m- and *p*-substituted derivatives.[11] In our studies with the (phosphinite–oxazoline)Ir complexes **11** a strong dependence of the enantioselectivity on the hydrogen pressure was observed (Table 2). The highest enantioselectivities (up to 88% *ee*) were obtained at ambient pressure, which compares favorably with the best results reported to date.[3, 10, 11]

Table 2. Hydrogenation of 2-(4-methoxyphenyl)butene (**18**).[a]

Ligand	Cat. [mol%]	H_2 [bar]	*ee* [%][b]
2a	0.2	50	46 (*S*)
2a	0.2	10	59 (*S*)
2a	0.1	1	78 (*S*)
2e	0.2	50	53 (*S*)
2e	0.2	10	77 (*S*)
2e	0.1	1	88 (*S*)

[a] Conditions: see Equation (1); 100% conversion in all reactions; experimental procedures: see ref. [2]. [b] Determined by HPLC, see ref. [2].

The new phosphinite–oxazoline ligands **2** significantly expand the scope of enantioselective hydrogenation to classes of substrates for which no efficient catalysts were previously available. The modular construction and the facile synthesis of these ligands should make it possible to tailor their structure for other substrates and other metal-catalyzed reactions.

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[7] X-Ray crystal structure analysis of **11e**: crystallized from CH_2Cl_2/Et_2O/pentane, formula: $C_{53}H_{62}Cl_2F_6Ir_1N_1O_2P_2$, $M = 1184.15$ ($[C_{52}H_{60}IrN_1O_2P] \cdot PF_6 \cdot Cl_2CH_2$), orange crystal $0.08 \times 0.11 \times 0.19$ mm, $a = 14.7714(3)$, $b = 14.9908(2)$, $c = 23.7541(5)$ Å, $\alpha = 90.0°$, $V = 5260.0$ Å^3, $\rho_{calcd} = 1.495$ g cm^{-3}, $\mu = 2.762$ mm^{-1}, $F(000) = 2386.186$, $Z = 4$, orthorhombic, space group $P2_12_12_1$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, graphite monochromator), $T = 293$ K, Θ scan range $1.00 < \Theta < 27.00°$. 32529 reflections collected ($\pm h$, $\pm k$, $\pm l$), 11878 independent reflections, 9652 observed reflections [$I = 2\sigma(I)$], 633 refined parameters. $R = 0.0411$, $Rw = 0.0494$, max. residual electron density $-1.57(1.99)$ e$^-$ Å^{-3}, located near the metal center. Restraints were applied to parts of the *tert*-butyl group, which was split due to disorder. Hydrogen atoms were calculated and refined as riding atoms. Data collection was performed with a Kappa CCD diffractometer. Programs used: structure solution: SIR92 (A. Altomare, G. Cascarano, C. Giaccovazzo, A. Gualgliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435), structure refinement: CRYSTALS (D. J. Watkin, *Crystals, Issue 11*, Chemical Crystallography Laboratory, Oxford, **2001**), weighting scheme: Chebychev polynominal (J. R. Carruthers, D. J. Watkin, *Acta Crystallogr. Sect. A* **1979**, *35*, 698). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-167319. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). We thank M. Neuburger and Dr. P. Mukherjee (University of Basel) for solving the crystal structure.

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Synthesis of Highly Magnetic, Air-Stable Iron–Iron Carbide Nanocrystalline Particles by Using Power Ultrasound[**]

Sergei I. Nikitenko, Yuri Koltypin, Oleg Palchik,
Israel Felner, Xiao N. Xu, and Aharon Gedanken[*]

Coated magnetic nanoparticles may have important applications as materials for magnetic data storage, xerography, and magnetic resonance imaging.[1] A protective layer on the surface of the particles prevents interactions between closely

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[*] Prof. Dr. A. Gedanken, Dr. Yu. Koltypin, O. Palchik
Department of Chemistry, Bar-Ilan University
Ramat-Gan 52900 (Israel)
Fax: (+972)3-5351250
E-mail: gedanken@mail.biu.ac.il

Prof. Dr. I. Felner
Racah Institute of Physics, Hebrew University
Jerusalem (Israel)

Dr. S. I. Nikitenko
Institute of Physical Chemistry, RAS
Leninskii Pr.31, 117915 Moscow (Russia)

Dr. X. N. Xu
Department of Physics, Nanjing University
Nanjing 210093 (China)

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spaced magnetic bits and provides oxidation resistance.[2] Coated iron nanoparticles are of particular interest, since iron has the highest magnetic moment among the ferromagnetic transition metals. Many different processes for obtaining carbon-coated iron nanoparticles have been tested, such as carbon arc, flowing gas plasma, laser-induced pyrolysis, mechanosynthesis, and thermal carbonization.[3] Recently, iron nanoparticles coated with gold,[4a] phosphate,[4b] and silica[4c] were prepared by reverse-micelle reduction and sol–gel techniques. These processes yield unstable iron nanoparticles, and the saturation magnetization of materials thus prepared does not exceed 120 emu g^{-1}.

Uncoated iron nanoparticles have been prepared by using high-intensity ultrasound to decompose [Fe(CO)$_5$] in alkane solutions.[5] The chemical effect of ultrasound is related to acoustic cavitation, that is, the formation, pulsation, and implosive collapse of microbubbles in liquids or other media with elastic properties. The bubble collapse generates transient temperatures of several thousand Kelvin and local pressures of one hundred atmospheres.[6] Such drastic conditions lead to homolytic dissociation of the molecules within the cavitating bubbles.

Iron nanoparticles obtained sonochemically from alkane solutions are not stable in contact with air. To prepare coated iron nanoparticles we studied the sonochemical decomposition of [Fe(CO)$_5$] in diphenylmethane (DPhM), an aromatic solvent with physicochemical properties (m.p. 25 °C, b.p. 265 °C, vapor pressure 1 hPa at 77 °C)[7] that are suitable for sonochemistry. Recently, we revealed that sonolysis of neat DPhM forms a polymerlike solid product. We assumed that small amounts of this product generated in situ would coat the surface of iron nanoparticles formed simultaneously from [Fe(CO)$_5$].

During sonication, the color of the solution changed rapidly from yellow to black. After sonication, the solution was transferred under argon into an inert glove box. The pyrophoric solid product was then removed by centrifugation, washed with pentane, dried under vacuum, and kept in the glove box. The as-prepared material contained 17.6 wt% C and 1.5 wt% H. The reaction yield was 53 % with respect to iron.

The presence of a significant amount of carbon and hydrogen indicates that as-prepared material contains the sonolytic decomposition products of DPhM. The FTIR spectrum reveals the presence of absorption bands at 3060–3020, 2900–2850, and 1100–1000 cm^{-1}, which were assigned to C–H stretching vibrations of aromatic and aliphatic groups and *p*-substituted phenyl groups, respectively.[8] It can be assumed that the structure of the sonopolymer is close to that of polystyrene. Further studies on the polymeric product are in progress.

The XRD diagram (Figure 1 a) showed that the as-prepared material is X-ray amorphous. According to low-resolution transmission electron microscopy (TEM; Figure 2 a), it consists of nanosized globular agglomerates in which very small (ca. 5 nm) dense particles are dispersed. It can be assumed that iron nanoparticles formed from [Fe(CO)$_5$] are included in a globular matrix of DPhM sonication products. As-prepared material is superparamagnetic ($M = 88$ emu g^{-1} at 15 kG external field). This observation confirms that the iron particles are smaller than 10 nm.[5]

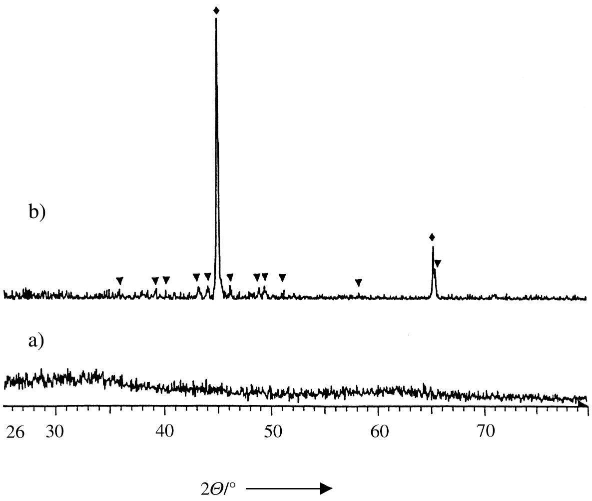

Figure 1. XRD diagrams of as-prepared (a) and annealed materials (b). ◆ bcc Fe, ▼ Fe_3C.

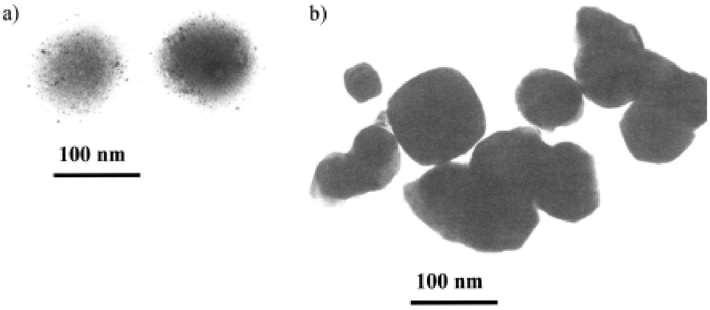

Figure 2. Low-resolution TEM images of as-prepared (a) and annealed materials (b).

An air-stable, dark gray magnetic powder is formed after annealing of the as-prepared pyrophoric sample at 700 °C in argon. The annealed material contains 5.6 wt% C and 0.08 wt% H. The low-resolution TEM image (Figure 2 b) showed that the annealed material consists of tetragonal and round nanoparticles with a particle size in the range of 20–100 nm. The Mössbauer spectrum (Figure 3) revealed the

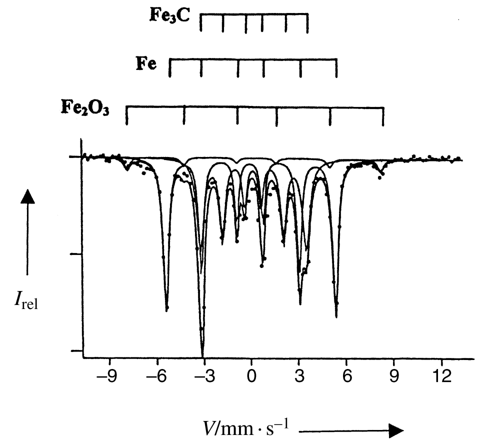

Figure 3. Mössbauer spectrum of annealed material at room temperature.

presence of bcc Fe, iron carbide Fe_3C (I.S. = 0.20 mm s^{-1} and $H_{eff} = (208 \pm 5)$ kOe), and small amounts of Fe_2O_3 (ca. 3 atom %). The ratio of Fe to Fe_3C is close to 4:1. The XRD patterns shown in Figure 1 b confirm the presence of bcc Fe and Fe_3C.

The annealed material is ferromagnetic, as follows from the magnetization curve presented in Figure 4. The saturation magnetization M_s and coercive force H_c are 212 emu g^{-1} and 40 Oe, respectively. The M_s value of the material is unexpectedly high and is close to that of bulk bcc Fe (222 emu g^{-1}[9]). Since the M_s value of bulk Fe_3C is small (14 emu g^{-1}[9]), the magnetization of the nanocomposite would be expected to be considerably lower than that of bcc Fe. Further studies are required to explain the high M_s value of the nanocomposite.

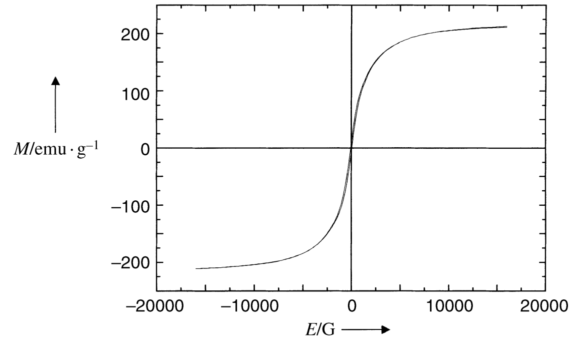

Figure 4. Magnetization curve of annealed material.

The nanocrystalline particles exhibit strong resistance to oxidation with oxygen. The Mössbauer spectrum, XRD data, and magnetic properties of the annealed material did not change after at least four months of contact with air (monthly measurements). The high stability of the nanoparticles could be related to the protective shell formed on the surface. The high-resolution TEM image (Figure 5) shows that iron particles are coated by a crystalline shell with a thickness of about 3 nm. The shell does not exhibit the layered structure typical of graphite. It can be assumed that the coat consists of Fe_3C or a mixture of Fe_3C and C.

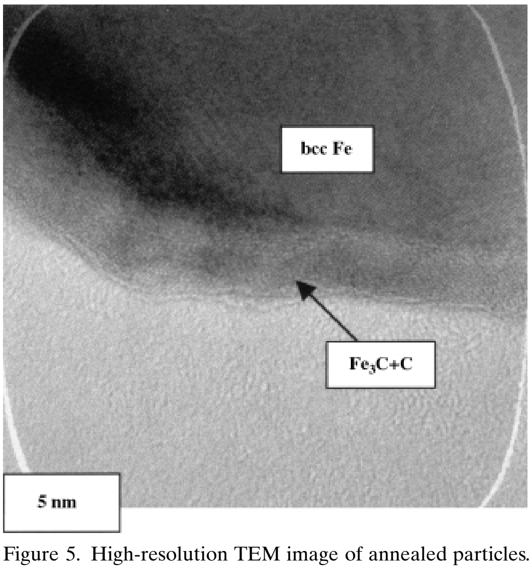

Figure 5. High-resolution TEM image of annealed particles.

Experimental Section

A 0.50 M solution of $[Fe(CO)_5]$ in DPhM was sonicated for 3 h in argon with a Sonics and Materials device ($f = 20$ kHz, $P_{el} = 600$ W, $S = 1$ cm^2, $P_{ac} = 0.45$ W cm^{-3}, measured by the thermal-probe method[6a]). The temperature was kept at 30 °C during sonication. The solids were annealed in an argon stream (99.996 %).

The XRD diagrams were recorded on a Bruker AXS D* Advanced Powder X-ray Diffractometer ($Cu_{K\alpha}$ radiation, $\lambda = 0.15418$ nm). Low-resolution TEM images were obtained with a JEOL-JEM100SX electron microscope with 80 kV accelerating voltage. High-resolution TEM images were obtained by employing a JEOL-3010 device with 300 kV accelerating voltage. Magnetization loops were measured with a Quantum Design MPMS SQUID magnetometer. Mössbauer spectra were recorded on a conventional constant-acceleration spectrometer (50 mCi ^{57}Co(Rh) source). FTIR spectra were recorded in KBr pellets on an Impact 410 Nicolet spectrometer. Elemental analysis was carried out in an Eager 200 CHN analyzer.

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