

Commercial edible oils as new solvents for ultrasonic synthesis of nanoparticles: the preparation of air stable nanocrystalline iron particles

Yury Kolytyn, Nina Perkas and Aharon Gedanken*

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel.
E-mail: gedanken@mail.biu.ac.il; Fax: +972 3 5351250; Tel: +972 3 5358315

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A simple sonochemical method for the preparation of air-stable iron nanoparticles has been developed employing commercial edible oils as solvents. Upon annealing of the as-prepared material in argon, an air-stable ferromagnetic nanocrystalline material with a saturation magnetization comparable to that of bcc Fe is obtained.

The synthesis of magnetic iron nanoparticles is of interest to research workers because of its application in magnetic and electronic devices,^{1–3} medicine,⁴ and new technologies such as environmental remediation,⁵ *etc.* Unfortunately, the high air sensitivity is the main problem in the technological application of this material, and for that reason many different methods have been developed to prevent iron nanoparticles from oxidation. They include: embedding the nanoparticles in polymer matrices,⁶ passivating them with an oxide shell,² the carbonization of iron powder with methane to obtain a different surface content of iron carbide in a carbon matrix,⁷ and high temperature annealing mixtures of hematite and carbon powders,¹ *etc.* Recently, an effective synthetic method for highly magnetic air-stable iron–iron carbide nanocrystalline particles was reported using ultrasound irradiation of iron pentacarbonyl.^{8–10} The process was carried out in a diphenylmethane (DPHM) solution, which formed a polymeric product as the result of the sonochemical decomposition of DPHM coating the surface of the iron nanoparticles. Annealing the as-prepared material at 700 °C resulted in the formation of a protective shell consisting of a mixture of Fe₃C and C. This synthesis of nanocrystalline iron (particle size 20–100 nm) yielded a material with magnetic properties comparable to, or even higher than, those for bulk bcc Fe. The annealed iron nanopowder is stable in air (for at least four months). The drawbacks to this synthesis are the production of some toxic by-products during the sonochemical decomposition of diphenylmethane,¹¹ and the high cost of this solvent (about 70 dollars per kg). Recently, we have found a cheap and environmentally friendly process to replace DPHM; the use of edible vegetable oils.¹² In this article we present the results for two such solvents, rapeseed and corn oil, employed for the sonochemical preparation of air stable, highly magnetic iron nanopowders. The importance of using a nonvolatile solvent in sonochemical processes has been emphasized by many authors, and these edible vegetable oils answer this requirement.

The methods of sonochemical synthesis and the material characterization are described below.¹³ The XRD analysis showed that the black, as-prepared material, obtained by using the commercial food oils as solvents, was amorphous. After annealing under Ar at 750 °C, the color of the material changed to dark gray, and diffraction patterns of bcc Fe were the sole detected peaks for both solvents [Fig. 1].

The TEM studies demonstrated the different changes in

particle size after annealing of the samples prepared in the rapeseed and corn oils [Fig. 2].

The material prepared in the rapeseed oil revealed a drastic increase in particle size upon annealing. Changes in size from 20–30 nm for the as-prepared sample to 180–200 nm after annealing [Fig. 2(a,b)] were observed. On the other hand, for the products obtained using the corn oil as a solvent, only slight changes in size were observed upon heating the as-prepared

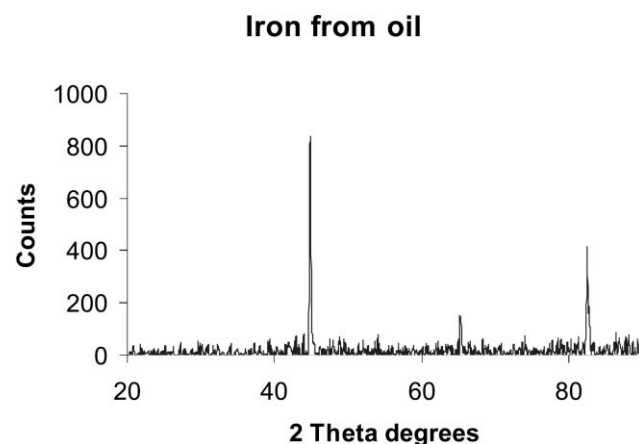


Fig. 1 XRD patterns of the annealed products.

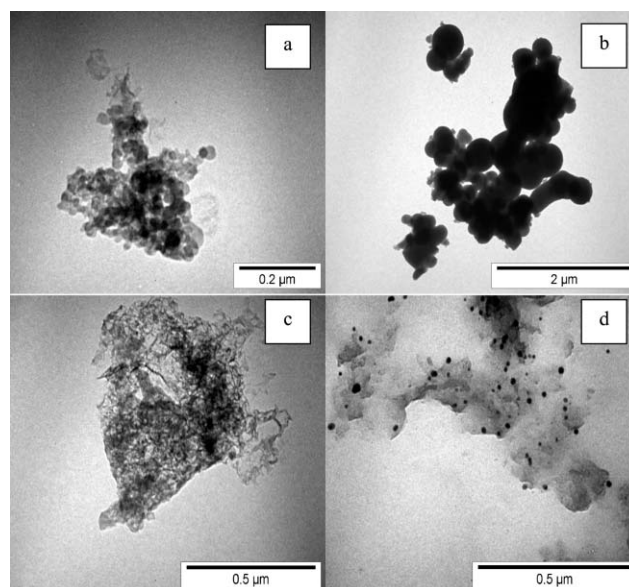


Fig. 2 TEM images of materials prepared in rapeseed oil (a, b) and in corn oil (c, d); (a, c) as-prepared samples, (b, d) annealed samples.

Table 1 Chemical analysis of iron prepared by sonication in commercial food oils

Solvent	Sample characterization	Content (wt.%)	
		C	H
Rapeseed oil	As-prepared	13.2	1.3
	Annealed 750 °C, Ar	5.8	—
Corn oil	As-prepared	19.5	2.1
	Annealed 750 °C, Ar	7.5	—

sample at 750 °C under Ar. Size changes from 10–15 nm to 20–25 nm [Fig. 2(c,d)] were measured. For both solvents, the as-prepared material represented nanoparticles of iron embedded in a matrix, which was a product of the sonochemical decomposition of the solvent [Fig. 2(a,c)]. During the annealing process the organic phase was partly removed and partly converted into another product, while the iron nanoparticles crystallized in a spherical form [Fig. 2(d)]. The organic residues were able to form a protective layer on the surface of the iron particles. The organic layer surrounding the iron obtained in the corn oil was more noticeable after the annealing, as observed in the TEM picture in [Fig. 2(d)]. The difference in the stabilization properties of rapeseed and corn oils can be explained in terms of their composition. The rapeseed oil is known to contain less polyunsaturated and more monounsaturated fats than any other commercial edible oil: about 2% polyunsaturated and 78% monounsaturated fats. In the corn oil the concentration of polyunsaturated oils is rather high: about 59% polyunsaturated and 24% monounsaturated fats. As usual, the polyunsaturated compounds are more inclined to undergo polymerization than the monounsaturated ones. Such polymerization could take place during the sonochemical reaction. The products of the polymerization process form the protection layer that keep iron nanoparticles stable to air oxidation. The higher concentration of polyunsaturated compounds makes the corn oil more effective for air-stabilization.

In Table 1 we present the result of the C, H analysis of the as-prepared and annealed products for both solvents. We believe that some hydrocarbons have evaporated from the surface upon annealing, which reduced the carbon content. The sample prepared in corn oil contained more carbon than the sample synthesized in the rapeseed oil. The larger amount of carbon perhaps caused the growth of smaller iron nanoparticles, arresting their growth.

The presence of an organic shell in the annealed samples was detected also by HR TEM (Fig. 3).

According to the HR TEM images, the iron nanoparticles

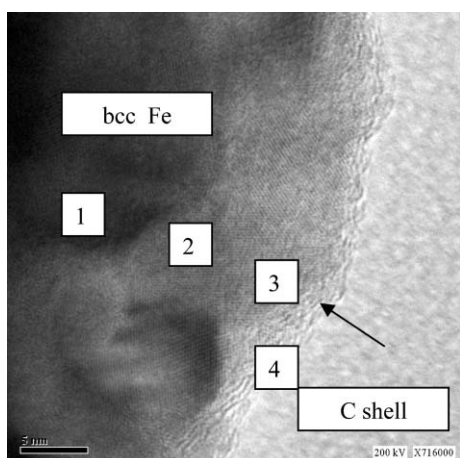


Fig. 3 An HR TEM image of an annealed iron sample prepared in corn oil.

Table 2 SAEDS analysis of an annealed iron sample prepared in the corn oil. The measured points are marked in Fig. 3

Spectrum location	Relative concentration (%)	
	C	Fe
Spectrum center 1	1.43	98.57
Spectrum center 2	2.41	97.59
Spectrum border 3	10.02	89.08
Spectrum border 4	22.83	77.17

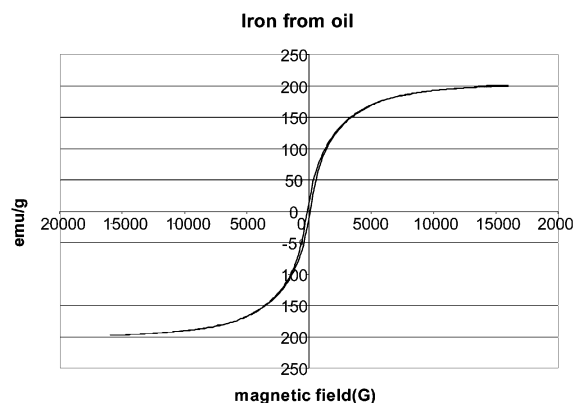


Fig. 4 A magnetization curve of annealed material prepared from the corn oil.

are coated with a non-crystalline layer with a thickness of about 2.5 nm. SAEDS analysis using a 25 nm beam determined a positive gradient of carbon concentration towards the edge of the particle (Table 2). This result shows that although we cannot detect a clear core-shell border separating the iron and the carbon, their concentrations change along the particle radius and a higher carbon content on the edge helps to protect the iron from oxidation.

To investigate the nature of the changes that the oil undergoes in the sonolysis process, and the way the protection layer is formed, FTIR and Raman studies are now in progress. Early results show that the strong carbonyl peak at 1730 cm^{-1} disappears during the sonication, and we could find some evidence that the unsaturated C–C bonds remain intact.

Both annealed materials demonstrated ferromagnetic properties, having a saturation magnetization (M_s) of about 200 emu g^{-1} . Taking into account the 7.5% carbon means that its M_s is very close to that of bulk bcc Fe (222 emu g^{-1}) [Fig. 4].

The magnetic properties of sonochemically prepared air-stable iron were highly stable and did not change during exposure to air for more than two months. Thus, we have reproduced the early sonochemical results obtained with an expensive solvent, DPhM, using much cheaper solvents such as edible vegetable oils.

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- 13 Commercial refined rapeseed and corn oils were used as purchased. Fe(CO)₅ (99.5% STREM) were used without additional purification. A 1 M solution of Fe(CO)₅ in oil was sonicated in the presence of argon by means of a “Sonics and Materials” ultrasonic device with a direct immersion titanium horn (working frequency 20 kHz, electric power of generator 600 W, irradiation surface area of the horn 1 cm²). The volume of the sonicated solution was 100 mL. Absorbed acoustic power, measured by the thermal probe method,¹⁴ was found to be equal to 0.45 W mL⁻¹. Sonolysis has been performed for 3 h. Temperature was kept at 0–10 °C during sonication by a “Julabo FT-901” cooler. All the sonochemical experiments were carried out under argon. The black solid product of sonication was removed by centrifugation, washed three times with pentane inside a N₂-filled glove box and dried under vacuum at room temperature. Annealing of the solids was performed at 750 °C for 3.5 h under an argon flow (99.996%) XRD was recorded on a Bruker AXS D8 Advance Powder X-ray Diffractometer (Cu–K_α radiation, λ = 0.15418 nm). The XRD of as-prepared material was measured in a tightly closed cell to avoid sample contact with air. Measurements of annealed samples were performed without special precautions. Low resolution TEM were obtained with a JEOL-JEM100SX electron microscope with 80–100 kV accelerating voltage. High resolution TEM (HR TEM) images were obtained by employing a JEOL-3010 device with 300 kV accelerating voltage. Magnetic measurements were performed at room temperature using a Quantum Design MPMS SQUID magnetometer. The error margin in weighing the samples for magnetic measurements did not exceed 0.5%. The saturation magnetization of commercial iron powder (d ≤ 5 μm) measured by the same procedure was found to be equal to 1.6 × 10⁶ A m⁻¹, which is very close to the M₀ value for bulk Fe (1.7 × 10⁶ A m⁻¹). Elemental analysis was carried out by an Eager 2000 CHN analyzer.
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