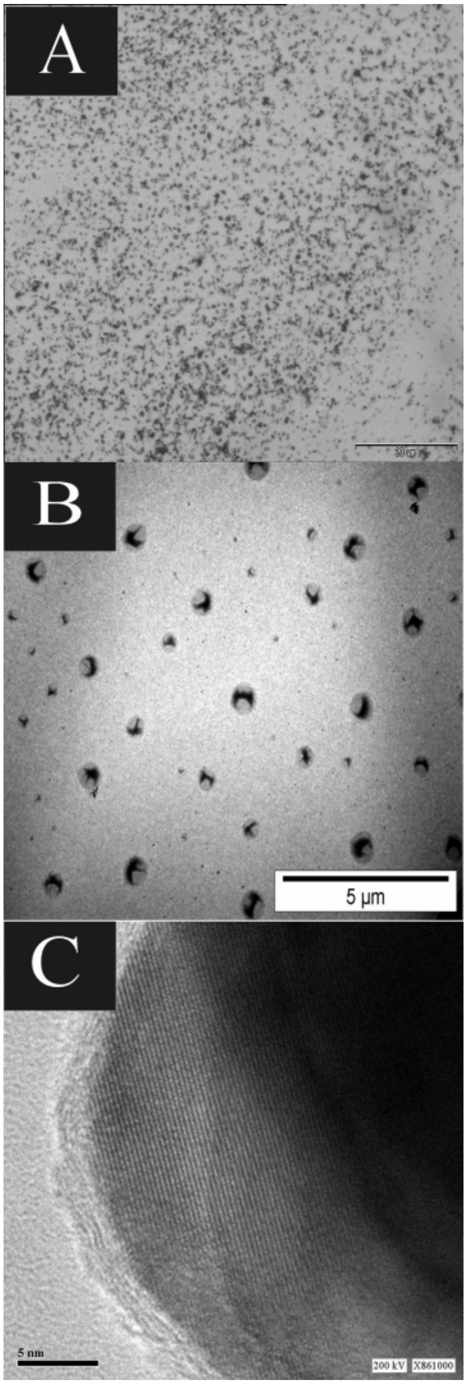

Figure 5. Light microscopy picture (scale bar 20 μm) (A), low-resolution TEM (B), and HRTEM (C) of the Fe/C nanoparticles. Fe/C nanoparticles were formed according to the Experimental Procedures by swelling the template PS microspheres with swelling solvent emulsion droplets composed of 0.7 mL of methylene chloride and 0.9 mL of $Fe(CO)_5$.

surface. XPS survey spectrum shows an intense carbon (C_{1s}) peak at ca. 286, oxygen (O_{1s}) at ca. 532 eV, and iron (Fe_{2p}) at ca. 710. The integration of these peaks indicates the atomic % surface fraction of Fe/C particles that contains 89.9% C, 9.1% O, and 1% Fe.

Elemental analysis of the Fe/C particles confirms that the particles contain 48.8 atom % C, 0.8 atom % H, 3.1 atom % O, and 47.3 atom % Fe. The relative small amount of Fe (47.3%) in the particle explains the low saturation magnetization value of these Fe/C particles.

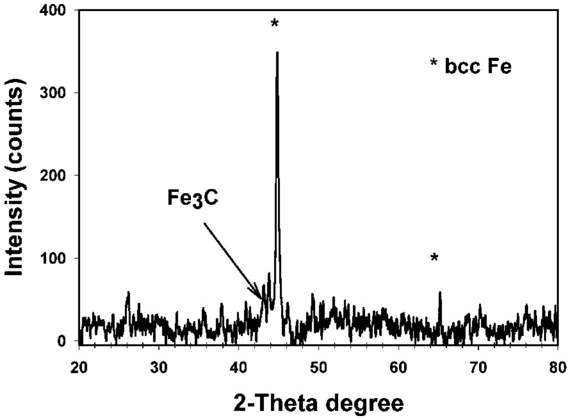

Figure 6. XRD pattern of the Fe/C nanoparticles. Fe/C nanoparticles were formed according to the Experimental Procedures by swelling the template PS microspheres with swelling solvent emulsion droplets composed of 0.7 mL of methylene chloride and 0.9 mL of $Fe(CO)_5$.

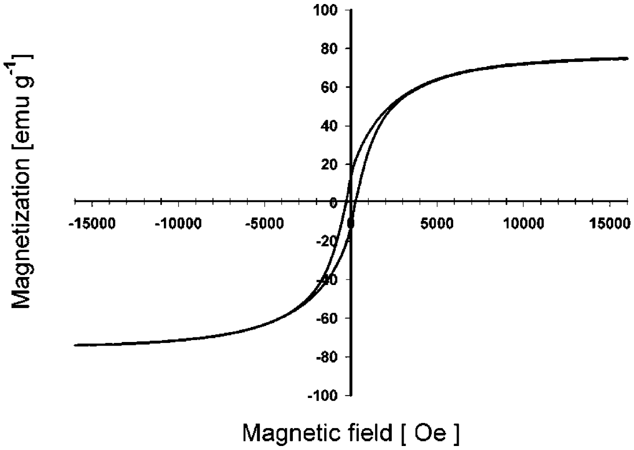

Figure 7. Magnetization curve for the Fe/C nanoparticles. Fe/C nanoparticles were formed according to the Experimental Procedures by swelling the template PS microspheres with swelling solvent emulsion droplets composed of 0.7 mL of methylene chloride and 0.9 mL of $Fe(CO)_5$.

TGA measurements have been performed to study the stability of annealed Fe/C particles (600 °C for 3 h) in air atmosphere. Figure 8 shows that the annealed sample Fe/C has good stability against oxidation below 300 °C, due to the formation of a carbon protective shell on the surface of the alloy nanoparticles during the annealing process. The loss of weight 400 °C is related to the burning of the carbon shell.

Conclusion

This paper describes a new method for preparing air-stable Fe crystalline magnetic nanoparticles. The first step consists of encapsulation of the precursor $Fe(CO)_5$ within uniform PS template microspheres by a single-step swelling process. Hemispherical biphase microspheres were observed by light microscopy after evaporation of methylene chloride from the swollen template particles containing both methylene chloride and $Fe(CO)_5$. Annealing of the as-prepared $Fe(CO)_5$ swollen PS particles in argon at 600 °C leads to the growth of

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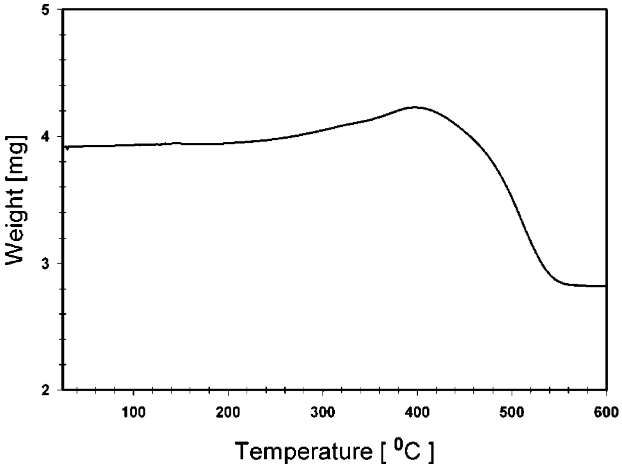

Figure 8. TGA curve for the Fe/C nanoparticles under air atmosphere. Fe/C nanoparticles were formed according to the Experimental Procedures by swelling the template PS microspheres with swelling solvent emulsion droplets composed of 0.7 mL of methylene chloride and 0.9 mL of Fe(CO)$_5$.

nonuniform air-stable iron nanocrystalline particles coated by a carbon and iron carbide protective layer. These air-stable nanocrystalline bcc Fe particles exhibit ferromagnetic behavior with a saturation magnetization of 75 emu g^{-1} and a large hysteresis with coercivity of 250 Oe. Studies concerning the precise composition of each phase of the hemispherical particles and the influence of various parameters (e.g., size and type of the template particles, type and concentration of the swelling solvent, annealing temperature, etc.) on the swollen template particles and the Fe/C composite nanoparticles are ongoing in our laboratory. Special care is taken to produce air-stable Fe nanoparticles of narrow size distribution. Similar studies concerning the preparation of other air-stable metal particles (e.g., Co and Ni) based on a single-step swelling process of the appropriate metal carbonyl complexes are also ongoing in our laboratory.

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