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Synthesis and Structure of Colloidal Bimetallic Nanocrystals: The Non-Alloying System Ag/Co

Nelli S. Sobal,^{†,‡} Michael Hilgendorff,^{*,‡} Helmuth Möhwald,[†] and Michael Giersig[‡]

Hahn-Meitner-Institut Berlin, Glienicker Strasse 100, 14109 Berlin, Germany, and Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Am Mühlenberg 1, 14476 Golm, Germany

Marina Spasova,[§] Tamara Radetic,^{||} and Michael Farle[§]

Technische Universität Braunschweig, Mendelssohnstrasse 3, 38106 Braunschweig, Germany, and The National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California

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ABSTRACT

Monodisperse bimetallic Ag/Co composite nanocrystals have been prepared using colloid chemistry methods. Transmission electron microscopy showed well isolated Ag/Co particles centered around 12 nm in diameter. The composition of the particles was determined by energy dispersive X-ray spectrometry. Bulk-like fcc-structures of both components were determined within the individual crystals using selected area electron diffraction. A Ag_{core}Co_{shell} structure of the bimetallic particles was observed by transmission electron microscopy and electron energy-loss spectroscopy.

The synthesis of ferrofluids has been state of the art for several decades because of the fluids' interesting properties for novel technological applications, e.g., new refrigerators using the magnetocaloric effect,¹ inks for inkjet printers,² novel spin valves,³ for new cancer therapies, such as hyperthermia⁴ and apheresis,⁵ and the enlargement of data storage capacity assuming that a magnetic particle of 10 nm in diameter can act as a spin up/spin down 1/0 binary code.⁶ Hence it is no wonder that the preparation of ferrofluids was intensely investigated in the past. Thousands of references and patents are listed in the magnetic fluids libraries.⁷

A decrease in the size of nanoparticles means an increase in reactivity, e.g., for oxidation and a decrease of the curie temperature of ferromagnetic (FM) materials.⁸ Most of the possible applications of ferrofluids require high remanent magnetization at room temperature, found in soft magnetic materials above a specific diameter, which depends on the material (> 10 nm for Co), and high anisotropies, found in hard magnetic materials which are usually alloys. The ability to prepare air-stable FM/noble metal (NM) bimetallic particles is therefore a challenge. Well-known ferromagnetic

alloys consisting of FM 3d- and NM elements of the platinum group are known to have large magnetic moments and large magnetic anisotropies.⁹

Ferrofluids of metallic nanocrystals are usually prepared using oil-in-water (micelles), or water-in-oil (reverse micelles) emulsion techniques.¹⁰ Another successful preparation procedure is the reduction or thermal decomposition of metal precursors in organic solvents in the presence of bulky stabilizers such as fatty acids.¹¹ As a result, ferrofluids with enhanced oxidation stability are formed. Fe-, Co-, or Ni-nanoparticles embedded in a metallic matrix were found to show a technologically important effect called giant magnetoresistance.¹² Many publications address the synthesis of Co/NM core-shell particles and alloys, but the successful preparation of these novel materials is not unambiguously verified in many cases.¹³ There are very few reports showing transmission electron microscopy (TEM) images of a core-shell structure of bimetallic NM particles combined with energy-dispersive X-ray spectrometry (EDX) and/or UV/VIS spectrometry, thereby clearly revealing the composition of core and shell.¹⁴ The determination of bimetallic core-shell particles by electron energy-loss spectroscopy (EELS) has not yet been presented to our knowledge.

Published results of TEM and magnetic measurements of Co/NM nanocrystals could also be explained assuming a

* Corresponding author: michael.hilgendorff@hmi.de.

[†] Hahn-Meitner-Institut Berlin.

[‡] Max-Planck-Institut für Kolloid- und Grenzflächenforschung.

[§] Technische Universität Braunschweig.

^{||} Lawrence Berkeley National Laboratory.

mixture of pure Co particles and pure NM particles. The high probability of an antiferromagnetic CoO shell around the Co particles could lead to magnetic properties not easily distinguished from properties of Co/NM bimetallic particles, which completes the uncertainty of published results.¹⁵

Colloid chemistry is rather complex: Small changes in synthesis procedures can give completely different results.^{8,11c,16} Moreover, the chemical synthesis of colloids can produce nanocrystals having a crystal structure never found in bulk materials. It is thought that colloid chemistry could produce alloys of elements well-known as non alloying systems in the bulk.

For our investigations we chose the Ag/Co system, which is known not to form alloys in the bulk and in thin films. Some reports about metastable phases of the Ag/Co system are available.¹⁷ Furthermore, silver perchlorate (AgClO_4) is soluble in toluene.

The scope of this journal does not allow for the discussion of different synthesis routes. Therefore, one route for the chemical synthesis of bimetallic FM/NM particles is presented along with structure investigations using (HR)TEM, EDX; EELS; selected area electron diffraction (SAED); and UV/VIS.

Here, the bimetallic colloids were prepared using standard Schlenck techniques. The method is based on the thermal decomposition of dicobalt octacarbonyl in combination with a transmetalation^{13b} reaction with water free AgClO_4 using oleic acid and tridodecylamine as surfactants following the overall reaction



As a result bimetallic Ag/Co particles were formed. The formation of $\text{Co}(\text{ClO}_4)_2$ seems to be logical from a chemical point of view but has not been verified.

In a typical synthesis, a mixture of 0.05 g (0.25 mmol) AgClO_4 , 0.085 g (0.24 mmol) $\text{Co}_2(\text{CO})_8$, 92 μL (0.40 mmol) oleic acid and 176 μL (0.27 mmol) tridodecylamine in 10 mL of deoxygenated toluene was heated under a N_2 atmosphere with vigorous stirring to 140 °C (oil bath temperature). After 30 min the dark-brown solution was cooled to room temperature and the particles were precipitated by adding ethanol to the dispersion. The supernatant was discarded by decanting. The magnetic precipitate was redispersed in 15 mL of toluene with 32 μL of oleic acid. This procedure was repeated two times without the addition of oleic acid. After this, the Co content remained constant and no chloride ions were present, as could be detected by EDX.

The composition of these nanocrystals could be controlled by varying the amount of $\text{Co}_2(\text{CO})_8$ (from 0.085 g (0.24 mmol) to 0.19 g (0.56 mmol)), while the amount of AgClO_4 remained constant. The stoichiometric ratio of both elements, given as AgCo_x , was determined by EDX after separation of the particles from " $\text{Co}(\text{ClO}_4)_2$ ".

Figure 1a shows the change of the optical density of colloidal Ag/Co solutions with increasing Co content for constant Ag concentrations. It is obvious that there is a

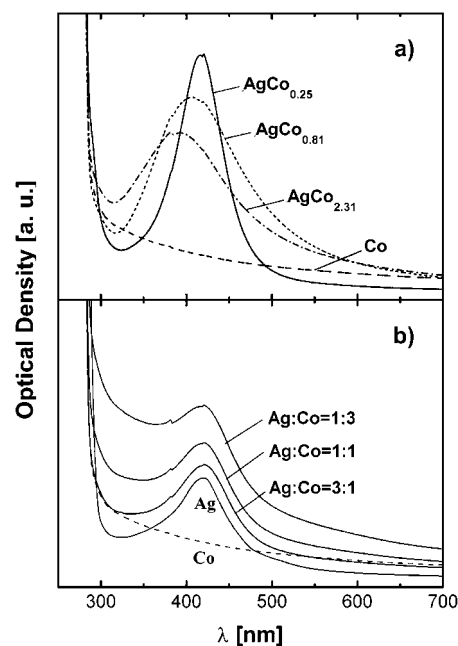


Figure 1. (a) Blue shift and quenching of the Ag plasmon band with increasing Co content for composite particles of constant Ag concentration in solution. The stoichiometric ratio is given as AgCo_x . (b) Optical density of different mixtures of pure Ag and Co particles. The size of the Ag particles (8 nm) is the same as in (a).

broadening and a blue shift of the Ag plasmon band with increasing Co content after removal of " $\text{Co}(\text{ClO}_4)_2$ " while the optical density is quenched. (The UV/VIS-spectrum of pure Co is also shown; spectra are not normalized for identical Co concentrations). A comparison with the optical spectra for mixtures of pure Co and Ag colloids (Figure 1b) indicates a strong interaction of the electrons of both elements in our composite particles. Neither a Ag/Co ratio dependent blue shift nor a broadening of the Ag plasmon wavelength is seen in Figure 1b. Quenching of the Ag-surface plasmon has been observed before, e.g. Ag-particles coated with a Au shell.^{14b}

TEM investigations were employed to obtain information about the morphology and the structure of the bimetallic particles. Figure 2 shows a typical TEM image of a monolayer of $\text{AgCo}_{0.81}$ particles on a carbon coated copper grid taken with a Philips CM12 (120 kV) at low magnification. The image demonstrates the spherical shape of the particles having a size distribution of $\sim 19\%$ determined by image analysis of about 250 particles. The core-shell structure of the particles was observable at higher magnification and can be viewed in the inset.

High-resolution TEM (HRTEM) (acceleration voltage 800 kV), SAED taken with a JEOL 3010 (300 kV), and EELS investigations with a JEOL 200CX (200 kV) equipped with a Gatan 666 EELS spectrometer (2.0 eV energy resolution) have been conducted to get information about the element distribution in the particles, their crystalline phases, and the nature of the core-shell structure.

Figure 3 shows the results of element mapping taken with EELS using the Ag $\text{M}_{4,5}$ edge and the strong white lines of

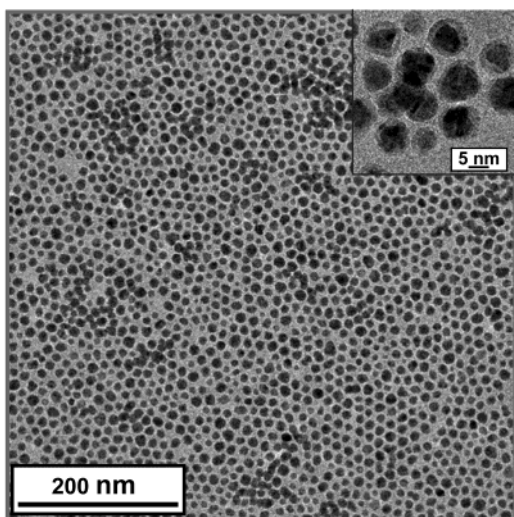


Figure 2. TEM image at low magnification of a monolayer of $\text{AgCo}_{0.81}$ particles deposited on a carbon coated copper grid by simply drying a drop of solution. The core-shell structure is visible at higher magnification (inset).

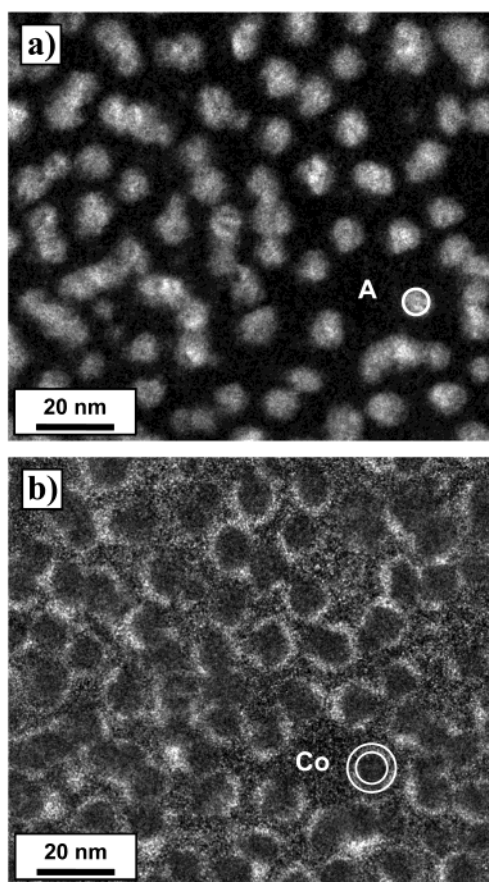


Figure 3. EELS element mapping of the Ag component (Ag $M_{4,5}$ edge) (a) and the Co component (Co $L_{2,3}$ edge) (b) in the bimetallic particles revealing an $\text{Ag}_{\text{core}}\text{Co}_{\text{shell}}$ structure. The element specific brightness of the same particle is marked by circles in both images.

the Co $L_{2,3}$ edge. The bright contrast in the images represents Ag (a) and Co (b), respectively. A typical result is an $\text{Ag}_{\text{core}}\text{Co}_{\text{shell}}$ structure with partially incomplete Co shells as can be seen in Figure 3b. The element specific brightness of the same particle is marked by circles in both images.

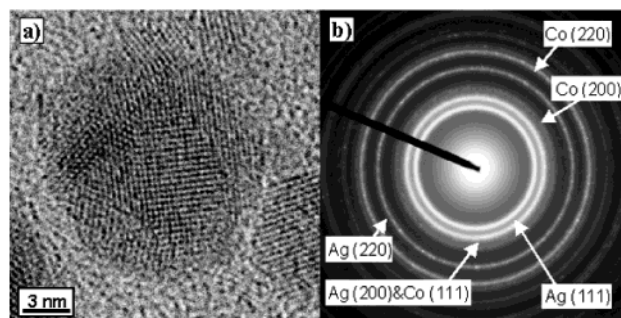


Figure 4. HRTEM image of a single polycrystalline bimetallic Ag/Co crystal showing a polycrystalline structure (a). The typical parameters of the fcc Ag phase and the Co phase could be calculated from the SAED pattern shown in 4b, taken from an ensemble of particles as presented in Figure 2.

This result can be explained by kinetically controlled crystal growth of the particles. To be more exact, the formation of “seed” Ag particles occurs before the formation of elemental Co in our synthesis. The size of the Ag core determined by TEM remained constant (8 nm, with a standard deviation $< 9\%$) while the thickness of the Co shell increased with increasing Co content in the particles. Thus there is no reason to discuss classical quantum size effects as the reason for the observed blue shift of the Ag-plasmon wavelength (Figure 1a).¹⁸

A second result was the fact that there was no evidence from EELS for the existence of CoO in the Co shell. The measured white line ratio of $L_3/L_2 = 4.0$ agrees with that of metallic Co for the particles and their surfaces.¹⁹ CoO would have given much lower values (3.6).²⁰ This result indicates again a strong interaction of both elements within the individual particles because it is well known that the surface of pure Co colloids usually consists of at least two monolayers of CoO.^{15a} The reason for the oxidation stability of the Co-shell in our bimetallic particles is not yet understood and will be discussed in the future, as well as more details of image processing using EELS, e.g., background subtraction, which is the content of a forthcoming paper.

HRTEM-investigations of single particles revealed a multiple twinned or “polycrystalline” structure of the nanocrystals (Figure 4a). The reason for the invisible core-shell structure in Figure 4a is a decreased contrast difference at the higher accelerating voltage used compared to the inset in Figure 2. The background theory of this behavior is discussed in detail by Reimer and Lippert.²¹

Fast Fourier transformation (FFT) was also performed on the HRTEM images of single particles as well as powder XRD investigations, which verified the existence of crystalline Ag with a typical fcc-structure. An unambiguous determination of the structure of Co was not possible because of reflex overlapping of Ag (200), $d = 2.044 \text{ nm}^{-1}$ and Co (111), $d = 2.047 \text{ nm}^{-1}$. These results are therefore not shown here.

SAED analysis of particle ensembles as presented in Figure 2 does not require the complete fulfillment of the Bragg condition and shows different intensities of the reflexes compared to the XRD pattern caused by secondary diffrac-

tion. This analysis was conducted to obtain information about the structure of Co (Figure 4b). It is evident from Figure 4b, that Co crystallizes in its fcc-phase and not in its hcp, ϵ , or bcc phase, as one might expect.^{11c,22,23}

Interestingly, the colloids also show a remanent magnetization at 90 K. A discussion of the magnetic properties goes beyond the scope of this letter and will be published elsewhere.

In summary, we can conclude that FM/NM bimetallic colloidal nanocrystals can be synthesized. As a result of a kinetically controlled crystal growth $\text{Ag}_{\text{core}}\text{Co}_{\text{shell}}$ particles were obtained, which show no surface oxidation and present magnetic properties, useful for magnetophoretic deposition experiments.^{23,24} UV/VIS-spectroscopy as well as methods of (HR)TEM and related spectroscopy like EDX or EELS were employed as suitable methods for the investigation of this kind of nanocrystalline materials. The formation of an Ag/Co alloy was not observed.

Sintering experiments, which could lead to interesting changes in the particle morphology, taking into account the decreased melting point of nanoparticles,²⁵ will be one aspect of our ongoing research, as well as similar investigations of alloying systems, e.g., Pd/Co or Pt/Co.

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References

- (1) (a) Shao, Y. Z.; Lai, J. K. L.; Shek, C. H. *J. Magn. Magn. Mater.* **1996**, *163*, 103. (b) Pecharsky, V. K.; Gschneidner, K. A., Jr. *J. Magn. Magn. Mater.* **1999**, *200*, 44. (c) Yamamoto, T. A.; Tanaka, M.; Misaka, Y.; Nakagawa, T.; Nakayama, T.; Niihara, K.; Numazawa, T. *Scr. Mater.* **2002**, *46*, 89.
- (2) (a) Ronay, M. *IBM Technol. Discl. Bull.* **1976**, *19*, 2753. (b) Kormann, C.; Schwab, E.; Raulfs, F.-W.; Beck, K. H. U.S. Patent 5,500,141, 1996.
- (3) Lodder, J. C.; Monsma, D. J.; Vlutters, R.; Shimatsu, T. *J. Magn. Magn. Mater.* **1999**, *198–199*, 119.
- (4) Jordan, A.; Scholz, R.; Wust, P.; Schirra, H.; Schiestel, T.; Schmidt, H.; Felix, R. *J. Magn. Magn. Mater.* **1999**, *194*, 1185.
- (5) Mapara, M. Y.; Körner, I. J.; Hildebrandt, M.; Bargou, R.; Krah, D.; Reichardt, P.; Dorken, B. *Blood* **1997**, *89*, 337.
- (6) (a) Weller, D.; Moser, A. *IEEE Trans. Magn.* **1999**, *35*, 4423. (b) Sellmyer, D. J.; Yu, M.; Kirby, R. D. *Nanostruct. Mater.* **1999**, *12*, 1021.
- (7) (a) Charles, S. W.; Rosensweig, R. E. *J. Magn. Magn. Mater.* **1983**, *39*, 190. (b) Kamiyama, S.; Rosensweig, R. E. *J. Magn. Magn. Mater.* **1987**, *65*, 401. (c) Blums, E.; Osols, R.; Rosensweig, R. E. *J. Magn. Magn. Mater.* **1990**, *85*, 303. (d) Cabuil, V.; Neveu, S.; Rosensweig, R. E. *J. Magn. Magn. Mater.* **1993**, *122*, 437. (e) Bhatnagar, S. P.; Rosensweig, R. E. *J. Magn. Magn. Mater.* **1995**, *149*, 199. (f) Vékás, L.; Sofonea, V.; Balau, O. *J. Magn. Magn. Mater.* **1999**, *201*, 454.
- (8) Yacamán, M. J.; Ascencio, J. A.; Liu, H. B.; Gardea-Torresdey, J. *J. Vac. Sci. Technol. B* **2001**, *19*, 1091.
- (9) (a) Shull, R. D.; Bennet, L. H. *Nanostruct. Mater.* **1992**, *1*, 83. (b) Harp, G. R.; Parkin, S. S. P.; O'Brian, W. L.; Tonner, B. P. *Phys. Rev. B* **1995**, *51*, 12037. (c) Moraitis, G.; Dreyssé, H.; Khan, M. A. *Phys. Rev. B* **1996**, *54*, 12037.
- (10) (a) Chen, J. P.; Sørensen, C. M.; Klabunde, K. J.; Hadjippanayis, G. C. *Phys. Rev. B* **1995**, *51*, 11527. (b) Pileni, M.-P. *Adv. Funct. Mater.* **2001**, *11*, 323.
- (11) (a) Osuna, J.; de Caro, D.; Amiens, C.; Chaudret, B.; Snoeck, E.; Respaud, M.; Broto, J.-M.; Fert, A. *J. Phys. Chem.* **1996**, *100*, 14572. (b) Papirer, E.; Horny, P.; Balard, H.; Anthore, R.; Petipas, C.; Martinet, A. *J. Colloid Interface Sci.* **1983**, *94*, 207. (c) Murray, C. B.; Sun, S.; Doyle, H.; Betley, T. *Mater. Res. Soc. Bull.* **2001**, *26*, 985.
- (12) Baibich, M. N.; Broto, J. M.; Fert, A.; Van Dau, N.; Petroff, F.; Eitenne, P.; Creuzet, G.; Friedrich, A.; Chazelas, J. *Phys. Rev. Lett.* **1988**, *61*, 2472.
- (13) (a) Rivas, J.; Sánchez, R. D.; Fondado, A.; Izco, C.; García-Bastida, A. J.; García-Otero, J.; Mira, J.; Baldomir, D.; González, A.; Lado, I.; López-Quintela, M. A.; Oserov, S. B. *J. Appl. Phys.* **1994**, *76*, 6564. (b) Park, J.-I.; Cheon, J. *J. Am. Chem. Soc.* **2001**, *123*, 5743. (c) O'Connor, C. J.; Kolesnichenko, V.; Carpenter, E.; Sangregorio, C.; Zhou, W.; Kumbhar, A.; Sims, J.; Agnoli, F. *Synth. Met.* **2001**, *122*, 547.
- (14) (a) Baddelley, C. J.; Jefferson, D. A.; Lambert, R. M.; Ormerod, R. M.; Rayment, T.; Schmid, G.; Walker, A. P. *Mater. Res. Soc. Symp. Prog.* **1992**, *272*, 85. (b) Mulvaney, P.; Giersig, M.; Henglein, A. *J. Phys. Chem.* **1993**, *97*, 7061. (c) Hodak, J. H.; Henglein, A.; Giersig, M.; Hartland, G. V. *J. Phys. Chem. B* **2000**, *104*, 11708. (d) Mizukoshi, Y.; Fujimoto, T.; Nagata, Y.; Oshima, R.; Maeda, Y. *J. Phys. Chem. B* **2000**, *104*, 6028.
- (15) (a) Wiedwald, U.; Spasova, M.; Farle, M.; Hilgendorff, M.; Giersig, M. *J. Vac. Sci. Technol. A* **2001**, *19*, 1773. (b) Meiklejohn, W. H.; Bean, C. P. *Phys. Rev.* **1957**, *105*, 904.
- (16) (a) Katsikas, L.; Eichmüller, A.; Giersig, M.; Weller, H. *Chem. Phys. Lett.* **1990**, *172*, 201. (b) Talapin, D. V.; Rogach, A. L.; Haase, M.; Weller, H. *J. Phys. Chem. B* **2001**, *105*, 12278.
- (17) (a) Li, Z. C.; Cheng, X. Q.; Liu, B. X. *J. Alloy. Comput.* **2001**, *327*, L1. (b) Liu, J. B.; Li, Z. F.; Zhang, J. X.; Liu, B. X.; Kresse, G.; Hafner, J. *Phys. Rev. B* **2001**, *64*, 54102.
- (18) (a) Doremus, R. H. *J. Chem. Phys.* **1965**, *42*, 414. (b) Lue, J.-T. *J. Phys. Chem. Solids* **2001**, *62*, 1599.
- (19) Fink, J.; Müller-Heinzerling, Th.; Scheerer, B.; Speier, W.; Hillebrecht, F. U.; Fuggle, J. C.; Zaanen, J.; Sawatzky, G. A. *Phys. Rev. B* **1985**, *32*, 4899.
- (20) Waddington, W. G.; Rez, P.; Grant, I. P.; Humphreys, C. J. *Phys. Rev. B* **1986**, *34*, 1467.
- (21) (a) Reimer, L. *Transmission electron microscopy*; Springer: Berlin, 1997. (b) Lippert, W. *Naturwissenschaften* **1963**, *50*, 219 (in German).
- (22) (a) Dinega, D. P.; Bawendi, M. G. *Angew. Chem.* **1999**, *111*, 1908. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1788. (b) Püntes, V. F.; Krishnan, K. M.; Alivisatos, A. P. *Appl. Phys. Lett.* **2001**, *78*, 2187.
- (23) Giersig, M.; Hilgendorff, M. *J. Phys. D.: Appl. Phys.* **1999**, *32*, L111.
- (24) (a) Giersig, M.; Hilgendorff, M. In *Cluster and Nanostructure Interfaces*; Jena, P., Khanna, S. N., Rao, B. K., Eds.; World Scientific: Singapore, 2000; p 203. (b) Hilgendorff, M.; Tesche, B.; Giersig, M. *Aust. J. Chem.* **2001**, *54*, 497.
- (25) (a) Xue, Y.; Zhao, Q.; Luan, C. *J. Colloid Interface Sci.* **2001**, *243*, 388. (b) Zhao, M.; Zhou, X. H.; Jiang, Q. *J. Mater. Res.* **2001**, *16*, 3304.

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