Magnetic Nanoparticle Superstructures

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The aim of this microreview is to present recent advances in the preparation of magnetic nanoparticle superstructures from ferrofluids and by nanosphere lithography. Different successes of methods presented in this article to create magnetic nanoparticles will be discussed in view of different requirements of available assembling techniques. Theoretical aspects of nanoparticle assemblies and their assembled layer magnetic properties are not reviewed here.
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1. Introduction

For the design of novel nanostructured devices one needs a technique for preparing highly symmetric periodic particle arrays (PPA) within the range of several microns, on an industrial scale. Different routes have been investigated in the past to obtain small particles, which can be assembled in large areas of high symmetry. These approaches typically apply "scale down" techniques, e.g. ball milling of bulk materials, and "bottom up" techniques, e.g. cluster or nanoparticle growth from precursors in gaseous or liquid phases. The latter, i.e. the wet chemical synthesis of inorganic colloidal particle fluids, is most elegant from a chemist's point of view.[1]

Inorganic colloidal fluids are stable dispersions of nanoscale clusters or fine particles – which can be crystalline or amorphous – in a solvent.[2] If the dispersed material is known to exhibit ferromagnetic behavior in the bulk material, colloidal suspensions thereof are called ferrofluids or magnetic fluids.[3] One can develop PPA with ferrofluids having a standard particle size distribution $< 10\%$ by simply drying a drop of solution on suitable substrates. This self-assembly technique has been improved through use of

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Michael Giersig studied at the A. Mickiewicz University of Poland. He carried out his diploma research work at the Fritz-Haber-Institute of the Max-Planck-Gesellschaft in Berlin and received his diploma in physics at the Freie Universität Berlin in 1984. He continued to work at the Fritz-Haber-Institute. He received his PhD in chemistry at the Freie Universität Berlin in 1988. Subsequently he continued with his postdoctoral work at the Institute for Molecular Genetics of the Max-Planck-Institut in Berlin. At the end of 1989 he took up a post at the Hahn-Meitner-Institute in Berlin, Department of Physical Chemistry, where he was awarded twice with a research prize. In 1995 he received an international accolade in the form of a 2-year stay at the University of Melbourne, Department of Physical Chemistry. After his return he habilitated at the University of Potsdam, Faculty of Physical Chemistry in 1999. In 2000 Michael Giersig was appointed professor at the Technological University, department of physics in Poznan, Poland. He is the author/co-author of over 140 scientific journal and conference articles and book chapters. He joined the research center caesar in April 2003 to establish the group "nanoparticle technology". The work of the group focuses on the creation of 2-D and 3-D nanostructures, based on single nanoparticles as well as the fabrication of nanostructured surfaces with a size of a number of square centimeters. A further focal point is the optical, structural as well as magnetic characterization of nanostructures.

Michael Hilgendorff received his diploma in chemistry in 1993 (University of Hannover), where he investigated the photocatalytic degradation of carbon tetrachloride on platinized titanium dioxide particles. He then worked on ZnO colloids and transparent electrical conductive electrodes at the University of Würzburg, where he received his PhD in 1999. In February 1999 he joined the group of Michael Giersig at the Hahn-Meitner-Institute in Berlin to work within the priority program of the Deutsche Forschungsgemeinschaft (DFG) on "Semiconductors and metal clusters as building blocks for nanostructured materials". He joined the group "nanoparticle technology" at caesar in April 2003, where he is responsible for the development of new and the optimization of existing inorganic colloid syntheses.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

different coating techniques (e.g. spin coating, dip coating, or spraying) in combination with applied external forces. The origin of these external forces is either mechanical, and is used for the preparation of Langmuir–Blodgett (LB) films,[4] or electrostatic, which is then used for layer-by-layer (LbL) assembly applying polyelectrolytes.[5] The use of external electric and magnetic fields to improve the self-assembly of charged and magnetic nanoparticles, respectively, has also been reported.[6,7]

Despite all those successes, there are some applications that cannot be solved by the use of ferrofluids. One reason is the limitation of perfectly ordered nanostructures to about one micron squared. A second result from the question: "How can we arrange highly ordered magnetic nanoparticles on substrates having a distance larger than 100 nm?". To overcome these problems, a lithographical technique applying organic colloids – Nanosphere Lithography (NSL) – has been further optimized.[8]

The formation of monolayers of self-assembled colloidal particles (mainly polystyrene and silica submicron-sized, monodisperse spheres) is well established and has been widely used in various fields of research.[9] Well-ordered latex particle films were used, among others, as masks that allow the production of regularly arranged triangular-shaped structures on almost arbitrary substrates. Through the evaporation of different materials through the mask, it was possible to prepare nano-sized particles with diverse optical[9,10] or magnetic properties.[10] There are many different monolayer fabrication methods based on electrophoresis,[6] electrostatic deposition,[11] the Langmuir–Blodgett technique, spin-coating,[12] the controlled evaporation of solvents from a solution containing latex particles on a hydrophilic substrate,[13] or non-photolithographic methods.[14] Many authors used the method of Micheletto et al.,[13a] or other drying-based methods and pointed out that a hydrophilic surface is crucial for monolayer depositions.[15] To deposit PS latex particles onto hydrophobic substrates it is necessary to use an alternative method that involves assembly onto a liquid–gas or a liquid–liquid interface.[8]

In this microreview we will provide an overview of assemblies of ferrofluids, as well as some improvements of NSL by changing the shadows below – and the interstices between – hexagonal-ordered monolayers of submicron spheres. For an overview of theoretical aspects of nanoparticle assemblies see.[16] Detailed information on magnetic properties are available by Leslie-Pelecky and Rieke,[17] Binns,[18] and Spasova and Farle.[19] A short summary is given in ref.[20].

2. Superstructures from Ferrofluids

Syntheses: The most important prerequisite for the preparation of magnetic nanoparticle superstructures from ferrofluids is the control over particle size and size distribution during syntheses. Many wet chemical routes have been developed in recent years. Syntheses of monometallic mag-

netic particles such as Fe,[21] Co,[7b,21a,21b,22] or Ni,[21a,21b,23] have been successfully done by electrochemical reduction,[22i,23d] chemical reduction by Li,[23c] hydroborides,[21b,22j–22l] or polyols[24] of metal salts, thermal decomposition (initiated by conventional methods[7b,21e,22a,22b,22e–22h,22m,23a,23b] or by ultrasound[21d]) of zero-valent metal-organic compounds in organic solvents in the presence of bulky stabilizers such as: *i*) fatty acids (in combination with organic amines or phosphanes); *ii*) polymers, or; *iii*) surfactants. In the case of *i*), the fatty acids act as stabilizing compounds, i. e. to overcome oxidation, Van der Waals, and dipole–dipole interactions, while the amines or phosphanes control the particle growth. Surfactants can be used as stabilizers for inorganic nanomaterials dispersed in organic solvents or as compounds forming stable micelles in heterogeneous oil-in-water systems, e.g. sodium dodecyl sulfate (SDS). Other surfactants, e.g. alkylammonium bromides (DDAB, CTAB) or Aerosol OT (AOT), form a stable emulsion of water droplets in hydrophobic solvents (reverse micelles). Figure 1 shows a typical result of Co-particles prepared by thermal decomposition of octacarbonyldicobalt in dichlorobenzene.
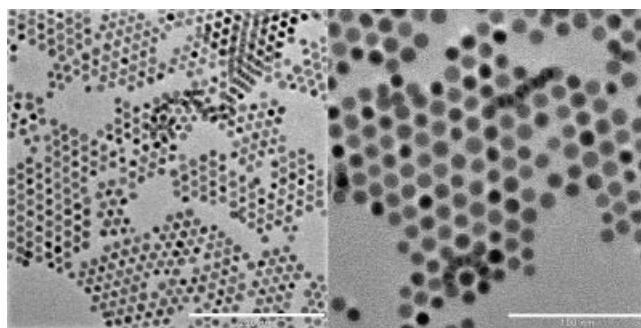

Figure 1. TEM images at different magnifications of monodisperse 10 nm Co particles self-assembled on a carbon-coated Cu grid.

The development of bimetallic ferrofluid syntheses has been based on existing synthetic procedures of monometallic ferrofluids. In general, they have been produced by thermal decomposition of bimetallic zero-valent metal-organic compounds[25] or in-situ or successive thermal decomposition of zero-valent monometallic metal-organic compounds,[26] as well as by in-situ or successive reduction of metal salts,[27,28] or combinations thereof.[29] In summary, bimetallic particles form alloys, core-shell particles, or cluster in cluster particles,[24] are all dependent largely, but not exclusively, on reaction kinetics. Applied methods and properties of these fluids have been summarized in ref.[20].

The most common preparation of magnetite (Fe_3O_4) ferrofluids was developed by Massart about 20 years ago and described in detail in 1987.[30] The synthesis was based on the co-precipitation of Fe^{II} and Fe^{III} salts in aqueous solutions stabilized by repulsive electrostatic forces. TEM investigations show typically aggregated particles, consisting usually of a mixture of ferrimagnetic magnetite, and maghemite (γ-Fe_2O_3), and paramagnetic hematite (αFe_2O_3). The ratio of the different iron oxide phases is directly compared to the expense associated with performing the synthe-

sis under oxygen free conditions, because γFe_2O_3 and α-Fe_2O_3 are oxidation products of Fe_3O_4. Figure 2 provides typical images of magnetite particles prepared in aqueous medium (a) and after their transfer to toluene (b).
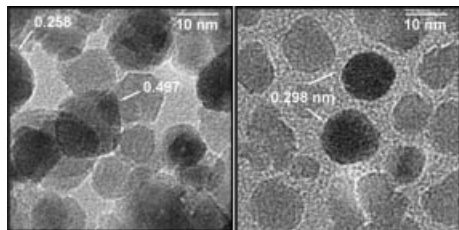

Figure 2. Typical TEM images of iron oxide particles; a) prepared in aqueous solution by Massart method and b) the same particles dried from a toluene solution after adsorbing oleic acid on their surface. The distances shown in the images are the result of fast Fourier analysis, indicating typical lattice planes of magnetite (redrawn with permission from ref.[16a]).

Since these reports, several optimizations have been discovered to produce ferrofluids useful for new applications. One of them was concerned with the possibility of changing the magnetic properties of the inverse Fe_3O_4 spinell by replacing Fe^{II} with Co^{II}, Ni^{II}, Mn^{II}, or Zn^{II} ions.[31]

Additionally, many reports dealt with solving the classic problem of nanoparticle aggregation in aqueous solutions (Figure 2, a). To overcome such aggregation, new preparations have involved micellar solutions,[32] as well as the transfer of iron oxide particles from aqueous to nonpolar solvents by hydrophobizing the surface by adsorbing bulky stabilizers such as fatty acids (Figure 2, b).[33]

Different methods have been applied to decrease particle size distribution. One method that has been successfully applied involves synthesis of iron oxides in reverse micelles. A second method dealt with a size selective precipitation after transfer of iron oxide particles to nonpolar organic solvents. Most recently, Sun et al.[34] have developed a very successful method to achieve monodisperse Fe_3O_4 nanoparticles without a size selection procedure. This method is based on the reduction of iron(III) acetylacetonate by 1,2-hexadecanediol and further thermal decomposition at high temperatures (solvent: diphenyl ether, b.p. 265°C) in the presence of oleic acid and oleylamine as stabilizers. As a result, small Fe_3O_4 nanoparticles (diameter ca. 4 nm) having a particle size distribution of ca. 5% are formed and can be further grown by seed-mediated growth.[35] A further method to obtain

monodisperse maghemite (γ-Fe_2O_3) particles based on the preparation of Fe particles by the thermal decomposition of carbonyliron and their further oxidation to the oxide has been published by Hyeon et al.[36] A detailed investigation of the structural, magnetic, and electronic properties of iron oxide nanoparticles prepared by decomposition of iron(II) and iron(0) precursors in the presence of different organic solvents and surfactants has been published in ref.[37].

Table 1 provides an overview of successful syntheses and surface properties, determining the applicability of different assembling methods, of various magnetic colloids.

General observations for wet chemical ferrofluid preparations are increasing particle sizes with decreasing precursor concentrations and decreasing chain length of the stabilizers, and increasing size distributions with increasing final particle sizes. As one challenge of syntheses is to achieve a narrow size distribution, the reverse micelle technique and the so-called "hot injection" technique have been successfully applied, especially for the preparation of larger particles (diameters > 5 nm – 15 nm). Using the latter method, standard size deviations < 10% have been experimentally demonstrated (standard size deviations of ca. 5% have been predicted theoretically by choosing a proper combination of solvent and stabilizers[38]). Moreover, the hot-injection technique has been employed to facilitate a further growth of primary prepared particles (seed particles) by reactive precipitation of precursors on the surface of seed particles.
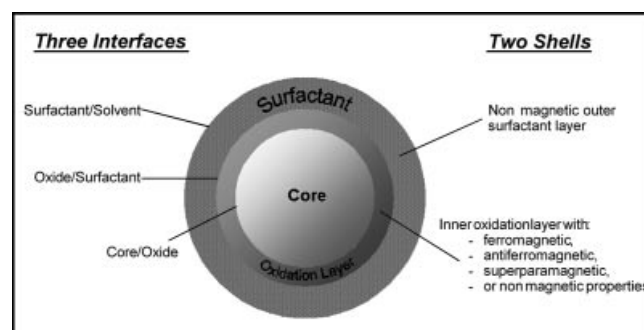

Figure 3. Sketch of a magnetic nanoparticle representing the usual result of colloid chemical synthesis. The desired core material is covered with an inner oxidation layer of the core material and an outer surfactant layer that is necessary to overcome attractive forces. As a result, three interfaces are present, which determine the nanoparticles properties (adapted with permission from ref.[16a]).

Table 1. Overview of successful syntheses and surface properties of various magnetic colloids.

Synthesis		Materials	Surface properties
D	Decomposition	metals, their alloys, and oxides prepared by post oxidation	uncharged, hydrophobic
E	Electrolysis	metals and their alloys	charged, hydrophobic
R	Reverse micelles	metals, their alloys, and oxides	charged, hydrophobic
M	Micelles	magnetic latex spheres formed by emulsion polymerization	charged, hydrophilic
O	Organohydroborate reduction.	metals and their alloys	charged, hydrophobic
P	Polyol reduction	metals and their alloys	various
C	Combination	metal alloys	uncharged, hydrophobic
H	Hydrolysis and condensation	iron oxides	charged, hydrophilic

Hydrophobic ←――――――――――――――――――→ **Hydrophilic**

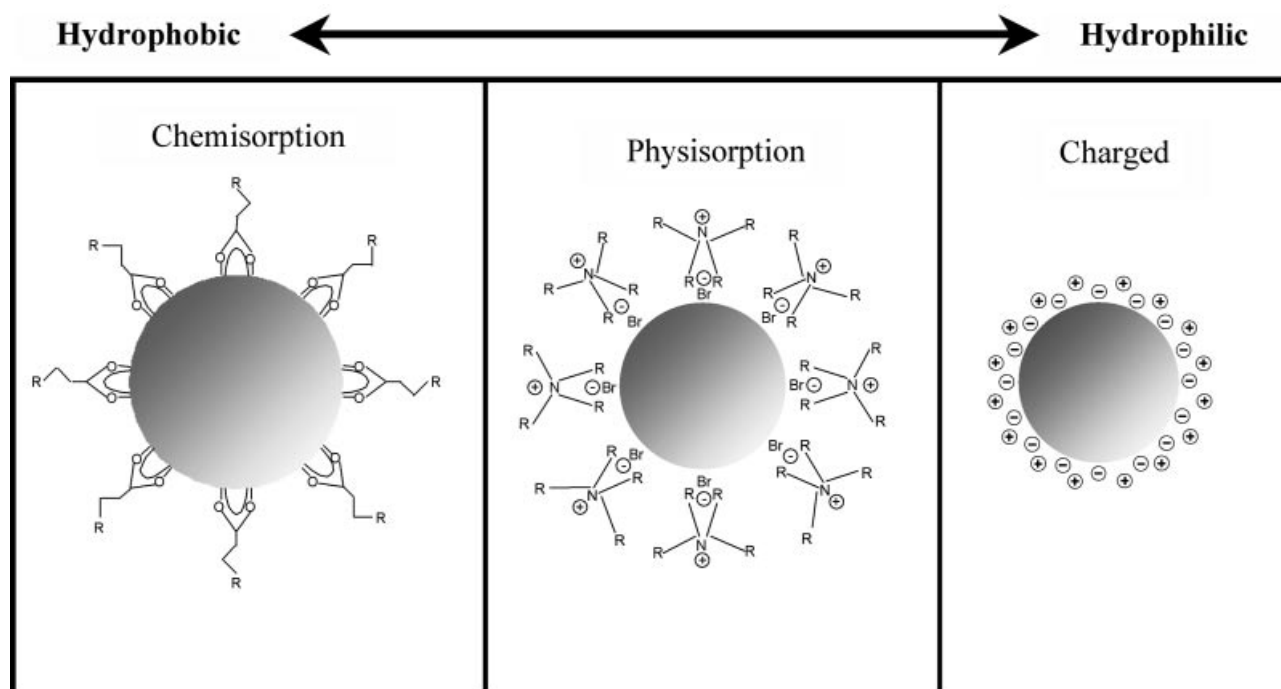| Chemisorption	Physisorption	Charged

Figure 4. Sketches of models describing the particle surface under different conditions. The chemisorption, i.e. the dissociative adsorption of stabilizers, is most often used in hydrophobic solvents (e.g. toluene). The physisorption has been successfully used to stabilize colloids by tetraalkyl ammonium salts in polar organic solvents (e.g. THF). Simply charged surfaces are in principle limited to aqueous suspensions.

The main result of wet chemical preparations of nano-particles is the fact that one produces composite particles consisting of a core of the desired material, a protecting outer surface layer, and an intermediate inner surface layer of – most often – unknown composition. Figure 3 and Figure 4 give a schematic overview of the "composite" nanoparticle and its different surface properties (with respect to different preparation routes) that are mainly determined by the outer protecting surface layer.

Assembly: Concerned with the control of particle evolution during syntheses by kinetic rather than thermodynamic control of particle size and particle size distribution, is the phenomenon of self-assembly, which was first investigated using submicron spheres of PS latex or SiO_2 dispersed in water. This work concluded that self-assembly is conditional on the narrow size distribution of the particles (standard deviation ca. 5%), i.e. a narrow distribution of the sum of repulsive and attractive forces between particles in a colloidal solution. Thus, this conclusion is not limited to well-separated single particles. It holds also for aggregates of particles often found in aqueous systems, assuming that equal forces interact between aggregates of similar size.

Various methods have been applied for assembling magnetic colloids in recent years. The different methods and their requirements – mainly concerned to the surface properties of the nanoparticles, which are different for different preparation conditions – are summarized in Table 2 (in view of Table 1).

2.1 Self-Assembly

The most simple particle layer preparation method, which allows the application of external forces, is drying a drop of solution on a flat substrate – solid or liquid. This procedure results in a particle monolayer if the inorganic material concentration of the fluid is in the order of about 10^{-4} M. The monolayer typically consists of particle *sheets* of high symmetry interrupted by *empty* areas containing excess stabilizer (Figure 5).

The particle sheets can self-assemble into hexagonal-ordered arrays as shown in Figure 1, or into cubic-ordered arrays[39,37] depending on the stabilizers nature and/or the particles shape, respectively. Increasing the ferrofluid concentration can increase the particle area density and the number of layers formed by self-assembly on a substrate. Increasing the concentration results in multilayers forming three-dimensional crystals of various symmetry, e.g. hcp, fcc, bcc, or tetragonal, but with multiple defects. Figure 6 shows a three-dimensional crystal prepared by drying a drop of a monodisperse Co-colloid shown in Figure 1.

One major requirement for technological applications of ferrofluids is their assembly into ordered structures of several mm² in size. Self-assembling of colloids on aqueous surfaces allows for the preparation of continuous layers of several mm² in size typically consisting of well-ordered *cores* interrupted by grain boundaries between cores of different orientation. There is no principle difference between nano-sized inorganic and micron-sized organic colloids.

Table 2. Overview of successful assembling methods, their requirements, and their applicability for colloids prepared by methods summarized in Table 1.

Assembling Method		Requirements	Applicable for
SA	**S**elf-**A**ssembly: self organization of colloidal particles into symmetric arrays during their deposition on flat substrates, i.e. flat solid- or liquid surfaces, or their precipitation into large particulate crystals from over-saturated liquids	narrow distribution of interacting forces between the colloidal particles	D, M (latex), R, and C
IA	External field **I**mproved **A**ssembly:		
	LB: mechanical force-improved assembly on aqueous surfaces	hydrophobic properties	D, E, R, O, P, and C
	MDT: magnetic force-improved assembly on flat surfaces	ferro- or superparamagnetic properties	D, R, M, C, and H[a]
	EDT: electric force-improved assembly on flat surfaces	charged colloids	R, M, and H[a] [b]
LbL	**L**ayer-**b**y-**L**ayer assembly: alternative deposition of polymers and colloids on solid surfaces of various geometry	charged colloids and aqueous solvents by use of polyelectrolytes	all[c]

[a] Particles available by the methods E, O, and P are typically too small to be influenced by external electric and magnetic fields during deposition at room temperature. [b] EDT approach has not yet been demonstrated for magnetic colloids to the authors' knowledge. [c] Applicability is dependent on the solubility of polymers in different solvents.
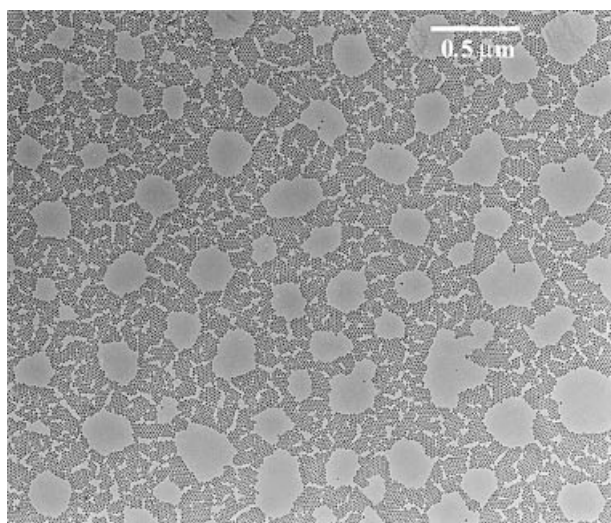

Figure 5. Typical TEM image of a sheet-like self-assembled film obtained by drying a drop of ferrofluid on a carbon-coated Cu grid (adapted with permission from ref.[16b]).
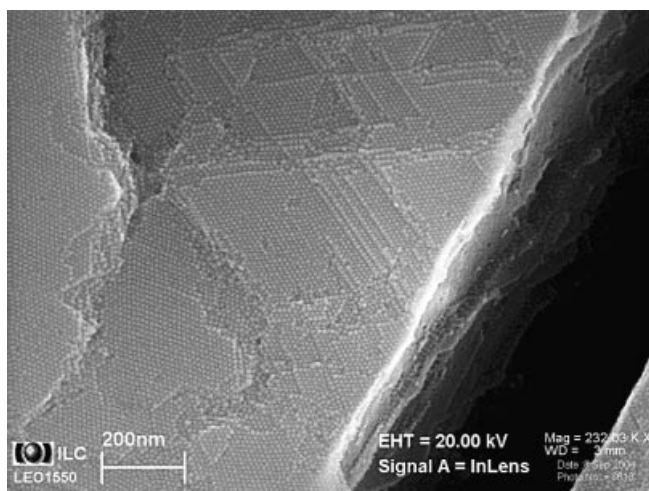

Figure 6. SEM image of a colloidal crystal prepared from a concentrated solution of highly monodispere Co nanoparticles (courtesy of E. Majkova).

The core size can be improved by adding special surfactants (or simply soap) to the aqueous phase that will change its surface tension and/or the interaction of the particulate depletion layer. The latter refers to theoretical descriptions developed by Debye, Hückel, and Onsager (see common textbooks of physical chemistry).

Figure 7 presents a typical result of particle assembly on a water surface. The visible structure results from isolated second layer islands. A perfect monolayer would not be visible at this magnification, demonstrating the problem of TEM investigations to show both, symmetry as well as large-area substrate coverage in case of nanoscale materials. It is obvious from Figure 8 that the symmetry of the assembled layer is decreased compared to the layer shown in Figure 1. Nevertheless, assembling on water surfaces allows (and is limited) to prepare monolayers of, for example, narrow symmetry distribution, but over several mm^2. Furthermore, this technique allows applying external magnetic fields during monolayer formation; static, as well as rotating magnetic fields. The latter may have some advantages in preparing assembled layers of circular geometry.
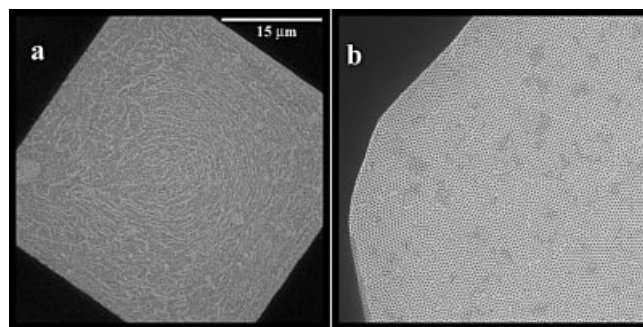

Figure 7. a) One mesh of a complete covered Cu grid. The structure results from islands of a double layer as can be seen in b. b) Higher magnified image showing the degree of ordering (adapted with permission from ref.[16b]).

Further optimizations have been available by applying the LB technique, dealing with mechanical force to increase the core size of self-assembled particle layers on water surfaces.[4] The preparation of large-scale three-dimensional
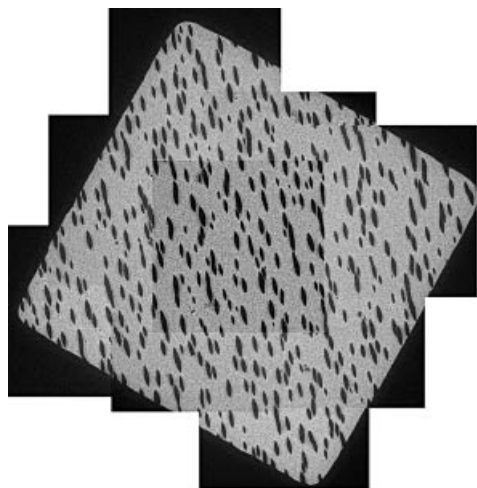
Figure 8. TEM image constructed from 11 micrographs. The mesh is 45 μm × 45 μm. The insert demonstrates that the structure is the same on at least four meshes (adapted with permission from ref.[16b]).

colloidal crystals grown from over-saturated fluids, has also been reported.[29j,29k]

2.2 Magnetophoretic Deposition Technique (MDT)

Ordering phenomenon in ferrofluids placed in external magnetic fields have been observed and theoretically calculated in literature. More recently, the formation of ordered stripes and hexagonal sheets has been experimentally observed while drying a thin liquid film of a ferrofluid on a substrate in an applied external magnetic field.[7b,16] Theoretical calculations of Lacoste and Lubensky showed that the shape of ordered structures, which are obtainable by drying a thin layer of ferrofluid under the influence of an external magnetic field applied in an identical plane to the liquid layer, can be completely different. Stripes as well as hexagonal sheets are available and can be made to coexist simply by changing the strength of the applied magnetic field and/or the concentration of the particles.[40] We found experimentally that the direction of the applied magnetic field is a further important parameter.[7b,16]

Figure 8 is shown for two reasons. Firstly, it demonstrates the coexistence of stripes (triple layers in this case) and sheets (monolayers, not really visible at this magnification) and confirms theoretical calculations. Secondly, it has been constructed from eleven single images to demonstrate large-area ordering within several μm², which is one major problem of TEM investigations of nanoscale materials. (One mesh of a carbon-coated copper grid, typically used in TEM investigations of colloids, 45 μm by 45 μm in size, is shown.).

Detailed investigations of MDT showed that the size of stripes (Figure 9) as well as sheets (as in Figure 5) of high symmetry, interrupted by isotropic regions of low (or no) symmetry and *empty* regions,[7b,16] can be increased by increasing the strength of the applied magnetic field. Figure 10 shows TEM images of the creation of multidimen-

sionally ordered diluted Co colloids of the same concentration using MDT with external applied magnetic fields of 0.8 T (monolayer, upper left), 1.5 T (double layer, upper right), and 6 T (triple layer, lower left). The lower right image shows a triple layer prepared in the absence of a magnetic field for comparison.
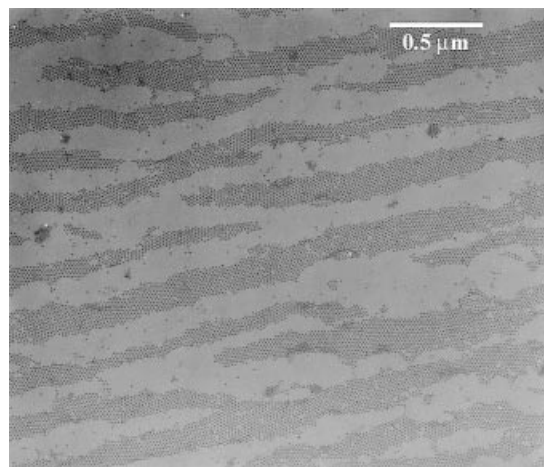

Figure 9. TEM image at low magnification showing a large-area of chains deposited at 0.8 T in perpendicular arrangement (adapted with permission from ref.[7b]).
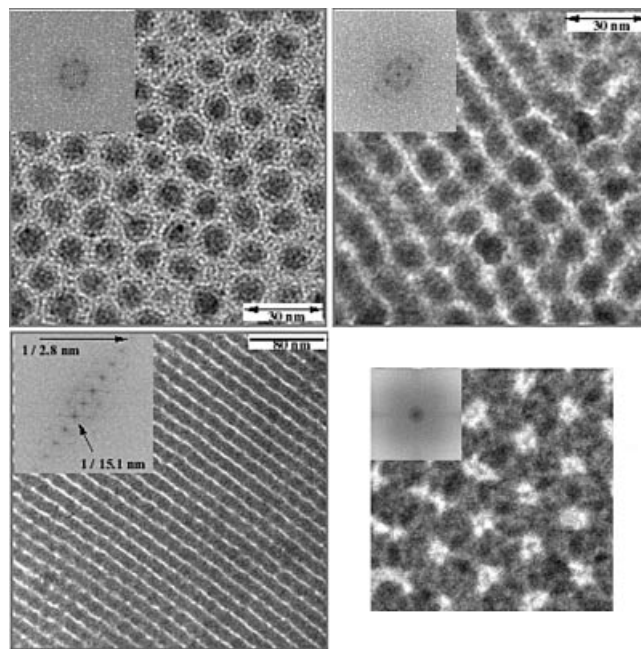

Figure 10. TEM images of the creation of multidimensionally ordered Co colloids of the same concentration using MDT with external applied magnetic fields of 0.8 T, mono layer (upper left), 1.5 T, double layer (upper right), and 6 T, triple layer (lower left). The lower right image shows a triple layer prepared in the absence of a magnetic field for comparison (redrawn with permission from ref.[7b]).

By increasing the concentration of colloids one can obtain micron-sized rod-shaped colloidal crystals by MDT grown perpendicular (magnetic field applied perpendicular to a substrate) or parallel (magnetic field applied parallel to

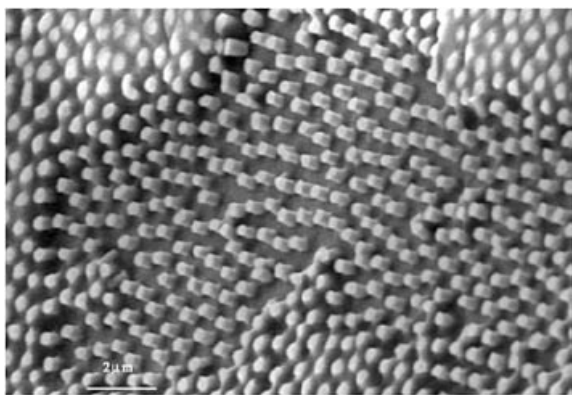a substrate) on a substrate as can be seen in Figure 11 and Figure 12.[41]

Figure 11. SEM picture of randomly distributed rods prepared by drying in air on substrate in a magnetic field of 0.8 T perpendicular to a Si/Si_3N_4 substrate (adapted with permission from ref.[41]).
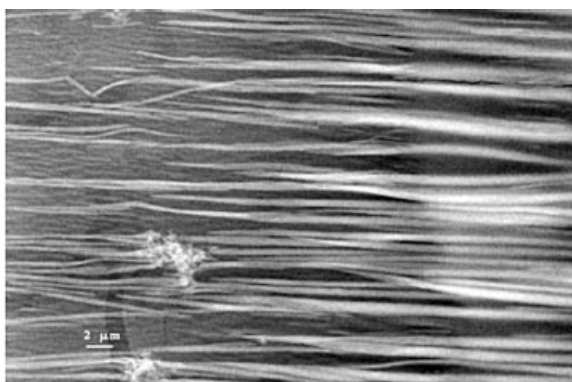

Figure 12. SEM picture of rods prepared like in Figure 11, however, with the magnetic field of 0.8 T parallel to the substrate (adapted with permission from ref.[41]).

Most recently, the perpendicular magnetic field-directed growth of such rods has been discussed in detail by the Pileni group.[42] Meanwhile, the magnetic field-directed growth of rods from bimetallic $CoPt_3$ colloids also has been published.[43]

Despite all those successes, the maximum size of defect-free inner superstructures available by applying MDT is limited to the lower µm range.[7b,16]

2.3 Layer-by-Layer Deposition (LbL)

Different to other assembling methods is the LbL technique, The LbL technique based on polymer-mediated self-assembly by alternatively adsorbing oppositely charged polymers (polyelectrolytes) or polymer and nanoparticles on solid substrates.[5,44] The LbL approach is, in principle, applicable for ferrofluids prepared by all methods presented in Table 1 with one restriction. Dealing with polyelectrolyte (the most common technique) requires typically aqueous solutions and charged colloids; therefore it is generally limited to ferrofluids containing iron oxide. The advantages of this technique are the availability of assembled layers

(mainly layers of aggregates in case of aqueous iron oxide colloids) on curved substrates, i.e. latex spheres, and free-standing films including hollow spheres. As a result, nanoparticle layers of different thicknesses alternatively divided by layers of polymer have been published to be available.

A certain number of articles concerning the preparation of photonic crystals from magnetized latex spheres are available.[5d–5f,45] Two different routes were used to prepare magnetic organic/inorganic hybrid spheres. One dealt with the synthesis of magnetite incorporated in polymeric microspheres produced by emulsion polymerization.[46] The second method applied the LbL approach to prepare latex particles covered with magnetite[5c–5f]

These microspheres have then been used for the preparation of three-dimensional crystals. The photonic band gap of these crystals could be varied by varying the distance between the microspheres within a colloidal crystal by applying MDT. Increasing the applied magnetic field resulted in decreasing particle distances and blue shift of the Bragg diffraction wavelength. Unidirectional shifts have been observed with increasing NaCl concentration in aqueous solutions and decreasing dielectric constants of non-aqueous solutions.

The Farle group has used the LbL approach to prepare magnetite-covered latex particles.[5d–5f] Figure 13 shows TEM micrographs of uncoated PS particles (a) and polyelectrolyte-modified PS particles with (b) one, (c) two, (d) three Fe_3O_4 nanoparticles/polyelectrolyte layers. The average diameters of the composite particles are 650, 770, and 960 nm, respectively. The insert pictures in (b) clearly show Fe_3O_4 particles on the PS particles, many of them existing as aggregates.
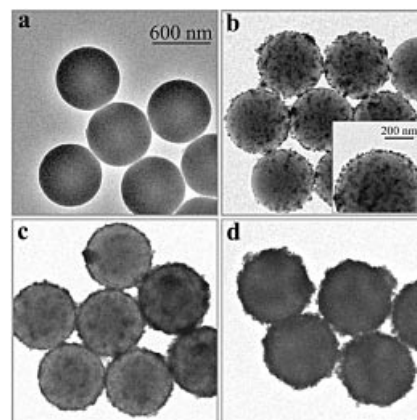

Figure 13. TEM micrographs of uncoated PS particles (a), and polyelectrolyte-modified PS particles with (b) one, (c) two, (d) three Fe_3O_4 nanoparticles/polyelectrolyte layers. The average diameters of the composite particles are 650, 770, and 960 nm, respectively. The insert pictures in (b) show clearly Fe_3O_4 particles on the PS particles; many of them existing as aggregates (adapted with permission from ref.[5g]).

These particles were then coated with SiO_2-covered Au particles.[5e,5f] The use of SiO_2-covered Au particles became necessary because the requirement of a negatively charged surface of Au colloids (as prepared Au particles by the applied method are positively charged). This approach in-

volves coating of microspheres with a high refractive material prior to the colloid crystal formation. Figure 14 demonstrates the successful preparation of latex@magnetite@gold core-shell nanostructured microspheres. Properties of photonic band gap behavior of colloidal crystals prepared from these particles are under investigation.
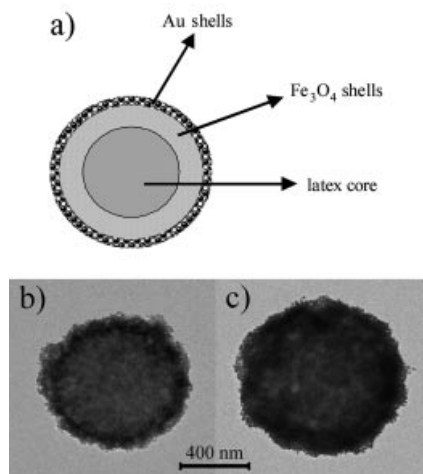

Figure 14. a) Schematic of a core (latex)-shell (Fe₃O₄ and Au nanoparticles) magnetic microsphere. b,c) TEM images of 640 nm PS microspheres: b) covered with two layers of magnetic Fe_3O_4 nanoparticles ($d = 750 \pm 20$ nm) and c) after additional coverage with three layers of Au nanoparticles ($d = 860 \pm 20$ nm) (redrawn with permission from ref.[5e]).

3. Superstructures by Nanosphere Lithography (NSL)

The main prerequisite to obtain highly symmetric nanostructured surfaces of large areas by use of NSL is the successful preparation of ordered monolayers of submicron spheres that are free of grain boundaries. To achieve this, we have developed a modified preparation technique based on the deposition of latex particles similar to a LB film on water. This method, involving surfactant-improved self-assembly on a liquid–gas interface (instead of a mechanical force-improved LB-assembly), allowed us to obtain large monolayers (a few cm²) that could be applied directly onto various surfaces. Using this simple fabrication technique, it was possible to prepare monolayers as large as a few cm² with grain sizes of 1 mm² and above (using latex particles with diameters between 1000 nm and 500 nm), and areas of even 50 μm² without other structural defects (like point defects). Figure 15 shows one typical result of our modified method (right) in comparison to typical results of other methods (left).[8]

Figure 16 shows AFM images of nanostructured surfaces after evaporation of Ni through different masks and further removal of the latex particles by dissolution in THF. The hexagonal symmetry of triangular-shaped Ni islands is clearly visible.[8]

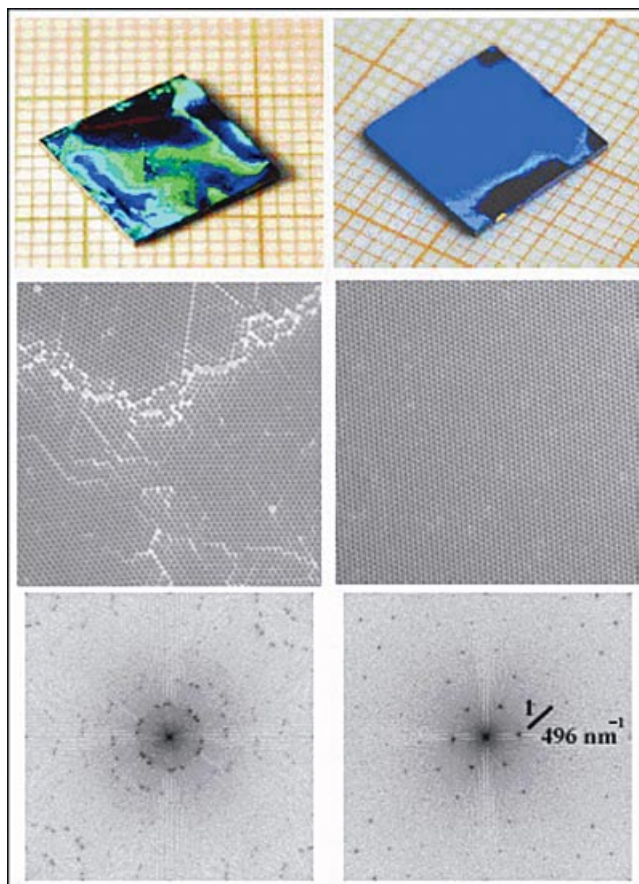Those nanostructured substrates have been successfully used for the growth of hexagonal-ordered carbon nano-

Figure 15. 1×1 cm² silicon wafers covered with 496 nm PS latex particles deposited as a monolayer. In contrast to the sample on the left side, most of the surface of the right one does not contain any grain boundaries, which are represented as a monochrome light interference (blue) color of the surface (right). In the second row, atomic force microscopy images are shown as representative examples for both samples. Additionally, quantitative information about the structures was obtained from a power spectrum of the pictures. Typical reflections for a polycrystalline structure are shown, in contrast to the right one which shows a power spectrum of perfectly ordered PS latex particles (adapted with permission from ref.[16a]).

tubes, grown perpendicular on a 1 cm² substrate, and having interstices > 100 nm (Figure 17). It has been found that the distance of perpendicular-aligned CNT's on substrates is a critical parameter in the preparation of field emission devices from CNT's.[47]

3.1 The Shadow Approach

The structures obtained by NSL can become much more complex by varying the shadows below the microspheres of masks during evaporation. We have first developed computer simulations that predicted the structures resulting from the variation of the angle between the evaporation beam and the sample by tilting and/or rotating the sample under process. Figure 18 shows the principle experimental setup of the shadow approach.[48]

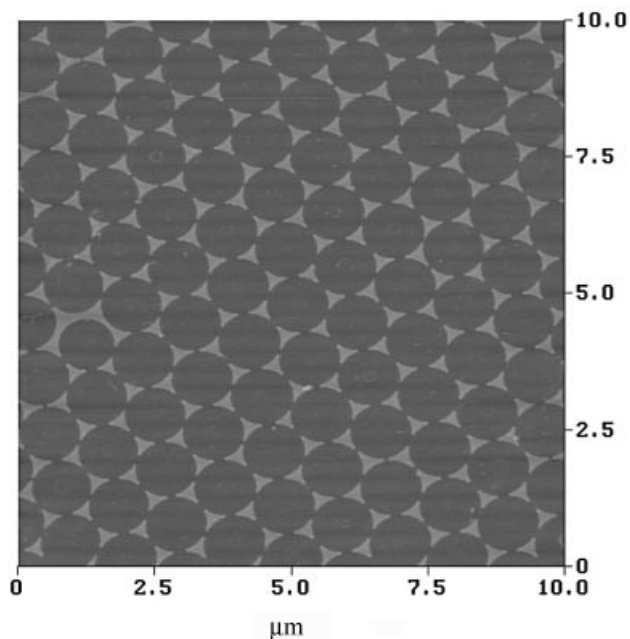Meanwhile, a variety of predicted complex morphologies, ranging from cup-like structures to rods and wires, have
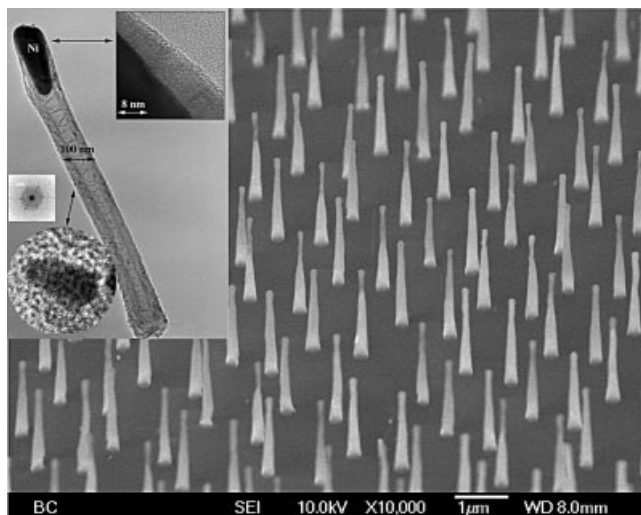
Figure 17. SEM image showing well-aligned carbon nanotubes grown perpendicular on a substrate that was pre-patterned with triangular Ni islands (courtesy of Z. F. Ren).

Figure 16. AFM image gallery showing 2-D magnetic Ni nanostructures created by deposition through different PS latex masks.
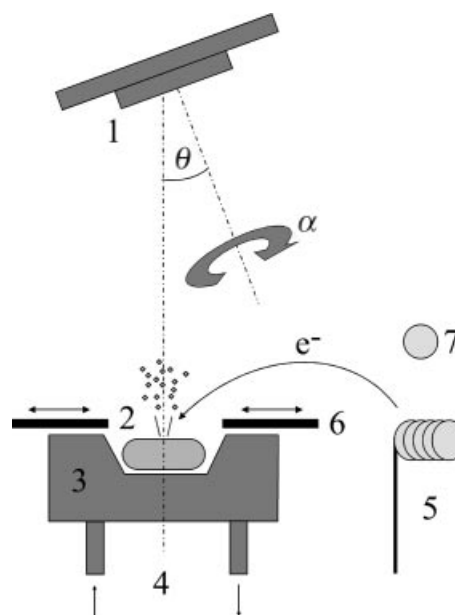
Figure 18. Schematic of the modified evaporation system. (1) Sample holder, (2) evaporation source, (3) crucible, (4) water cooling system, (5) electron beam source, (6) shutter, (7) magnetic field. The evaporation angle is *q*, and *R* the rotation angle of the sample (adapted with permission from ref.[48]).

been successfully prepared using this technique. Figure 19 and Figure 20 give examples of simulation and realization for one experimental setup, respectively.[48]

(A) 1, (B) 2, (C) 4, (D) 6, (E) 7, and (F) 10 microwave pulses.[49]

Applying temperature-treated masks in the shadow approach allowed for the preparation of particles with morphologies such as rings and rods. The combination of both processes allows an outstanding control of size and morphology of particles deposited on substrates. This efficient way is shown to scale down the size of metallic nanoparticles from 200 nm to 30 nm, while preserving the original nanosphere spacing and order. Nano-sized Fe rings produced by this method, having a diameter of 150 nm, show

3.2 Fine Tuning of Interstices

The shadow approach could be further improved by changing the mask morphology, i.e. by decreasing the size and by changing the form of the interstices between the spheres through temperature processing. Figure 21 demonstrates the changes of size and form of interstices and the change of the interferometric color of a 540-nm PS latex mask annealed in 25 mL water/ethanol/acetone mixture by
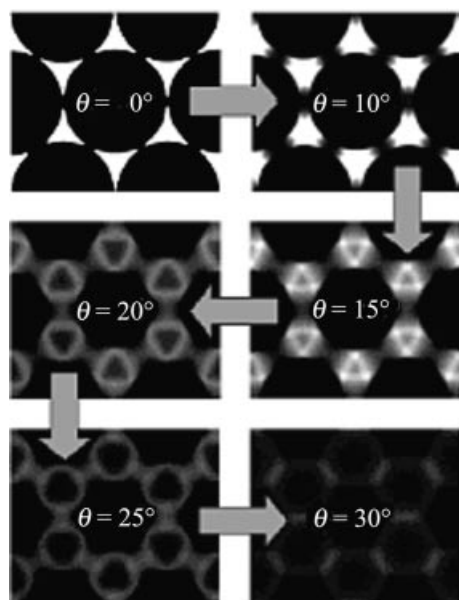
Figure 19. Simulation results for the evaporation through an hcp mask of ordered spheres, with evaporation angles q varying from 0° (perpendicular evaporation) to 30° (adapted with permission from ref.[48]).
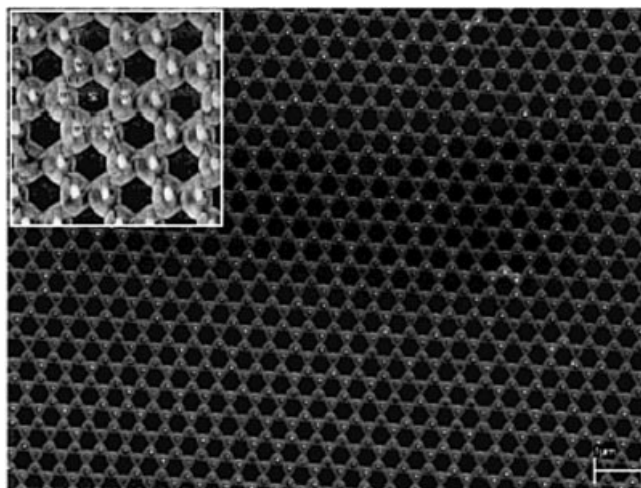

Figure 20. SEM image of a bimetallic structure, obtained by a two-step evaporation process. First step, evaporation of 150 nm Cr (with sample rotation at $q = 25°$), followed by a normal evaporation ($q = 0°$) of 15 nm Ni. The inset presents the scan in the AFM tapping phase mode of the same sample, which shows well-separated Ni spots inside the cup-like Cr structures. The diameter of the mask spheres was 540 nm (adapted with permission from ref.[48]).

ferromagnetic behavior, which has been predicted by mathematical modeling. Figure 22 shows a SEM picture of ordered Fe nanorings evaporated over an annealed 540-nm PS latex mask. The outer diameter of single rings is 150 nm and the width of the rings is 20–30 nm.[49]

Computer simulations that showed the possibility of creating periodic arrays of any other geometrical shapes confirmed all experimental results. Some examples are given in Figure 23.[49]
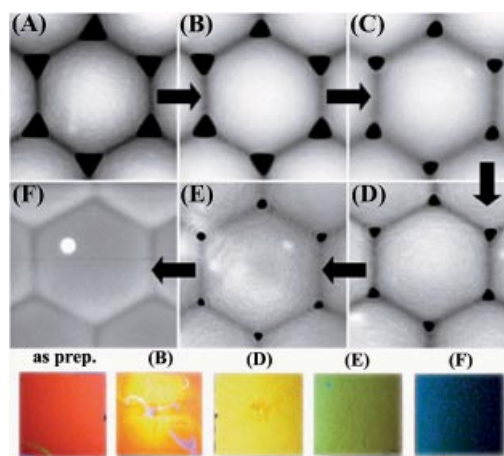

Figure 21. Change of interstices and interferometric color of a 540-nm PS latex mask annealed in 25 mL water/ethanol/ acetone mixture by (A) 1, (B) 2, (C) 4, (D) 6, (E) 7, and (F) 10 microwave pulses (redrawn with permission from ref.[49]).
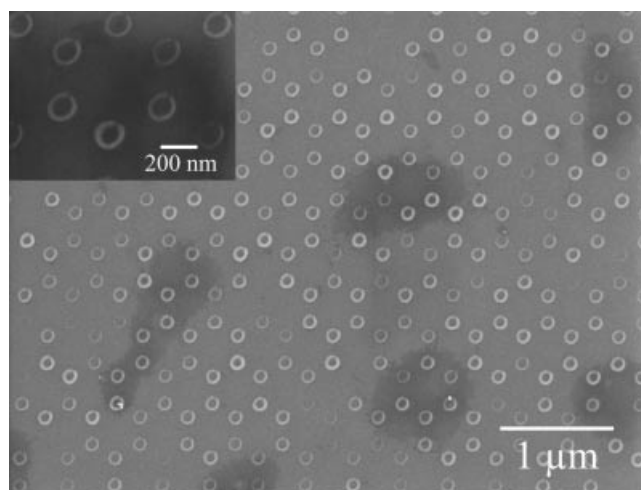

Figure 22. SEM picture of ordered Fe nanorings evaporated over an annealed 540-nm PS latex mask. The outer diameter of the single ring is 150 nm and the width of the ring is 20–30 nm (adapted with permission from ref.[49]).

Concluding Remarks

We have presented some principles of syntheses of inorganic colloidal magnetic particles, their properties, and recent advances in preparing assembled layers thereof on different substrates. The results are, of course, not necessarily limited to magnetic particles. The only restriction for non-magnetic materials is the applicability of MDT. Furthermore, we have shown, that organic colloids, used as lithographic masks, are interesting tools for the development of mm²-sized nanostructured devices. As reduced size means increased reactivity, colloid chemistry is not able to provide solutions in all fields of device development.

Moreover, the applicability of inorganic colloidal magnetic particles is limited by their composite nature, the NSL is limited to two-dimensional structures and the quality of perfect NSL masks prepared from organic colloids is still a
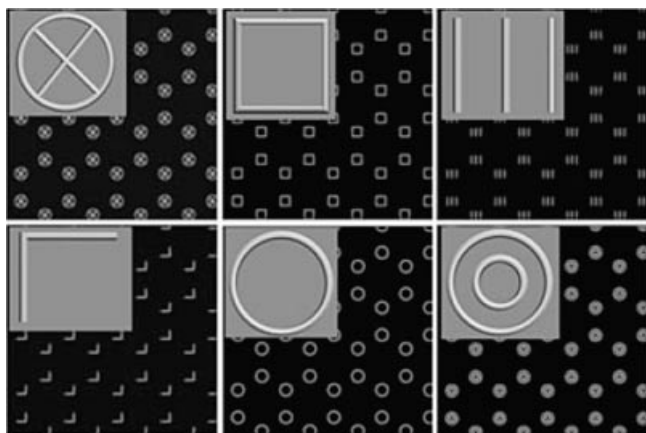
Figure 23. Computer simulation of some structures that should be available theoretically by evaporation through annealed PS masks (adapted with permission from ref.[49]).

challenge when PS latex particles $1000\ \mathrm{nm} > d > 400\ \mathrm{nm}$ are used.

Nevertheless, from the point of view of the ease of sample handling all the methods presented here have great promise in aiding the development of devices relevant to electronic, pharmaceutical, and bioscience technologies.

Acknowledgments

[1] a) C. J. Brinker, G. W. Scherer, *Sol-Gel Science*, Academic Press, San Diego, **1990**; b) H.-D. Dörfler, *Grenzflächen- und Kolloidchemie,* Wiley-VCH, Weinheim, **1994** (written in German); c) G. Schmid (Ed.), *Clusters and Colloids: From Theory to Applications*, Wiley-VCH, Weinheim, **1994**; d) J.-H. Fendler (Ed.), *Nanoparticles and Nanostructured Films*, Wiley-VCH, Weinheim, **1998**; e) H. S. Nalwa (Ed.), *Handbook of Surfaces and Interfaces of Materials*, Academic Press, San Diego, **2001**; f) P. Moriarty, *Rep. Prog. Phys.* **2001**, *64*, 297–381; g) L. M. Liz-Marzan, D. Norris (Guest Eds.) New Aspects of Nanocrystal Research, *Mater. Res. Soc. Bull.* **2001**, *26*; h) G. Schmid (Ed.), *Nanoparticles: From Theory to Applications*, Wiley-VCH, Weinheim, **2004**.

[2] W. Ostwald, *Die Welt der vernachlässigten Dimensionen*, Steinkopf, Dresden, **1915** (written in German).

[3] a) R. E. Rosensweig, *Sci. Am.* **1982**, *247*, 124–132; b) R. E. Rosensweig, *Ferrohydrodynamics*, Dover Publishing, New York, **1998**.

[4] a) S. A. Iakovenko, A. S. Trifonov, M. Giersig, A. Mamedov, D. K. Nagesha, V. V. Hanin, E. C. Soldatov, N. A. Kotov, *Adv. Mater.* **1999**, *11*, 388–392; b) T. Fried, G. Shemer, G. Markovich, *Adv. Mater.* **2001**, *13*, 1158–1161.

[5] a) M. A. Correa-Duarte, M. Giersig, N. A. Kotov, L. M. Liz-Marzán, *Langmuir* **1998**, *14*, 6430–6435; b) F. G. Aliev, M. A. Correa-Duarte, A. Mamedov, J. W. Ostrander, M. Giersig, L. M. Liz-Marzán, N. A. Kotov, *Adv. Mater.* **1999**, *11*, 1006–1010; c) F. Caruso, M. Spasova, A. Susha, M. Giersig, R. A. Caruso, *Chem. Mater.* **2001**, *13*, 109–116; d) E. L. Bizdoaca, M. Spasova, M. Farle, M. Hilgendorff, F. Caruso, *J. Magn. Magn. Mater.* **2002**, *240*, 44–46; e) E. L. Bizdoaca, M. Spasova,

M. Farle, M. Hilgendorff, L. M. Liz-Marzan, F. Caruso, *J. Vac. Sci. Technol. A* **2003**, *21*, 1515–1518; f) M. Spasova, V. Salguei-riño-Maceira, A. Schlachter, M. Hilgendorff, M. Giersig, L. M. Liz-Márzan, M. Farle, *J. Mater. Chem.* **2005**, *15*, 2095–2098; g) F. Caruso, A. S. Susha, M. Giersig, H. Möhwald, *Adv. Mater.* **1999**, *11*, 950–953.

[6] M. Giersig, P. Mulvaney, *J. Phys. Chem.* **1993**, *97*, 6334–6336.

[7] a) M. Giersig, M. Hilgendorff, *J. Phys. D: Appl. Phys.* **1999**, *32*, L111–L113; b) M. Hilgendorff, B. Tesche, M. Giersig, *Aust. J. Chem.* **2001**, *54*, 497–501.

[8] J. Rybczynski, M. Hilgendorff, M. Giersig, in: *NATO Science Series II*, vol. 91, *Low-Dimensional Systems: Theory, Preparation, and some Applications* (Eds.: L. M. Liz-Marzán, M. Giersig), Kluwer Academic Publishers, Dordrecht, **2003**, pp. 163–172.

[9] S. H. Park, B. Gates, Y. Xia, *Adv. Mater.* **1999**, *11*, 462–466.

[10] B. Gates, Y. Xia, *Adv. Mater.* **2001**, *13*, 1605–1608.

[11] a) H. W. Deckman, J. H. Dunsmuir, *Appl. Phys. Lett.* **1982**, *41*, 377–379; b) A. Rogach, A. Susha, F. Caruso, G. Sukhorukov, A. Kornowski, S. Kershaw, H. Möhwald, A. Eychmüller, H. Weller, *Adv. Mater.* **2000**, *12*, 333–337.

[12] a) J. C. Hulteen, P. R. Van Duyne, *J. Vac. Sci. Techn. A* **1995**, *13*, 1553–1558; b) J. C. Hulteen, D. A. Treichel, M. T. Smith, M. L. Duval, T. R. Jensen, R. P. Van Duyne, *J. Phys. Chem. B* **1999**, *103*, 3854–3863; c) M. Winzer, M. Kleiber, N. Dix, R. Wiesendanger, *Appl. Phys. A* **1996**, *63*, 617–619.

[13] a) R. Micheletto, H. Fukuda, M. Ohtsu, *Langmuir* **1995**, *11*, 3333–3336; b) J. Boneberg, F. Burmeister, C. Schäfle, P. Leiderer, *Langmuir* **1997**, *13*, 7080–7084; c) F. Burmeister, W. Badowsky, T. Braun, S. Wieprich, J. Boneberg, P. Leiderer, *App. Surf. Sci.* **1999**, *144–145*, 461–466; d) F. Burmeister, C. Schäfle, B. Keilhofer, K. M. Bechinger, J. Boneberg, P. Leiderer, *Adv. Mater.* **1998**, *10*, 495–497; e) N. D. Denkov, O. D. Velev, P. A. Kralchevsky, I. B. Ivanov, H. Yoshimura, K. Nagayama, *Langmuir* **1992**, *8*, 3183–3190; f) S. Rakers, L. F. Chi, H. Fuchs, *Langmuir* **1997**, *13*, 7121–7124; g) E. Adachi, A. S. Dimitrov, K. Nagayama, *Langmuir* **1995**, *11*, 1057–1060.

[14] a) Y. Lu, Y. Yin, B. Gates, Y. Xia, *Langmuir* **2001**, *17*, 6344–6350; b) S. H. Park, Y. Xia, *Langmuir* **1999**, *15*, 266–273.

[15] F. Burmeister, C. Schäfle, T. Matthes, M. Böhmisch, J. Boneberg, P. Leiderer, *Langmuir* **1997**, *13*, 2983–2987.

[16] a) M. Giersig, M. Hilgendorff, in: *Nanoscale Materials* (Eds.: P. Kamat, L. M. Liz-Marzán), Kluwer Academic Publishers, Boston, **2003**, pp. 335–370; b) M. Hilgendorff, M. Giersig, in: *Nanoparticle Assemblies and Superstructures* (Ed.: N. Kotov), CRC Press LLC, Boca Raton, **2005**, pp. 385–409.

[17] D. L. Leslie-Pelecky, R. D. Rieke, *Chem. Mater.* **1996**, *8*, 1770–1783.

[18] C Binns, in: *Handbook of Surfaces and Interfaces of Materials,* vol. 2 (Ed.: H. S. Nalwa), Academic Press, San Diego, **2001**, pp. 357–392.

[19] M. Spasova, M. Farle, in: *NATO Science Series II*, vol. 91, *Low-Dimensional Systems: Theory, Preparation, and Some Applications* (Eds.: L. M. Liz-Marzán, M. Giersig), Kluwer Academic Publishers, Dordrecht, **2003**, pp. 173–192.

[20] M. Hilgendorff, in: *Encyclopedia of Nanoscience and Nanotechnology*, vol. 1 (Ed.: H. S. Nalwa), American Scientific Publishers, Stevenson Ranch, **2004**, pp. 213–233.

[21] a) C. B. Murray, S. Sun, H. Doyle, T. Betley, *Mater. Res. Soc. Bull.* **2001**, *26*, 985–991; b) H. Bönnemann, W. Brijoux, R. Brinkmann, E. Dinjus, T. Joussen, B. Korall, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1312–1314; c) J. Rivas, M. A. López-Quintela, M. G. Bonome, R. J. Duro, J. M. Greneche, *J. Magn. Magn. Mater.* **1993**, *122*, 1–5; d) K. S. Suslick, M. Fang, T. Hyeon, *J. Am. Chem. Soc.* **1996**, *118*, 11960–11961; e) T. W. Smith, D. Wychick, *J. Phys. Chem.* **1980**, *84*, 1621–1629.

[22] a) N. Buske, H. Sonntag, T. Götze, *Colloids Surfaces* **1984**, *12*, 195–202; b) M. Respaud, J. M. Broto, H. Rakoto, A. R. Fert, L. Thomas, B. Barbara, M. Verelst, E. Snoeck, P. Lecante, A. Mosset, J. Osuna, T. Ould Ely, C. Amiens, B. Chaudret, *Phys.*

Rev. B **1998**, *57*, 2925–2935; c) D. P. Dinega, M. G. Bawendi, *Angew. Chem. Int. Ed.* **1999**, *38*, 1788–1791; d) V. F. Puntes, K. M. Krishnan, P. Alivisatos, *Appl. Phys. Lett.* **2001**, *78*, 2187–2189; e) P. H. Hess, P. H. Parker Jr., *J. Appl. Polym. Sci.* **1966**, *10*, 1915–1927; f) E. Papirer, P. Horny, H. Balard, R. Anthore, C. Petipas, A. Martinet, *J. Colloid Interface Sci.* **1983**, *94*, 207–228; g) J. Osuna, D. de Caro, C. Amiens, B. Chaudret, E. Snoeck, M. Respaud, J.-M. Broto, A. Fert, *J. Phys. Chem.* **1996**, *100*, 14571–14574; h) C. Pathmamanoharan, A. P. Philipse, *J. Colloid Interface Sci.* **1998**, *205*, 340–353; i) J. A. Becker, R. Schäfer, R. Festag, W. Ruland, J. H. Wendorff, J. Pebler, S. A. Quaiser, W. Helbig, M. T. Reetz, *J. Chem. Phys.* **1995**, *103*, 2520–2527; j) G. N. Glavee, K. J. Klabunde, C. M. Sørensen, G. C. Hadjipanayis, *Inorg. Chem.* **1993**, *32*, 474–477; k) S. Sun, C. B. Murray, *J. Appl. Phys.* **1999**, *85*, 4325–4330; l) C. Petit, A. Taleb, M. P. Pileni, *J. Phys. Chem. B* **1999**, *103*, 1805–1810; m) J. P. Stevenson, M. Rutnakornpituk, M. Vadala, A. R. Esker, S. W. Charles, S. Wells, J. P. Dailey, J. S. Riffle, *J. Magn. Magn. Mater.* **2001**, *225*, 47–58.

[23] a) A. S. R. Hoon, M. Kilner, G. J. Russell, B. K. Tanner, *J. Magn. Magn. Mater.* **1983**, *39*, 107–110; b) N. Cordente, M. Respaud, F. Senocq, M.-J. Casanove, C. Amiens, B. Chaudret, *Nano Lett.* **2001**, *1*, 565–568; c) D. L. Leslie-Pelecky, S.-H. Kim, M. Bonder, X. Q. Zhang, R. D. Rieke, *Chem. Mater.* **1998**, *10*, 164–171; d) M. T. Reetz, M. Winter, R. Breinbauer, T. Thurn-Albrecht, W. Vogel, *Chem. Eur. J.* **2001**, *7*, 1084–1094.

[24] N. Toshima, T. Yonezawa, *New J. Chem.* **1998**, *22*, 1179–1201.

[25] a) D. B. Lambrick, N. Mason, N. J. Harris, G. J. Russell, S. R. Hoon, M. Kilner, *IEEE Trans. Magn.* **1985**, *21*, 1891–1893; b) D. B. Lambrick, N. Mason, S. R. Hoon, M. Kilner, *J. Magn. Magn. Mater.* **1987**, *65*, 257–260; c) D. B. Lambrick, N. Mason, S. R. Hoon, M. Kilner, J. N. Chapman, *IEEE Trans. Magn.* **1988**, *24*, 1644–1646; d) T. Ould Ely, C. Pan, C. Amiens, B. Chaudret, F. Dassenoy, M.-J. Casanove, A. Mosset, M. Respaud, J.-M. Broto, *J. Phys. Chem. B* **2000**, *104*, 695–702; e) M. C. Fromen, A. Serres, D. Zitoun, M. Respaud, C. Amiens, B. Chaudret, P. Lecante, M. J. Casanove, *J. Magn. Magn. Mater.* **2001**, *242–245*, 610–612; f) D. Zitoun, M. Respaud, M. C. Fromen, M. J. Casanove, P. Lecante, C. Amiens, B. Chaudret, *Phys. Rev. Lett.* **2002**, *89*, 037203(4).

[26] Y. Li, J. Liu, Y. Wang, Z. L. Wang, *Chem. Mater.* **2001**, *13*, 1008–1014.

[27] H. Ago, S. Ohshima, K. Uchida, M. Yumura, *J. Phys. Chem. B* **2001**, *105*, 10453–10456.

[28] a) M. T. Reetz, W. Helbig, S. A. Quaiser, *Chem. Mater.* **1995**, *7*, 2227–2228; b) P. M. Paulus, H. Bönnemann, A. M. van der Kraan, F. Luis, J. Sinzig, L. J. de Jongh, *Eur. Phys. J. D* **1999**, *9*, 501–504; c) H. Bönnemann, W. Brijoux, R. Brinkmann, M. Wagener, *World Patent*, Studiengesellschaft Kohle mbH. **1999**, WO 99/41758; d) H. Bönnemann, in: *Handbook of Surfaces and Interfaces of Materials*, vol. 3 (Ed.: H. S. Nalwa), Academic Press, San Diego, **2001**, pp. 41–64; e) W. Yu, Y. Wang, H. Liu, W. Zheng, *J. Mol. Catal. A* **1996**, *112*, 105–113; f) N. Nunomura, T. Teranishi, M. Miyake, A. Oki, S. Yamada, N. Toshima, H. Hori, *J. Magn. Magn. Mater.* **1998**, *177–181*, 947–948; g) N. Nunomura, H. Hori, T. Teranishi, M. Miyake, S. Yamada, *Phys. Lett. A* **1998**, *249*, 524–530; h) T. Teranishi, M. Miyake, *Chem. Mater.* **1999**, *11*, 3414–3416; i) P. Lu, T. Teranishi, K. Asakura, M. Miyake, N. Toshima, *J. Phys. Chem. B* **1999**, *103*, 9673–9682; j) J. Rivas, R. D. Sánchez, A. Fondado, C. Izco, A. J. García-Bastida, J. García-Otero, J. Mira, D. Baldomir, A. Gonzáles, I. Lado, M. A. López-Quintela, S. B. Oseroff, *J. Appl. Phys.* **1994**, *76*, 6564–6566; k) A. J. García-Bastida, R. D. Sánchez, J. García-Otero, J. Rivas, A. González-Penedo, J. Solla, M. A. López-Quintela, *Mater. Sci. Forum* **1998**, *269–272*, 919–924; l) R. D. Sánchez, M. A. López-Quintela, J. Rivas, A. González-Penedo, A. J. García-Bastida, C. A. Ramos, R. D. Zysler, S. Ribeiro-Guevara, *J. Phys.: Condens. Matter* **1999**, *11*, 5643–5654; m) N. Duxin, N. Brun, P. Bonville, C. Colliex, M. P. Pileni, *J. Phys. Chem. B* **1997**, *101*,

8907–8913; n) N. Duxin, N. Brun, C. Colliex, M. P. Pileni, *Langmuir* **1998**, *14*, 1984–1989; o) E. E. Carpenter, C. T. Seip, C. J. O'Connor, *J. Appl. Phys.* **1999**, *85*, 5184–5186; p) C. J. O'Conner, V. Kolesnichenko, E. E. Carpenter, C. Sangregorio, W. Zhou, A. Kumbhar, J. Sims, F. Agnoli, *Synth. Met.* **2001**, *122*, 547–557; q) B. Ravel, E. E. Carpenter, V. G. Harris, *J. Appl. Phys.* **2002**, *91*, 8195–8197.

[29] a) B. Warne, O. I. Kasyutich, E. L. Mayes, J. A. L. Wiggins, K. K. W. Wong, *IEE Trans. Magn.* **2000**, *36*, 3009–3011; b) S. Sun, C. B. Murray, D. Weller, L. Folks, A. Moser, *Science* **2000**, *287*, 1989–1992; c) S. Yamamuro, D. Farrell, K. D. Humfeld, S. A. Majetich, *Mater. Res. Soc. Symp. Proc.* **2001**, *636*, D.10.8.1(6); d) D. Farrell, S. Yamamuro, S. A. Majetich, *Mater. Res. Soc. Symp. Proc.* **2001**, *674*, U.4.4.1(6); e) K. D. Humfeld, A. K. Giri, E. L. Venturini, S. A. Majetich, *IEEE Trans. Magn.* **2001**, *37*, 2194–2196; f) R. V. Chamberlin, K. D. Humfeld, D. Farrell, S. Yamamuro, Y. Ijiri, S. A. Majetich, *J. Appl. Phys.* **2002**, *91*, 6961–6963; g) S. Yamamuro, D. Farrell, S. A. Majetich, *Phys. Rev. B* **2002**, *65*, 224431(9); h) M. Chen, D. E. Nikles, *Nano Lett.* **2002**, *2*, 211–214; i) M. Chen, D. E. Nikles, *J. Appl. Phys.* **2002**, *91*, 8477–8479; j) K. Ono, Y. Kakefuda, R. Okuda, Y. Ishii, S. Kamimura, A. Kitamura, M. Oshima, *J. Appl. Phys.* **2002**, *91*, 8480–8482; k) E. V. Shevchenko, D. V. Talapin, A. Kornowski, F. Wiekhorst, J. Kötzler, M. Haase, A. L. Rogach, H. Weller, *Adv. Mater.* **2002**, *14*, 287–290; l) E. V. Shevchenko, D. V. Talapin, A. L. Rogach, A. Kornowski, H. Weller, *J. Am. Chem. Soc.* **2002**, *124*, 11480–11485; m) J.-I. Park, J. Cheon, *J. Am. Chem. Soc.* **2001**, *123*, 5743–5746; n) N. S. Sobal, M. Hilgendorff, H. Möhwald, M. Giersig, M. Spasova, T. Radetic, M. Farle, *Nano Lett.* **2002**, *2*, 621–624; o) M. Spasova, T. Radetic, N. Sobal, M. Hilgendorff, U. Wiedwald, M. Farle, M. Giersig, U. Dahmen, *Mater. Res. Soc. Symp. Proc.* **2002**, *721*, 195–200; p) N. S. Sobal, U. Ebels, H. Möhwald, M. Giersig, *J. Phys. Chem. B* **2003**, *107*, 7351–7354; q) N. S. Sobal, M. Giersig, *Aust. J. Chem.* **2005**, *58*, 307–310.

[30] R. Massart, V. Cabuil, *J. Chim. Phys.* **1987**, *84*, 967–973, (in french).

[31] a) R. V. Upadhyay, K. J. Davies, S. Wells, S. W. Charles, *J. Magn. Magn. Mater.* **1995**, *139*, 249–254; b) K. J. Davies, S. Wells, R. V. Upadhyay, S. W. Charles, K. O'Grady, M. El Hilo, T. Meaz, S. Mørup, *J. Magn. Magn. Mater.* **1995**, *149*, 14–18; c) P. C. Fannin, S. W. Charles, J. L. Dormann, *J. Magn. Magn. Mater.* **1999**, *201*, 98–101.

[32] a) M.-P. Pileni, *Adv. Funct. Mater.* **2001**, *11*, 323–336; b) L. Liz, M. A. López Quintela, J. Mira, J. Rivas, *J. Mater. Sci.* **1994**, *29*, 3797–3801; c) J. A. López Pérez, M. A. López Quintela, J. Mira, J. Rivas, S. W. Charles, *J. Phys. Chem. B* **1997**, *101*, 8045–8047.

[33] a) K. J. Davies, S. Wells, S. W. Charles, *J. Magn. Magn. Mater.* **1993**, *122*, 24–28; b) I. Mălăescu, L. Gabor, F. Claici, N. Ştefu, *J. Magn. Magn. Mater.* **2000**, *222*, 8–12; c) T. Fried, G. Shemer, G. Markovich, *Adv. Mater.* **2001**, *13*, 1158–1161.

[34] S. Sun, H. Zeng, *J. Am. Chem. Soc.* **2002**, *124*, 8204–8205.

[35] a) K. R. Brown, M. J. Natan, *Langmuir* **1998**, *14*, 726–728; b) N. R. Jana, L. Gearheart, C. J. Murphy, *Chem. Mater.* **2001**, *13*, 2313–2322; c) H. Yu, P. C. Gibbons, K. F. Kelton, W. E. Buhro, *J. Am. Chem. Soc.* **2001**, *123*, 9198–9199.

[36] a) T. Hyeon, S. S. Lee, J. Park, Y. Chung, H. B. Na, *J. Am. Chem. Soc.* **2001**, *123*, 12798–12801; b) J. Park, K. An, Y. Hwang, J.-G. Park, H.-J. Noh, J.-Y. Kim, J.-H. Park, N.-M. Hwang, T. Hyeon, *Nat. Mater.* **2004**, *3*, 891–895.

[37] F. X. Redl, C. T. Black, G. C. Papaefthymiou, R. L. Sandstrom, M. Yin, H. Zeng, C. B. Murray, S. P. O'Brian, *J. Am. Chem. Soc.* **2004**, *126*, 14583–14599.

[38] D. V. Talapin, A. L. Rogach, M. Haase, H. Weller, *J. Phys. Chem. B* **2001**, *105*, 12278–12285.

[39] C. B. Murray, S. Sun, W. Gaschler, H. Doyle, T. A. Betley, C. R. Kagan, *IBM J. Res. Dev.* **2001**, *45*, 47–56.

[40] D. Lacoste, T. C. Lubensky, *Phys. Rev. E* **2001**, *64*, 41506(8).

[41] Y. Chushkin, L. Chitu, S. Luby, E. Majkova, A. Satka, V. Holy, J. Ivan, M. Giersig, M. Hilgendorff, T. Metzger, O. Konovalov, *Mater. Res. Soc. Symp. Prog.* **2005**, *877*, accepted.

[42] a) V. Germain, J. Richardi, D. Ingert, M. P. Pileni, *J. Phys. Chem. B* **2005**, *109*, 5541–5547; V. Germain, M. P. Pileni, *J. Phys. Chem. B* **2005**, *109*, 5548–5553.

[43] P. Beecher, E. V. Shevchenko, H. Weller, A. J. Quinn, G. Redmond, *Adv. Mater.* **2005**, *17*, 1080–1083.

[44] a) J. H. Fendler, *Chem. Mater.* **1996**, *8*, 1616–1624; b) G. Decher, *Science* **1997**, *277*, 123–127; c) T. Cassagneau, T. E. Mallouk, J. H. Fendler, *J. Am. Chem. Soc.* **1998**, *120*, 7848–7859; d) G. B. Sukhorukov, E. Donath, H. Lichtenfeld, E. Knippel, M. Knippel, A. Budde, H. Mohwald, *Colloid. Surf. A* **1998**, *137*, 253–266; e) G. B. Sukhorukov, E. Donath, S. Davis, H. Lichtenfeld, F. Caruso, V. I. Popov, H. Möhwald, *Polym. Adv. Technol.* **1998**, *9*, 759–767; f) F. Caruso, R. A. Caruso, H. Möhwald, *Science* **1998**, *282*, 111–1114; g) J. Schmitt, P. Mächtle, D. Eck, H. Möhwald, C. A. Helm, *Langmuir* **1999**, *15*, 3256–3266; h) B. H. Sohn, B. H. Seo, *Chem. Mater.* **2001**, *13*, 1752–1757.

[45] X. Xu, G. Friedman, K. D. Humfeld, S. A. Majetich, S. A. Asher, *Adv. Mater.* **2001**, *13*, 1681–1684.

[46] a) K. Wormuth, *J. Colloid Interface Sci.* **2001**, *241*, 366–377; b) Y. Deng, L. Wang, W. Yang, S. Fu, A. Elaïssari, *J. Magn. Magn. Mater.* **2002**, *257*, 69–78.

[47] a) Z. P. Huang, D. L. Carnahan, J. Rybczynski, M. Giersig, M. Sennett, D. Z. Wang, J. G. Wen, K. Kempa, Z. F. Ren, *Appl. Phys. Lett.* **2003**, *82*, 460–462; b) J. Rybczynski, M. Giersig, *Nano Lett.* **2003**, *3*, 13–18.

[48] A. Kosiorek, W. Kandulski, P. Chudzinski, K. Kempa, M. Giersig, *Nano Lett.* **2004**, *4*, 1359–1363.

[49] A. Kosiorek, W. Kandulski, H. Glaczynska, M. Giersig, *Small* **2005**, *1*, 439–444.