Synthesis of Nanosized Magnetic Ferrite Particles Inside Hollow Polyelectrolyte Capsules

Dmitry G. Shchukin,* Igor L. Radtchenko, and Gleb B. Sukhorukov

Max Planck Institute of Colloids and Interfaces, D14424 Potsdam/Golm, Germany

Received: July 15, 2002; In Final Form: October 22, 2002

Different ferrites ($CoFe_2O_4$, $ZnFe_2O_4$, $MnFe_2O_4$) and magnetite were synthesized from corresponding salts exclusively inside poly(styrenesulfonate)/poly(allylamine hydrochloride) polyelectrolyte capsules of 10 μm diameter. Polyelectrolyte capsules with synthesized ferrite (magnetite) particles possess enough magnetic activity to be easily manipulated in water solution by an external magnetic field. These composites were characterized by TEM, SEM, and WAXS techniques. The influence of the initial concentration of inorganic salts and inner capsule composition on the characteristics of the resulting inorganic precipitates was investigated.

Introduction

A continued interest in the synthesis of inorganic compounds with well-defined properties such as shape, size, polymorph modification, etc. exists in inorganic chemistry and material science. Inorganic materials produced by this mode will have advantages in areas of application where uniform size distribution and specific surface and bulk properties are key factors. There are a number of approaches to control different synthetic parameters for achieving these goals. Examples of them include

(i) control of reaction conditions (temperature, concentration of reagents, pressure) during the formation of inorganic materials,[1−3]

(ii) usage of organic additives such as biopolymers, surfactants, polyelectrolytes, and block copolymers forming supramolecular templates to modify the crystallization process,[4−7] and

(iii) strategies based on the utilization of the restricted (microscale as well as nanoscale) reaction environment.[8−13]

In the last approach different systems such as vesicles,[8−10] proteins,[12] and reverse micelles[13] were utilized for producing nanoscale metal or metal oxide particles. Hollow polyelectrolyte capsules, introduced in refs 14 and 15 (for review, see ref 16) as an extension of polyelectrolyte multilayers on the flat surfaces,[17,18] can also act as microreactors for spatially restricted inorganic synthesis. These capsules are made by layer-by-layer adsorption of oppositely charged polyelectrolytes on the surface of colloidal template particles[19] of 0.1−10 μm diameter with sequential removal of the template core. A great variety of materials including synthetic and natural polyelectrolytes,[20] proteins,[21−23] multivalent ions,[24] inorganic and organic nanoparticles,[25,26] and lipids[27] were used to build walls of hollow capsules. Many of them can be functionalized to provide special surface properties of technical or biological relevance. Capsules can be filled by either using encapsulated material as template[28−30] or incorporating material inside the hollow capsule by precipitation[31] or polymer synthesis.[32] The permeability of the capsule walls can be controlled by changing solvents,[33] ionic strength, and pH.[34] Capsules might be applied as microscale containers for delivery of inorganic and organic matter, e.g. drugs, colloidal particles, macromolecules. For this purpose they are given

defined fluorescent or magnetic characteristics by embedding quantum dot nanoparticles inside capsules,[35] using magnetite nanoparticles as one of the components of the polyelectrolyte shell introduced by alternating adsorption with polyions[20,36−38] or by permeability regulation.[39] These capsules carrying important material inside can be driven by external magnetic fields to deliver it to certain sites. However, procedures of magnetizing capsules described previously have several restrictions in terms of types of adsorbed magnetic particles, their quantity, and core decomposition conditions.

The presence of the polyelectrolytes such as poly(styrenesulfonate) and poly(allylamine hydrochloride) either inside or outside the capsule causes a pH gradient across the capsule shell.[40] This phenomenon can be utilized to perform selective physicochemical processes in the capsule interior (e.g., pH-sensitive dye precipitation[31] or inorganic synthesis[41,42]).

In this paper the formation of different magnetic ferrites ($CoFe_2O_4$, $ZnFe_2O_4$, $MnFe_2O_4$) and magnetite (Fe_3O_4) exclusively inside poly(allylamine hydrochloride)-loaded polyelectrolyte capsules of micron scale without any traces of precipitates in the surrounding media is accomplished by employing gradients in the pH across the capsule wall as the main force for performing the reaction. The deposition of magnetic materials within the capsule interior is carried out from the corresponding inorganic salts and their mixtures. To examine the resulting ferrite (magnetite)/polyelectrolyte capsule composites, SEM, TEM, and WAXS techniques are employed. The influence of the initial concentration of the inorganic precursors as well as of the positively charged PAH molecules on the precipitation process and final characteristics of the resulting magnetic composites is also investigated.

Experimental Section

Materials. Sodium poly(styrenesulfonate) (PSS, MW ∼ 70 000), poly(allylamine hydrochloride) (PAH, MW ∼ 50 000), rhodamine isothiocyanate, and citric acid were obtained from Aldrich. For the synthesis of the magnetic ferrites $Fe_2(SO_4)_3 \cdot 7H_2O$, $MnSO_4 \cdot H_2O$, $CoSO_4 \cdot 3.5H_2O$, $ZnSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 7H_2O$, and NaOH were utilized. These chemicals were all purchased from Fluka. Monodispersed weakly cross-linked melamine formaldehyde particles (MF) with a diameter of 5.6 μm were employed as template cores for polyelectrolyte shell assembly and purchased from Microparticles GmbH (Berlin, Germany).

* To whom correspondence should be addressed. E-mail: Dmitry.Shchukin@mpikg-golm.mpg.de. Tel.: +49-331-567-9428. Fax: +49-331-567-9202.

Nanosized Magnetic Ferrite Particles

J. Phys. Chem. B, Vol. 107, No. 1, 2003 **87**

All chemicals except PSS were used as received. PSS was dialyzed against Milli-Q water using a Spectra/Por membrane (MWCO: 14 000) and then lyophilized. The water used in all experiments was prepared in a three-stage Millipore Milli-Q Plus 185 purification system and had a resistivity higher than 18 MΩ·cm.

Formation of Polyelectrolyte Capsules. Hollow PAH/PSS capsules containing 0.1 M of PAH monomers inside were prepared in two steps. At first a mixture of MF suspension (5×10^8 cm^{-3}) with 5×10^{-3} M solution of citric acid was made and then the PAH solution (1 mg/mL) was dropped (10 μL each droplet) into the continuously stirred MF/citric acid mixture until the final PAH concentration reached a certain value high enough for the formation of approximately 80 monolayers on the MF particle surface (ca. 1.5 mL of PAH solution per 1 mL of MF/citric acid mixture[14]). Because of poor stability of the deposited PAH/citrate complex against acidic (<1) and basic (>10) pH the assembly of stable polyelectrolyte PAH/PSS multilayers on the top of the obtained MF/PAH particles was further performed by applying the layer-by-layer technique.[37] After formation of PAH/PSS shells the MF core was dissolved in 0.1 M HCl and hollow capsules composed of inner PAH/citrate shell and outer PAH/PSS one were formed. To dissolve the inner PAH/citrate shell, the capsules were then exposed to 2 M NaCl solution for 7 days; after washing, freely floating PAH molecules were uniformly distributed inside the polyelectrolyte capsule,[43] which undergoes osmotic swelling up to 10 μm in diameter, as confirmed by confocal fluorescence microscopy. A more detailed description of the synthesis of hollow PAH/PSS capsules can be found elsewhere.[15,16]

Characterization. Scanning electron microscopy (Zeiss DSM 940 instrument) and confocal laser scanning microscopy (Leica TCS SP equipped with a 100x oil immersion objective) were used for the investigation of the original structure of the synthesized polyelectrolyte shell/ferrite core particles. To view the nanoparticles composing the interior of the capsules, the samples were embedded in LR-White resin and then ultrathin sections (30−100 nm in thickness) were obtained using a Leica ultracut UCT ultramicrotome. Carbon or noncoated copper grids were used to support the thin sections and a Zeiss EM 912 Omega transmission electron microscope was employed for analysis. The crystal structure of the resulting ferrites and magnetite was determined from wide-angle X-ray scattering, Enraf-Nonius PDS-120.

The pH gradient between the surrounding solution and the interior of PAH-loaded capsules was evaluated from the fluorescence intensity of rhodamine molecules placed inside the capsules.[41] In these measurements a Fluorolog Spex spectrofluorometer was used. Excitation was performed at 492 nm.

Results and Discussion

The PAH/PSS shells are known as permeable toward multivalent ions and small organic molecules whereas large polymer molecules such as PAH can be entrapped inside.[40] Capture of the cationic PAH leads to establishing a pH gradient across the capsules.[41] Due to electroneutrality in inner capsule micronsized volume,[40] the hydroxide anions OH$^-$ act as counterions for PAH. Exposing PAH-containing capsules to 0.01 M NaOH solution leads to the deprotonation of the PAH amine groups and increasing pH inside the capsules. After washing in distilled water, the PAH molecules buffer capsule interior keeping hydroxide ions. The presence of OH$^-$ ions maintains the pH value inside the capsule close to the pK of PAH. As estimated in ref 41, the pH value in the capsules filled with 0.1 monoM
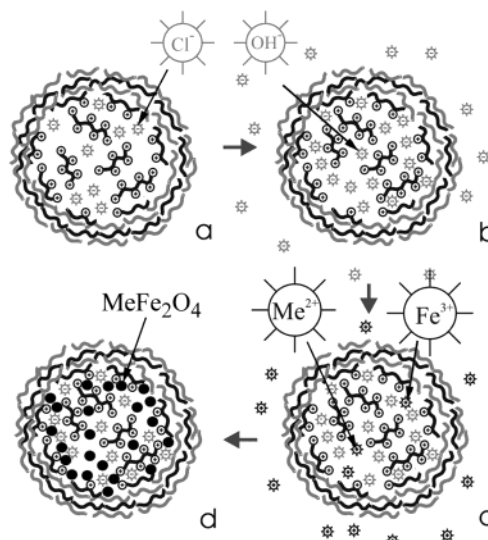

Figure 1. Schematic illustration of the selective inorganic synthesis inside polyelectrolyte capsules. Me^{2+} is Co^{2+}, Mn^{2+}, Zn^{2+}, or Fe^{2+} cation.

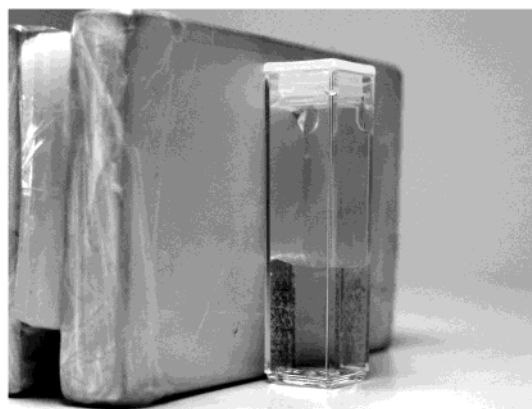**Figure 2.** Photograph of the CoFe$_2$O$_4$-filled polyelectrolyte capsules attached to the permanent magnet (Nd−Fe−B magnet, Reihnmagnet GmbH).

PAH is about 8.8 in pure water. The presence of salt partially equalizes the pH difference inside and outside.[40] However, due to certain buffer capacity of encapsulated PAH, there is always higher pH inside that outside.

The pH gradient between the capsule interior and surrounding solution is a major cause of the selective deposition from corresponding inorganic salts of magnetic ferrites and Fe$_3$O$_4$ only inside the capsules. Figure 1 illustrates a schematic overview of the deposition procedure. The precipitation of magnetic ferrites (CoFe$_2$O$_4$, MnFe$_2$O$_4$, ZnFe$_2$O$_4$) and magnetite (Fe$_3$O$_4$) inside PAH/PSS capsules was carried out as follows: at first polyelectrolyte capsules were immersed in 0.01 M NaOH for 4 h (Figure 1a,b); then, after washing, 3 mL of 0.1 M MeSO$_4$ (Me = Mn, Co, or Zn) + 0.2 M Fe$_2$(SO$_4$)$_3$ solution was added to 200 μL of suspension containing 5% v/v of capsules for 6 h (Figure 1c,d). In the case of magnetite precipitation the concentration of precursor salts was varied from 0.66 M FeSO$_4$ + 0.62 M Fe$_2$(SO$_4$)$_3$ to 10^{-4} M FeSO$_4$ + 9.4×10^{-5} Fe$_2$(SO$_4$)$_3$, keeping the Fe(II):Fe(III) ratio at a constant level. After synthesis, the excess of metal cations was removed from the bulk solution by repeated magnetic decantation. As shown in Figure 2, the resulting precipitates possess magnetic properties and can be easily attracted from water solution by an external magnetic field.
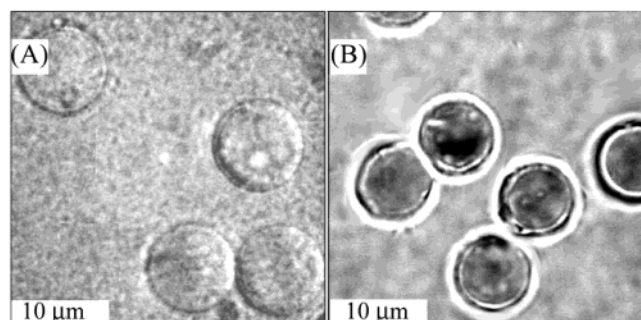
Figure 3. Transmission microscopy images of polyelectrolyte capsules in water (a) and during the reaction in solution containing a mixture of precursor salts (0.66 M $FeSO_4$ + 0.62 M $Fe_2(SO_4)_3$) (b). A 100× oil immersion objective was employed; the aperture was the same for both images.
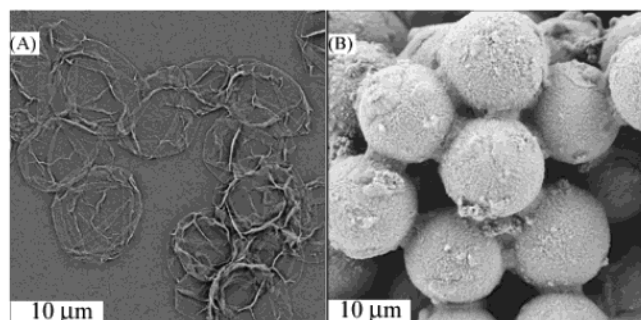

Figure 4. SEM images of hollow polyelectrolyte capsules (a) and polyelectrolyte capsules filled with Fe_3O_4 (b, deposited from 0.66 M $FeSO_4$ + 0.62 M $Fe_2(SO_4)_3$ solution).

It is important to point out that the selective precipitation inside polyelectrolyte capsules loaded with PAH occurs not only because of the differences in pH but also due to specific interaction between PAH molecules and dissolved metal cations. Addition of acidic PAH solution (pH = 0.8) in the absence of polyelectrolyte capsules to the 1 M $FeSO_4$ + 0.92 M $Fe_2(SO_4)_3$ solution having the same pH promotes the appearance of the Fe_3O_4 sol. The influence of PAH on the rate of the hydrolysis can be explained by incorporation of the PAH molecule into the hydrate shell of the Fe^{3+} ion producing an unstable PAH−Fe^{3+} complex, which then readily decomposes with the formation of the hydroxide. Adding polyelectrolytes with functional groups capable of acting as ligands for metal ions decreases of the minimum pH, at which the hydrolysis starts for this metals and leads to formation of unstable metal complexes.[44−46]

A transmission microscopy image of capsules in solution containing appropriate precursor salts ($Fe_2(SO_4)_3$ and $FeSO_4$) is shown in Figure 3. It is seen that the capsules become dark after the addition of precursor salts and magnetite formation occurs exclusively inside the capsules without any traces of the precipitate in the surrounding solution (as confirmed by light scattering analysis of precursor solution after the reaction). The presence of dissolved PAH inside the capsules is an ultimate condition for performing the reaction and the precipitation does not occur when hollow capsules without PAH are used. A typical SEM image of polyelectrolyte capsules filled with Fe_3O_4 is shown in Figure 4. Dried Fe_3O_4/PAH/PSS capsules have a rough surface reproducing the shape of the inorganic core. Inorganic material in the capsule interior also prevents capsule collapse during drying, which is typical for empty polyelectrolyte capsules without inorganic or organic interior frame (Figure 4a), maintaining original bulky shape (Figure 4b).

To investigate the inner structure and particle size of precipitated magnetic compounds, filled polyelectrolyte capsules were ultramicrotomed and analyzed using TEM (Figures 5 and
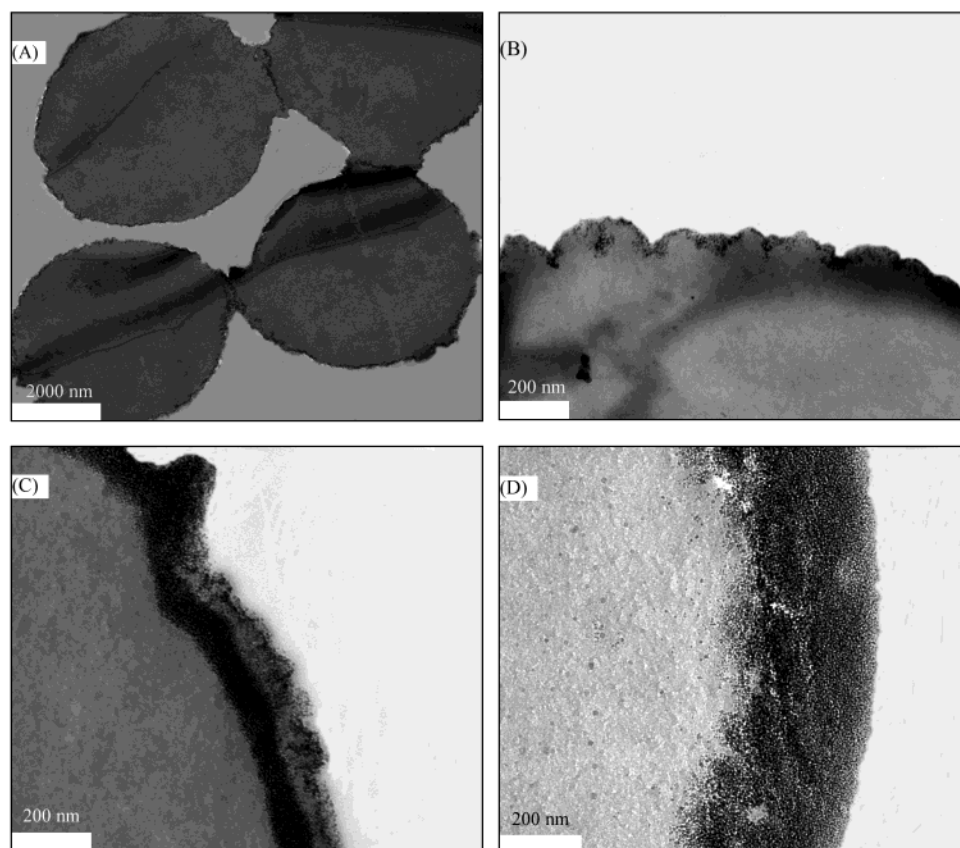

Figure 5. TEM images of polyelectrolyte capsules filled with $ZnFe_2O_4$ (a, b), $MnFe_2O_4$ (c), and $CoFe_2O_4$ (d) deposited from 0.1 M $MeSO_4$ (Me = Mn, Co, or Zn) + 0.2 M $Fe_2(SO_4)_3$ solution.

Nanosized Magnetic Ferrite Particles
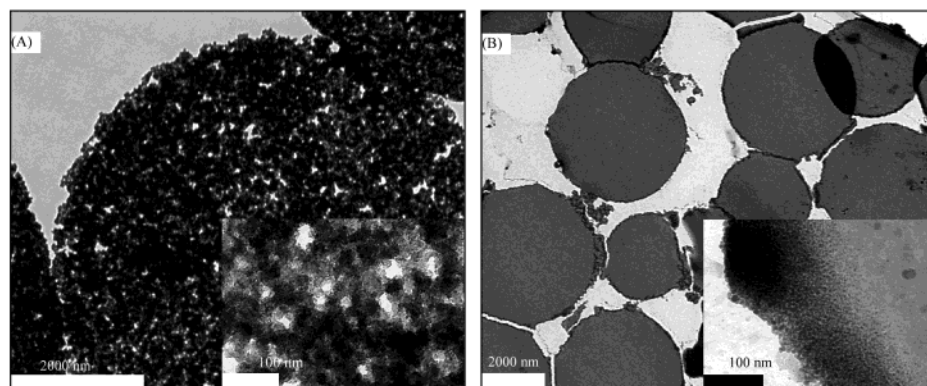
J. Phys. Chem. B, Vol. 107, No. 1, 2003 **89**

Figure 6. TEM images of polyelectrolyte capsules with Fe_3O_4 formed from 0.66 M $FeSO_4$ + 0.62 M $Fe_2(SO_4)_3$ (a) and 0.01 M $FeSO_4$ + 0.0092 M $Fe_2(SO_4)_3$ (b) solutions.

6). The deposition of the magnetic ferrites and magnetite from moderately concentrated solutions of inorganic precursors (0.1 M $MeSO_4$ (Me = Mn, Co, or Zn) + 0.2 M $Fe_2(SO_4)_3$) occurs on the inner side of the PAH/PSS wall (Figure 5) where PAH molecules, which make the first layer of PAH/PSS shell, are at the highest concentration. If the initial concentration of the precursor salts is increased, both the quantity and particle size of the formed magnetic material will also be increased. Almost total filling of the capsule interior with Fe_3O_4 aggregates of particles with average size 25−30 nm was observed (Figure 6a) when concentrated 0.66 M $FeSO_4$ + 0.62 M $Fe_2(SO_4)_3$ precursor solution was used for the precipitation. On the other hand, decreasing the precursor concentrations reduces the amount of inorganic material deposited on the inner side of the PAH/PSS wall (for 0.01 M $FeSO_4$ + 0.0092 M $Fe_2(SO_4)_3$ mixture see Figure 6b) and, at a concentrations below 10^{-5} M, the formation of ferrites or magnetite inside the polyelectrolyte capsules does not occur.

In view of the results described, it can be suggested that ferrite (magnetite) deposition and capsule filling is performed in the radial direction from the wall to the center of the capsule. At small concentrations of inorganic salts, the reaction proceeds presumably near the capsule wall, where the hydrolysis reaction starts; further increasing the precursor concentration results in gradual filling of the capsule interior.

The identification of the synthesized magnetic ferrites ($CoFe_2O_4$, $ZnFe_2O_4$, $MnFe_2O_4$) and magnetite was performed using the wide-angle X-ray scattering technique. As shown in Figure 7, the obtained magnetic compounds are weakly ordered magnetic ferrites of the corresponding metals and magnetite with traces of nonmagnetic individual metal oxides and α-Fe_2O_3. The crystallite size, estimated from the broadening of the XRD peaks, varies within the range 8−12 nm, which is in good agreement with the particle size estimated from TEM images.

Conclusions

We demonstrated that complex inorganic oxides ($CoFe_2O_4$, $ZnFe_2O_4$, $MnFe_2O_4$, Fe_3O_4) possessing magnetic properties without additional annealing could be synthesized inside hollow polyelectrolyte capsules of 10 μm diameter. Depending on the initial concentration of inorganic salts, ferrites and magnetite are formed gradually in the radial direction from the inner side of the capsule wall to the capsule center. It was established that the presence of PAH dissolved in the capsule interior is necessary for the formation of metal oxides from salt precursors. The PAH dissolved creates a pH gradient across the capsule wall. However, the specific interaction between PAH molecules and aqua complexes of metal cations resulting in the formation
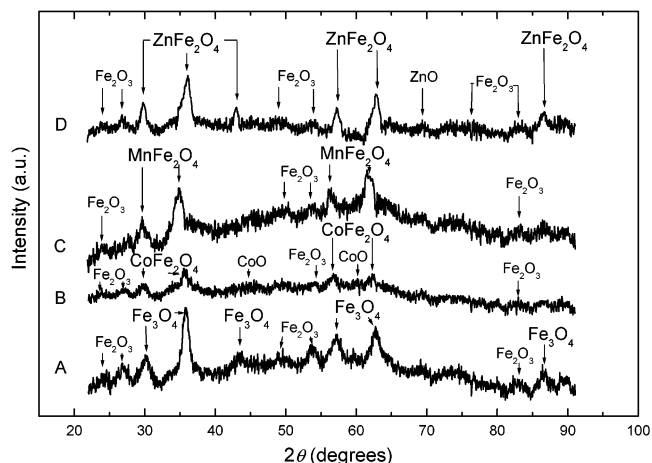

Figure 7. XRD patterns of the synthesized magnetite (a), $CoFe_2O_4$ (b), $MnFe_2O_4$ (c), and $ZnFe_2O_4$ (d). Arrows indicate peak positions corresponding to certain metal oxides. Peak assignment was made using the Powder Diffraction Database (http://merkur. mpikg-golm.mpg.de/pdf2/).

of metal oxide should also be taken into consideration. The developed approach of magnetite and ferrite synthesis inside polyelectrolyte capsules illustrates possibilities for using these capsules in spatially restricted inorganic synthesis. The influence of the micron-scale volume and capsule content on performing chemical reactions as well as on the structure and properties of the final product is a subject for further investigation.

References and Notes

(1) Goia, D. V.; Matijevic, E. *New J. Chem.* **1998**, *98*, 1203.
(2) Matijevic, E. *Chem. Mater.* **1993**, *5*, 412.
(3) Sugimoto, T. *Adv. Colloid Interface Sci.* **1987**, *28*, 65.
(4) Heuer, A. H.; Fink, D. J.; Laraia, V. J.; Arias, J. L.; Calvert, P. D.; Kendall, K.; Messing, G. L.; Blackwell, J.; Rieke, P. C.; Thompson, D. H.; Wheeler, A. P.; Veis, A.; Caplan, A. I. *Science* **1992**, *255*, 1098.
(5) Addadi, L.; Weiner, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 153.
(6) Antonietti, M. *Curr. Opin. Colloid Interface Sci.* **2001**, *6*, 244.
(7) Cölfen, H.; Qi, L. M. *Chem.−Eur. J.* **2001**, *7*, 106.
(8) Mann, S.; Hannington, J. P.; Williams, R. J. P. *Nature* **1986**, *324*, 565.
(9) Tricot, Y.-M.; Fendler, J. H. *J. Phys. Chem.* **1986**, *90*, 3369.

(10) Bhandarker, S.; Bose, A. *J. Colloid Interface Sci.* **1990**, *135*, 531.

(11) Meldrum, F. C.; Wade, V. J.; Nimmo, D. L.; Heywood, B. R.; Mann, S. *Nature* **1991**, *349*, 684.

(12) Bronstein. L.; Kraemer, E.; Berton, B.; Burger, C.; Foerster, S.; Antonietti, M. *Chem. Mater.* **1999**, *11*, 1402.

(13) O'Connor, C. J.; Kolesnichenko, V.; Carpenter, E.; Sangregorio, C.; Zhou, W.; Kumbhar, A.; Sims, J.; Agnoli, F. *Synth. Met.* **2001**, *122*, 547.

(14) Sukhorukov, G. B.; Donath, E.; Davis, S.; Lichtenfeld, H.; Caruso, F.; Popov, V. I.; Mohwald, H. *Polym. Adv. Technol.* **1998**, *9*, 759.

(15) Donath, E.; Sukhorukov, G. B.; Caruso, F.; Davis, S.; Möhwald, H. *Angew. Chem. Int. Ed.* **1998**, *37*, 2202.

(16) Sukhorukov, G. B. Designed Nano-engineered Polymer Films on Colloidal Particles and Capsules. In *Novel Methods to Study Interfacial Layers*; Mobius, D., Miller, R., Eds.; Elsevier Science B.V.: Amsterdam, 2001; pp 384−414.

(17) Decher, G.; Hong, J. D.; Schmitt, J. *Thin Solid Films* **1992**, *210/211*, 831.

(18) Decher, G. *Science* **1997**, *277*, 1232.

(19) Sukhorukov, G. B.; Donath, E.; Lichtenfeld, H.; Knippel, M.; Budde, A.; Möhwald, H. *Colloids Surf. A* **1998**, *137*, 253.

(20) Sukhorukov, G. B.; Donath, E.; Moya, S.; Susha, A. S.; Voigt, A.; Hartmann, J.; Mohwald, H. *J. Microencapsulation* **2000**, *17*, 177.

(21) Caruso, F. *Chem. Eur. J.* **2000**, *6*, 413.

(22) Prokop, A.; Hunkeler, D.; DiMari, S. *Adv. Polym. Sci.* **1998**, *136*, 1

(23) Schüler, C.; Caruso, F. *Biomacromolecules* **2001**, *2*, 921.

(24) Radtchenko, I. L.; Sukhorukov, G. B.; Leporatti, S.; Khomutov, G. B.; Donath, E.; Möhwald, H. *J. Colloid Interface Sci.* **2000**, *230*, 272.

(25) Caruso, F.; Caruso, R. A.; Möhwald, H. *Science* **1998**, *282*, 1111.

(26) Caruso, F.; Lichtenfeld, H.; Giersig, M.; Möhwald, H. *J. Am. Chem. Soc.* **1998**, *120*, 8523.

(27) Moya, S.; Donath, E.; Sukhorukov, G. B. *Macromolecules* **2000**, *33*, 4538.

(28) Balabushevitch, N. G.; Sukhorukov, G. B.; Moroz, N. A.; Donath, E.; Möhwald, H. *Biotech., Bioeng.* **2001**, *76*, 207.

(29) Shi, X.; Caruso, F. *Langmuir* **2001**, *17*, 2036.

(30) Antipov, A. A.; Sukhorukov, G. B.; Donath, E.; Möhwald, H. *J. Phys. Chem. B* **2001**, *105*, 2281.

(31) Sukhorukov, G.; Dähne, L.; Hartmann, J.; Donath, E.; Möhwald, H. *Adv. Mater.* **2000**, *12*, 112.

(32) Dähne, L.; Leporatti, S.; Donath, E.; Mohwald, H. *J. Am. Chem. Soc.* **2001**, *123*, 5431.

(33) Lvov, Y.; Antipov, A. A.; Mamedov, A.; Möhwald, H.; Sukhorukov, G. B. *Nano Lett.* **2001**, *1*, 125.

(34) Sukhorukov, G. B.; Antipov, A. A.; Voigt, A.; Donath, E.; Möhwald, H. *Macromol.. Rapid Commun.* **2001**, *22*, 44.

(35) Radtchenko, I. L.; Sukhorukov, G. B.; Gaponik, N.; Kornowski, A.; Rogach, A. L.; Möhwald, H. *Adv. Mater.* **2001**, *13*, 1684.

(36) Caruso, F.; Susha, A.; Giersig, M.; Mohwald, H. *Adv. Mater.* **1999**, *11*, 950.

(37) Voigt, A.; Lichtenfeld, H.; Sukhorukov, G. B.; Zastrow, H.; Donath, E.; Baumler, H.; Mohwald, H. *Ind. Eng. Chem. Res.* **1999**, *38*, 4037.

(38) Bizdoaca, E. L.; Spasova, M.; Farle, M.; Hilgendorff, M.; Caruso, F. *J. Magnetism Magnet. Mater.* **2002**, *240*, 44.

(39) Ibarz, G.; Dahne, L.; Donath, E.; Mohwald, H. *Adv. Mater.* **2001**, *13*, 1324.

(40) Sukhorukov, G. B.; Brumen, M.; Donath, E.; Möhwald, H. *J. Phys. Chem. B* **1999**, *103*, 6434.

(41) Radtchenko, I. L.; Giersig, M.; Sukhorukov, G. B. *Langmuir* **2002**, *18*, 8204.

(42) Sukhorukov, G. B.; Susha, A. S.; Davis, S.; Leporatti, S.; Donath, E.; Hartmann, J.; Möhwald, H. *J. Colloid Interface Sci.* **2002**, *247*, 251.

(43) Radtchenko, I. L.; Sukhorukov, G. B.; Mohwald, H. *Colloids Surf., A* **2002**, *202*, 127.

(44) Sokoll, L.; Robert, H. *J. Catal.* **1992**, *134*, 409.

(45) Ishikawa, T.; Takeda, T.; Kandori, K. *J. Mater. Sci.* **1992**, *27*, 4531.

(46) Napper D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic Press Inc.: London, 1983.