Photo-Switching

Reversible Photo-Switching of the Magnetization of Iron Oxide Nanoparticles at Room Temperature**

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Optically switchable magnetic materials are becoming increasingly important in the field of high-density information storage media.[1–3] We have been trying to prepare new types of magnets in which the magnetic properties can be controlled by photo-illumination. Our previous work has shown that cobalt–iron cyanide exhibits photoinduced magnetization effects due to an internal electron transfer.[4] However, practical examples of such photo-magnetic systems are limited in number[5] because the strategies that are necessary to achieve photoinduced switching in the solid state are yet to be clarified.

The use of organized organic assemblies to direct the formation of mesoscopic inorganic structures under mild conditions and the attempts to intercalate inorganic materials into functional organic molecules are also of topical interest.[6] We have focused our attention on composite materials as a novel strategy for realizing such photo-functional magnetic systems. These include the incorporation of organic photochromes into magnetic systems, for example, photo-controllable magnetic vesicles and Langmuir–Blodgett films containing Prussian blue (a ferromagnet at low temperature) and azobenzene.[7]

Although the examples described above show interesting photo-responsive phenomena, the results were only achieved at low temperature. It is evident that the temperature at which photo-switching occurs needs to be increased to room temperature in order to realize devices for practical applications. In the present work we have focused on iron oxide

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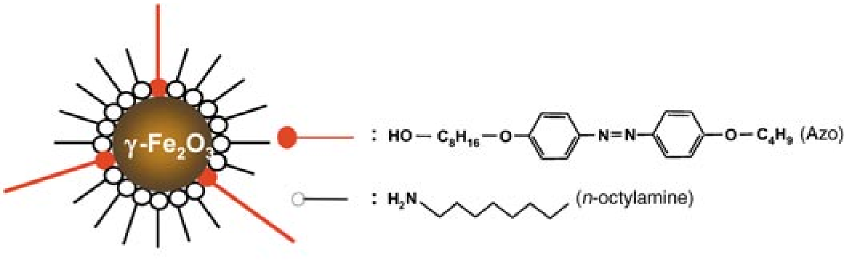
nanoparticles as magnetic materials that can function at room temperature. We recently reported our results for photo-responsive spiropyran vesicles containing iron oxide particles.[8] Although we were able to increase the magnetization values of these materials by carrying out photo-illumination at room temperature, the reversible photo-switching of their magnetic properties was far below our expectations. This was because the photoinduced increase in the magnetization was due to aggregation of the iron oxide particles, and we guess that it is difficult for aggregated particles to be separated.

To realize reversible photo-switching of magnetization at room temperature, we have now focused on a surface modification of nano-scale iron oxide particles and a combination of azobenzene-containing amphiphilic compounds and γ-Fe_2O_3 magnetic nanoparticles. Surface modification of nanoparticles is a useful technique for functionalizing the material properties.[9] For example, Rotello et al. reported that alkylamines in a monolayer could be displaced by harder Lewis base ligands such as alcohols.[9b]

Our strategy was to synthesize an appropriate azobenzene derivative for preparing the target photo-responsive nano-magnetic materials. In addition to encapsulating the surface of the γ-Fe_2O_3 nanoparticles with the azo moiety, we incorporated *n*-octylamine. The amphiphilic azo compound 8-[4-{4-butoxy-phenyl(azo)-phenoxy}octan-1-ol] (Azo) was synthesized according to literature methods[10] and then used to prepare the photo-responsive composite magnetic nanoparticles **1** (see the Experimental Section).



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The transmission electron microscope (TEM) image of **1** indicates the global presence of γ-Fe_2O_3 nanoparticles with almost homogeneous diameters (5 nm, Figure 1). We estimated the diameter of **1**, including the encapsulating agent, to be 9 nm by means of a dynamic light-scattering method.

The photoisomerization of **1** on the quartz substrates was monitored by UV/Vis absorption spectroscopy at room temperature (Figure 2a). Before illumination, **1** exhibited two absorption peaks at about $\lambda = 360$ nm and a weak band at about 480 nm, which correlate to the π–π^* and the n–π^* transitions, respectively, in the *trans* form of the azo compound. The spectra demonstrate that the π–π^* absorption at 360 nm remains invariant with respect to passivation of the nanoparticles, which proves that the azo components are protected during the synthesis of the γ-Fe_2O_3 nanoparticles. The absence of any shift in the absorption bands also indicates that there was no π stacking between the azo molecules (black line). After 5 min of UV illumination, the intensity of the band at 360 nm decreased and the intensity of the band at 480 nm increased, indicating the *trans*-to-*cis* photoisomerization (blue line). A photostationary state was obtained after 5 min of illumination, that is, the photoisomerization had saturated. Following subsequent illumination with visible light for 5 min, the reverse process, the *cis*-to-*trans* isomerization, proceeded to completion (red line). The *trans*-to-*cis* photoisomerization cycles were repeated several times by alternately illuminating with UV and visible light (Figure 2b).

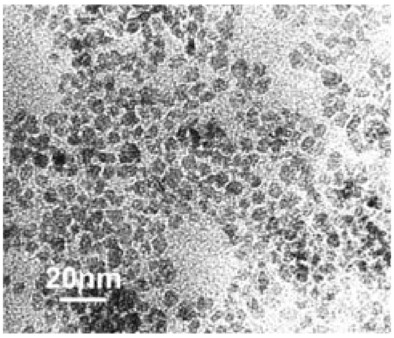

Figure 1. The TEM image of **1**.

Because the photoisomerization of azobenzene derivatives (in particular the *trans*-to-*cis* isomerization) is normally accompanied by an increase in molecular volume, the solid-state reaction is greatly inhibited due to the close packing of the chromophores. In practical terms, when the solid-state compound contains only Azo, it does not exhibit any photoisomerization behavior. In the case of **1**, sufficient free volume is guaranteed by the dilution of the azo moieties with *n*-octylamine to allow photoisomerization to take place. Another important point is the Lewis basicity of the capping ligands. *n*-Octylamine, which functions as an encapsulating agent for the γ-Fe_2O_3 nanoparticles,[11] contains an amino group, while Azo contains a harder Lewis basic hydroxy group. This means that Azo takes precedence over *n*-octylamine, resulting in the successful preparation of composite nanoparticles **1**.

The magnetic properties of **1** on a glass substrate were studied by SQUID measurements. The temperature dependence of the magnetization of **1** exhibits a cusp around 12 K in the zero field cooled (ZFC) susceptibility as well as a blocking temperature T_B determined from the branching of the ZFC and field-cooled (FC) data (Figure 3); thus, **1** exhibits superparamagnetic behavior. According to Néel's superparamagnetic model[12] at high temperatures, the magnetic moments of spin clusters are free to respond to an external field but freeze when the temperature is low enough. This freezing of the spin clusters over a wide temperature range can be visualized in terms of the progressive blocking of the cluster moments, depending on their size and magnetocrystalline anisotropy. Below the freezing temperature, the clusters freeze in random orientations dictated by the magnetocrystalline anisotropy.

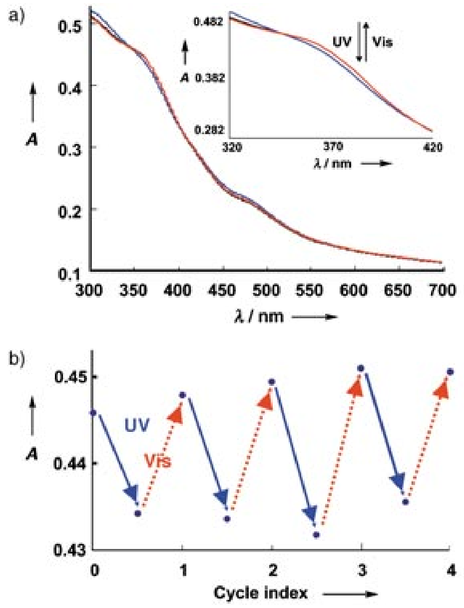

Figure 2. a) Changes in the optical absorption spectra due to photo-isomerization for **1** cast on quartz substrates at room temperature: before illumination (black line), after illumination with UV light for 5 min (blue line), after subsequent illumination with visible light for 5 min (red line). The inset shows a magnified region. b) Changes in the absorbance *A* at 360 nm by alternating illumination with UV and visible light (5 min each).

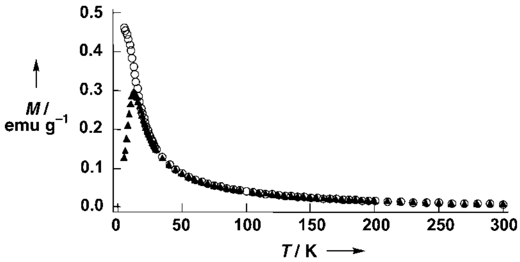

Figure 3. The plot of magnetization *M* versus temperature *T* for **1** at 5 G: ▲: zero-field cooled (ZFC), ○: field cooled (FC).

Since the magnetic moments of the spin clusters are frozen in a direction where magnetization occurs easily at low temperatures, this gives rise to a low value of magnetization. In contrast, the magnetization decreases (as T^{-1}) at high temperatures due to thermal fluctuations of the magnetic moments. Therefore, a peak occurs in ZFC susceptibility between these two regions.[13] The ^{57}Fe Mössbauer spectra for **1** at room temperature and at 8 K revealed the presence of γ-Fe_2O_3 nanoparticles (see the Supporting Information).

Based on these data, **1** exhibits typical superparamagnetic behavior of magnetic particles, with a particle size that is consistent with that observed by TEM (5 nm).[14] Generally speaking, iron oxide nanoparticles exhibit superparamagnetic behavior because of the infinitely small coercivity arising from the negligible energy barrier in the hysteresis of the magnetization loop of the particles.[12,15]

The magnetization curve of **1** was measured at 5 K (Figure 4a) in the field-cooled (FC) state. A small hysteresis loop with remanence (5.67 emu g^{-1}) and coercivity (300 G) was observed. Below T_B the superparamagnetic transition is blocked, that is, the magnetization cannot relax during the time frame of the measurement and therefore cannot appear on the plot of magnetization as a function of the magnetic field.

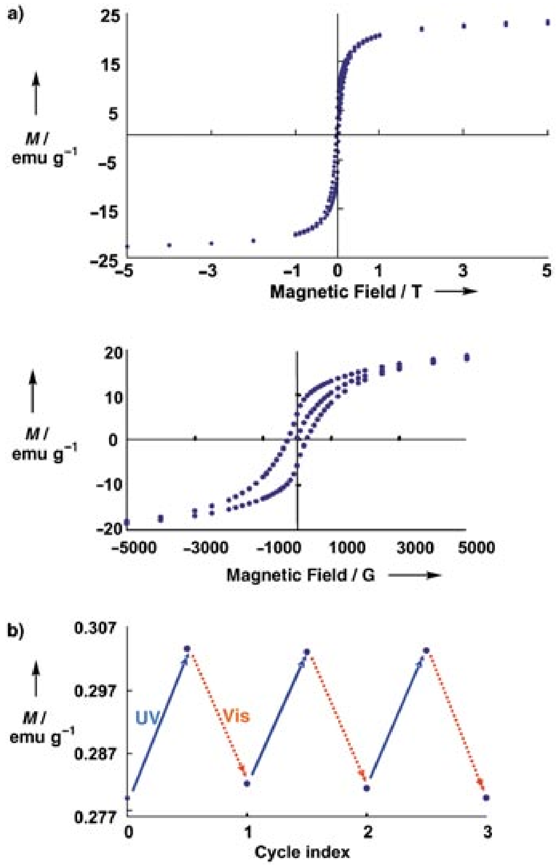

Figure 4. a) The plot of magnetization *M* versus applied magnetic field for **1** at 5 K and a magnified region (1 G = 10^{-4} T). b) Change in the magnetization for **1** induced by alternating illumination with UV and visible light (10 min each) at 5 K with an external magnetic field of 10 G.

We next investigated the influence of photo-illumination on the magnetic properties of **1** at 5 K (Figure 4b). Compound **1** was cooled from room temperature to 5 K in an external magnetic field of 10 G. The initial magnetization value of **1** at 10 G increased from 0.279 to 0.305 emu g^{-1} upon UV illumination. The sample was exposed to UV light until saturation, that is, until the change in magnetization was complete (10 min). Even after the illumination was stopped, this increased magnetization was maintained for several hours. Compound **1** was then illuminated with visible light for a further 10 min. The magnetization value decreased from 0.305 to 0.280 emu g^{-1}. This UV light induced increase and visible light induced decrease in the level of magnetization was repeated several times. The total change of the magnetization value resulting from photoinduced switching was about 9.3 %, which is larger than that achieved by our first photo-functional magnetic vesicles system.[7a]

To investigate the feasibility of using **1** for practical applications, corresponding measurements were performed at room temperature (300 K). No saturation of the magnetization was found at 300 K with a field of 50000 G. Characteristics that are typical of superparamagnetic behavior were observed, such as almost immeasurable coercivity and remanence (Figure 5a). This was consistent with the notion that, above T_B, the magnetization should be free to align with the field during the measurement time.

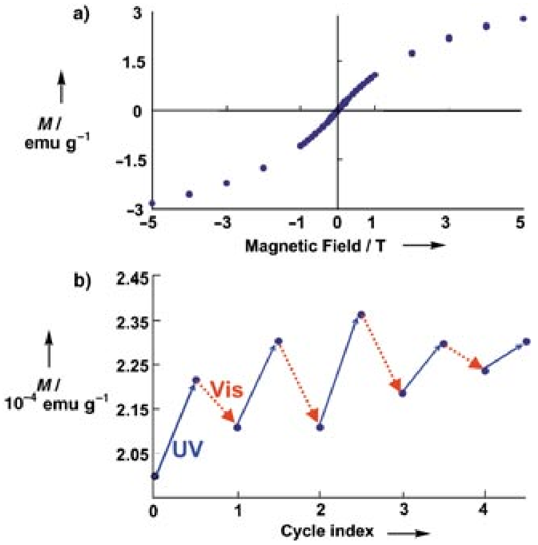

Figure 5. a) The plot of magnetization *M* versus applied magnetic field for **1** at 300 K. b) Change in the magnetization for **1** induced by alternating illumination with UV and visible light (30 min each) at 300 K with an external magnetic field of 10 G.

Next, the influence of photo-illumination on the magnetic properties of **1** at 300 K was examined. The same changes in magnetization upon photo-illumination were noted, that is, the magnetization increased upon illumination with UV light and decreased upon illumination by visible light (Figure 5b). The changes in the magnetization values do not give rise to a distinct trace because of the superparamagnetic properties. These changes in magnetization are consistent with the changes in the UV/Vis spectra and can be explained in the same fashion. The reversible control of the magnetic properties of **1** at room temperature was also confirmed by EPR and ^{57}Fe Mössbauer spectroscopy (see the Supporting Information).

To confirm the effect of the azo moiety, γ-Fe_2O_3 nanoparticles that were only encapsulated with *n*-octylamine were prepared (**2**). The TEM image of **2** also showed the presence of global γ-Fe_2O_3 nanoparticles with almost homogeneous diameters (5 nm), and **2** exhibited almost the same magnetic properties as **1** (not shown). However, when **2** was illuminated with UV or visible light, no changes were observed in the total magnetization. This result suggests that the azo moiety in **1** plays an important role in the photocontrol of the magnetization.

It appears that photoinduced changes in the electrostatic field around the γ-Fe_2O_3 magnetic nanoparticles affect the magnetization. Examples from our previous work could also be explained by similar interactions.[7] Changes in the dipole moments induced by the photoisomerization of the Azo moieties resulted in magnetic fields and moments in the materials. We have previously observed that the change in the dipole moments of the azo compounds did not affect the magnetization value in the paramagnetic region.[7] Those results were consistent with the present results in terms of the temperature dependence (at 5 K and room temperature): The stronger the magnetic exchange interactions between spins are, the greater the effect the dipole moment has on the magnetization values.

The relationship between the electronic polarization (including the charge or the dipole moments) and the magnetization has been discussed by several physicists.[16,17] The origins of the behavior of magneto-electric materials are the electric field induced g shift, the spin-orbit interactions, the exchange energies, and the electric field induced shift in the single-ion anisotropy energy. The underlying electrodynamics are complicated by induced fields interacting with electric and magnetic moments. That is, the spin orientation is coupled to the electric multi-pole through the lattice. Morup et al. also discussed the existence of significant collective effects in a magnetic nanoparticle system and made several speculations regarding a spin-glass-like phase at low temperatures on dipole–dipole interacting systems.[17b] Moreover, the surface magnetic phase diagram of the tetragonal manganites depends on the electrostatic interactions caused by the surface environment, such as surface termination.[15]

In 1999 Alivisatos et al. described the preparation of soluble crystalline γ-Fe_2O_3 nanoparticles by high-temperature organic-phase decomposition of an iron precursor.[18] The process was then extended to the synthesis of monodisperse MFe_2O_4 (M = Fe, Co, Mn) nanoparticles by Sun et al.[19] through the use of oleic acid and oleylamine. They studied the stability of the nanoparticles by varying the ratio of the capping agents and described how γ-Fe_2O_3 nanoparticles can be stabilized by alkylamine surfactants,[9b,11] suggesting that NH_2 coordinates with Fe^{III} on the surface of the particles. Furthermore, Zhang et al. studied the effects of surface coordination chemistry on the magnetic properties of $MnFe_2O_4$ nanoparticles.[20a,b] They observed that the coercivity of magnetic nanoparticles decreased upon coordination of the ligands on the nanoparticle surface, whereas the saturation magnetization increased. They concluded that the magnetic properties of the nanoparticles change with the functional group bound onto the nanoparticle surface. The correlation suggests a decrease in the spin-orbital coupling and surface anisotropy of magnetic nanoparticles due to surface coordination.

Gedanken et al. also studied the magnetic properties, especially the blocking temperature T_B, of iron nanoparticles coated by various surfactants.[20c] They observed large variations in T_B for various functional groups attached to the iron nanoparticles. For example, the magnetization values for alcohols and carboxylic acids were different from those for sulfonic and phosphonic acid. These differences could be explained by the variation in particle size as well as the effect of the iron-bound functional group on the *d* electrons of iron. The functional groups interact strongly with the *d* electrons and cause a large splitting of the doubly and triply degenerate *d* levels. This affects the spin state and the magnetization values as a result of exchange interactions between the spins of the iron center.

The above discussion also suggests that photoinduced changes in the electrostatic field around the γ-Fe_2O_3 magnetic nanoparticles affect the magnetization. Photo-switchable magnetic films—Prussian blue intercalated in Langmuir–Blodgett films consisting of an amphiphilic azobenzene and a clay mineral,[7c] which was one of our previous photo-functional systems—supplied data that support these mechanisms. A band corresponding to intervalence charge transfer (IVCT) between Fe^{II} to Fe^{III} in the Prussian blue layer was changed reversibly by alternate UV and visible illumination, accompanied by photoisomerization of the azo compound. That is, changes in the electrostatic field driven by the photoisomerization of the azobenzene chromophore led to changes in the Coulomb energy (which is necessary to transfer an electron) and this might affect the superexchange interaction between the spins in the Prussian blue magnet.

In conclusion, we have designed novel photoresponsive γ-Fe_2O_3 nanoparticles that are encapsulated by an azo compound and *n*-octylamine. To photo-control the magnetization, the design of the interfaces between the photoresponsive materials and the magnetic materials is important. The advantage of the current system is that nano-scale particles, from which much larger areas of photoresponsive interfaces might be expected, were used as the magnetic materials. Another important aspect was the dilution of the azo moieties with *n*-octylamine. The free volume gained is responsible for the ideal photoreaction. Use of azo compounds with appropriate end groups and alkyl chain length for direct interaction with the metal oxide surface was also mportant. Finally, we have succeeded in switching the magnetization value of composite magnetic nanoparticles by photo-illumination in the solid state at room temperature.

Experimental Section

The amphiphilic compound Azo[10] and the γ-Fe_2O_3 nanoparticles[11] were synthesized according to literature methods.

1: $FeCl_3 \cdot 6H_2O$ (0.47 g), sodium acetate (0.43 g, used as a hydrolyzing agent), H_2O (0.35 ml), *n*-octylamine (0.61 mL), and Azo (0.01 g) in 1,2-propanediol (6 mL) were heated under reflux at 150 °C for 5 h. The materials were then precipitated by the addition of a large volume of 2-propanol (ca. 20 mL). After being washed with 2-propanol, the solids were collected by centrifugation, washed with Et_2O, and dried in air. The crude product was re-dissolved in toluene (5 mL) containing a small amount of the encapsulating agents *n*-octylamine and Azo (0.3 mL, 100:1). Most of the crude product went into solution within 13 h. A solution of **1** in toluene was then cast onto the substrates for further study.

The UV/Vis spectra were recorded on a V-560 spectrophotometer (JASCO). UV illumination (filtered light, $\lambda_{max} = 360$ nm, 1.0 mW cm^{-2}) was applied with an ultra-high pressure mercury lamp (HYPERCURE 200, Yamashita Denso). Visible light (400–700 nm, 1.0 mW cm^{-2}) was provided by a xenon lamp (XFL-300, Yamashita Denso). The magnetic properties were investigated with a SQUID magnetometer (model MPMS-5S Quantum Design). The lamps were guided into the SQUID magnetometer by an optical fiber to study the photomagnetic effects. The ^{57}Fe Mössbauer spectra were measured at room temperature and at low temperature with a Topologic Systems Model 222 constant-acceleration spectrometer with a ^{57}Co/Rh source in transmission mode. A closed-cycle helium refrigerator (Nagase Electronic Equipments Service Co., Ltd.) was used for measuring the spectra at low temperature.

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[1] W. Kuch, *Nat. Mater.* **2003**, *2*, 505.

[2] C. Thirion, W. Wernsdorfer, D. Mailly, *Nat. Mater.* **2003**, *2*, 524.

[3] P. Gütlich, Y. Garcia, T. Woike, *Coord. Chem. Rev.* **2001**, *219–221*, 839.

[4] a) O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto, *Science* **1996**, *272*, 704; b) O. Sato, Y. Einaga, T. Iyoda, A. Fujishima, K. Hashimoto, *J. Electrochem. Soc.* **1997**, *144*, L11.

[5] S. Hayami, Z.-Z. Gu, M. Shiro, Y. Einaga, A. Fujishima, O. Sato, *J. Am. Chem. Soc.* **2000**, *122*, 7126.

[6] a) J. H. Fendler, *Chem. Rev.* **1987**, *87*, 877; b) S. Mann, D. D. Archibald, J. M. Didymus, T. Douglas, B. R. Heywood, F. C. Meldrum, N. J. Reeves, *Science* **1993**, *261*, 1286; c) K. Nakatani, P. Yu, *Adv. Mater.* **2001**, *13*, 1411; d) N. Kimizuka, *Adv. Mater.* **2000**, *12*, 1461.

[7] a) Y. Einaga, O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto, *J. Am. Chem. Soc.* **1999**, *121*, 3745; b) Y. Einaga, T. Yamamoto, T. Sugai, O. Sato, *Chem. Mater.* **2002**, *14*, 4846; c) T. Yamamoto, Y. Umemura, O. Sato, Y. Einaga, *Chem. Mater.* **2004**, *16*, 1195.

[8] a) Y. Einaga, M. Taguchi, G. Li, T. Akitsu, Z.-Z. Gu, T. Sugai, O. Sato, *Chem. Mater.* **2003**, *15*, 8; b) M. Taguchi, G. Li, Z.-Z. Gu, O. Sato, Y. Einaga, *Chem. Mater.* **2003**, *15*, 4756.

[9] a) A. Manna, P.-L. Chen, H. Akiyama, T.-X. Wei, K. Tamada, W. Knoll, *Chem. Mater.* **2003**, *15*, 20; b) A. K. Boal, K. Das, M. Gray, V. M. Retello, *Chem. Mater.* **2002**, *14*, 2628; c) S. Thimmaiah, M. Rajamathi, N. Singh, P. Bera, F. Meldrum, N. Chandrasekhar, R. A. Seshadri, *J. Mater. Chem.* **2001**, *11*, 3215.

[10] W.-H. Wei, T. Tomohiro, M. Kodaka, H. Okuno, *J. Org. Chem.* **2000**, *65*, 8979.

[11] M. Rajamathi, M. Ghosh, R. Seshadri, *Chem. Commun.* **2002**, 1152.

[12] L. Neel, *Ann. Geophys.* **1949**, *5*, 99.

[13] M. D. Mukadam, S. M. Yusuf, P. Sharma, S. K. Kulshreshtha, *J. Magn. Magn. Mater.* **2004**, *269*, 317.

[14] A. B. Bourlinos, A. Simopoulous, C. Petridis, *Chem. Mater.* **2002**, *14*, 899.

[15] J. C. Mallinson, *The Foundations of Magnetic Recording*, Academic Press, Berkeley, **1987**, ch. 3.

[16] V. K. Sharma, F. Waldner, *J. Appl. Phys.* **1977**, *48*, 4298.

[17] a) J. Baker-Jarris, P. Kabos, *Phys. Rev. E* **2001**, *64*, 056127-1; b) S. Morup, E. Tronc, *Phys. Rev. Lett.* **1994**, *72*, 3278.

[18] J. Rockenberger, E. C. Scher, P. A. Alivasatos, *J. Am. Chem. Soc.* **1999**, *121*, 11595.

[19] a) S. Sun, H. Zeng, *J. Am. Chem. Soc.* **2002**, *124*, 8204; b) S. Sun, H. Zeng, D. B. Robinson, S. Raoux, P. M. Rice, S. X. Wang, G. Li, *J. Am. Chem. Soc.* **2004**, *126*, 273.

[20] a) C. R. Vestal, Z. J. Zhang, *J. Am. Chem. Soc.* **2003**, *125*, 9828; b) C. Liu, B. Zou, A. J. Rondinone, Z. J. Zhang, *J. Am. Chem. Soc.* **2000**, *122*, 6263; c) G. Kataby, Y. Koltypin, A. Ulman, I. Felner, A. Gedanken, *Appl. Surf. Sci.* **2002**, *201*, 191.