Synthesis of Monodisperse Magnetic Methacrylate Polymer Particles**

By *Benedikt Lindlar, Monica Boldt, Stefanie Eiden-Assmann,* and *Georg Maret*

The synthesis of colloidal particles with tailored shapes and controlled chemical composition and physical properties is one prerequisite for the formation of self-assembled photonic crystals. Three-dimensional photonic crystals can be seen as the optical analog of semiconductors. Owing to their periodic order, both photonic bandgap materials and electronic semiconductors possess a bandgap. In the case of photonic crystals this bandgap is mainly defined by the index of refraction and the structure of the colloidal crystals used.

An important focus of the research on photonic bandgap materials is, therefore, the fabrication of periodic structures that have been predicted to show a suitable bandgap.[1,2] The tailored colloidal crystallization of such structures can be achieved either by a layer-by-layer method[3] or by bulk crystallization.[4] The former method may offer the possibility of better control of the crystal growth. However, both methods still yield crystals with unwanted defects. Therefore, as the latter pathway is less complicated and faster, it warrants further development. In this respect, the self-assembly of strongly interacting particles might be a promising approach to optimize the colloidal crystal structure.[5] Previous reports on two-dimensional systems[6,7] suggest that the use of magnetic colloids may open the way to tailored bulk crystallization assisted by an external magnetic field.

Magnetic colloidal particles of the required quality and a size between 500 and 700 nm are not commercially available. Therefore, an easily reproducible synthetic procedure had to be developed in order to obtain particles that are monodisperse in size and in their distribution of the magnetite nanoparticles. Our synthetic pathway is based on the preparation of commercially available particles 2.8 and 4.5 µm in diameter[8] and our previous investigations of polystyrene colloids.[9]

Here we describe the synthesis of tailored magnetic polymer colloids 400–800 nm in diameter. The synthesis involves the preparation of parent methyl/glycidyl methacrylate copolymer particles, their chemical modification with ethylenediamine in order to obtain internal anchor groups, and the generation of superparamagnetic magnetite nanoparticles by impregnation and subsequent hydrolysis of ferric and ferrous chloride inside the methacrylate matrix.

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The synthesis of the parent polymer colloids yields particles with very narrow size distribution as illustrated by the scanning electron microscopy (SEM) image shown in Figure 1a. Depending on the amount of monomer in the reaction mix-
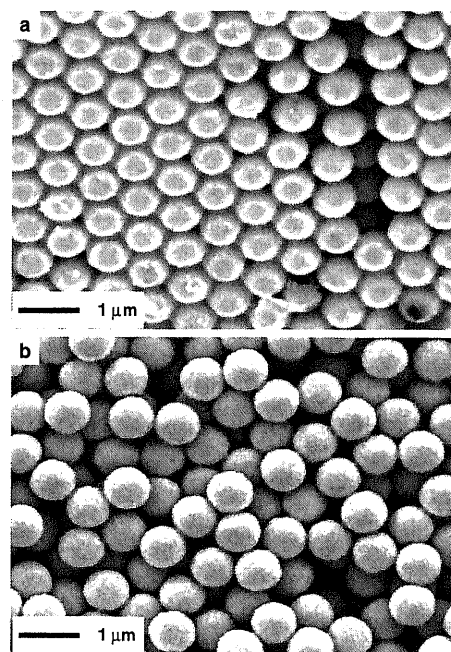

Fig. 1. SEM images of polymer particles: a) 700 nm particles obtained by polymerization and b) 700 nm particles swollen with ethylendiamine.

ture, the particle size can be varied between 400 and 700 nm. Due to the presence of the glycidyl methacrylate comonomer, the reaction of these dispersions with ethylenediamine produces particles with covalently attached, homogeneously distributed amino groups. As a consequence of this procedure, the diameter of the particles increases by about 7–9 %, indicating that the beads are swollen by the ethylenediamine (Fig. 1b). The nitrogen content of the colloids was found by elemental analysis to be 3 wt.-%. This is far below the maximum theoretical amount of 17 wt.-% and can be explained by the large number of glycidyl groups that are buried inside the polymer, and are thus hidden from chemical attack.

The impregnation of the polymer beads with iron salts and the conversion of the latter to magnetite was successful, as proven by microscopy, thermogravimetric analysis (TGA), enhanced X-ray adsorption fine structure analysis (EXAFS), and superconducting quantum interference device (SQUID) magnetometry. Although the diameter of the particles increases upon reaction with ethylenediamine, no noticeable change in size is observed upon incorporation of magnetite. Transmission electron microscopy (TEM) of cross-sectional cuts of the beads revealed distribution of the magnetite over the whole area (Fig. 2). The Fe_3O_4 content of the polymer beads was found to be 25 wt.-% as determined by TGA. Comparison of the X-ray absorption near edge structure (XANES) data with those of pure iron oxide standard materials showed that the iron oxide species obtained was the desired Fe_3O_4 (Fig. 3).

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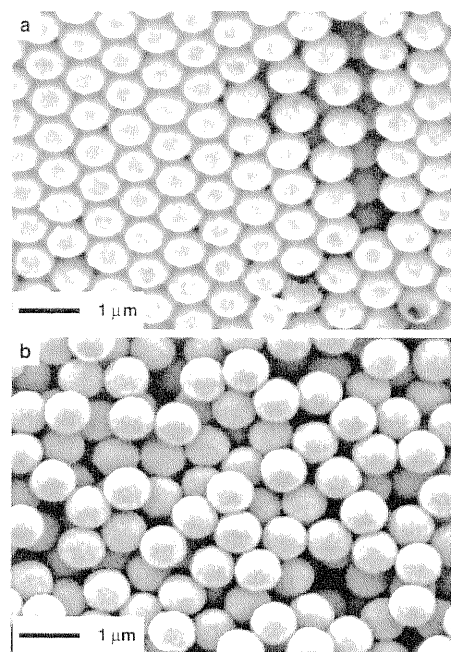

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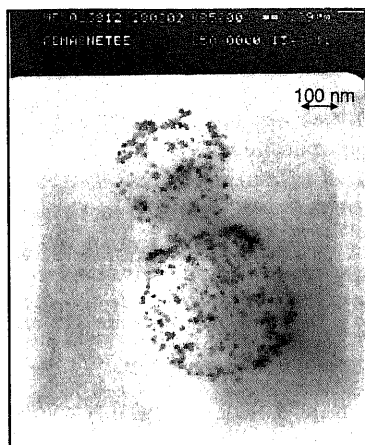
Fig. 2. TEM image of a cross-sectional cut through the magnetic beads revealing a uniform distribution of magnetite over the whole area.
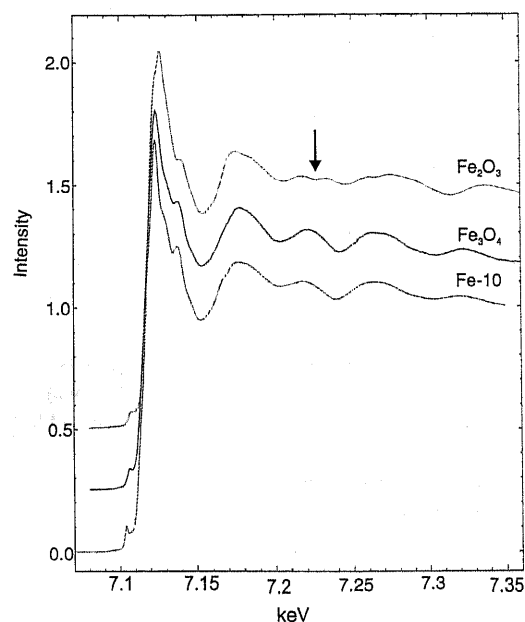

Fig. 4. Chains formed by the magnetic particles in a magnetic field of 125 mT.

Fig. 3. Normalized Fe K XANES spectra of Fe_2O_3, Fe_3O_4, and the magnetic particles (Fe-10).

Fig. 5. Temperature dependence of the magnetization of the magnetic particles. The magnetic properties are derived from zero-field-cooled (dotted line) and field-cooled (solid line) magnetization measurements as a function of temperature.

The behavior of the magnetic beads in a magnetic field was examined by optical microscopy. In a magnetic field of 125 mT, chains of particles form (Fig. 4), but the beads immediately redistribute randomly when the magnetic field is switched off. This phenomenon is in good agreement with the results from SQUID measurements at 20 mT, which proved that the iron oxide particles are superparamagnetic at ambient temperature (Fig. 5) and that they have a blocking temperature of about 150 K. The magnetic properties were derived from zero-field-cooled (dotted line) and field-cooled (solid line) magnetization measurements as a function of temperature. The sample was initially cooled to 2 K in a zero field. Then a magnetic field was applied, and the magnetization was recorded with increasing temperature. When the temperature reached 340 K, the sample was progressively

cooled and the magnetization recorded. The magnetization curve at 5 K (Fig. 6, open circles) shows a hysteresis indicative of ferrimagnetic behavior. The curve recorded at 200 K (Fig. 6, filled squares) exhibits no hysteresis, in line with superparamagnetic properties. This feature of the magnetic beads is a prerequisite for their application in controlled colloidal crystallization.

An easy and reproducible procedure for the synthesis of magnetic particles that are suitable starting materials for tailored colloidal crystals has been developed. Using this method, exclusively magnetite is formed inside the polymer beads. Owing to the size of these magnetite particles, the magnetic polymer colloids exhibit excellent properties for their desired application in tailored crystallization, namely, magnetic behavior, distribution of the magnetite particles within the polymer matrix, and uniform particle size.

Experimental

Polymethacrylate Colloids: The parent polymethacrylate (PMA) colloids were synthesized from a mixture of 3.40–5.10 mL methyl methacrylate (purum, Fluka), 6.20–9.30 mL glycidyl methacrylate (purum, Fluka), 100.0 mL water

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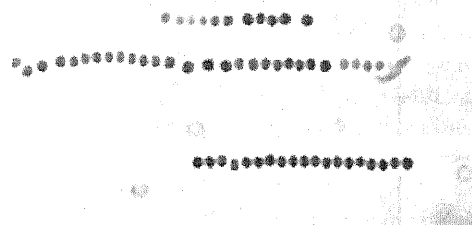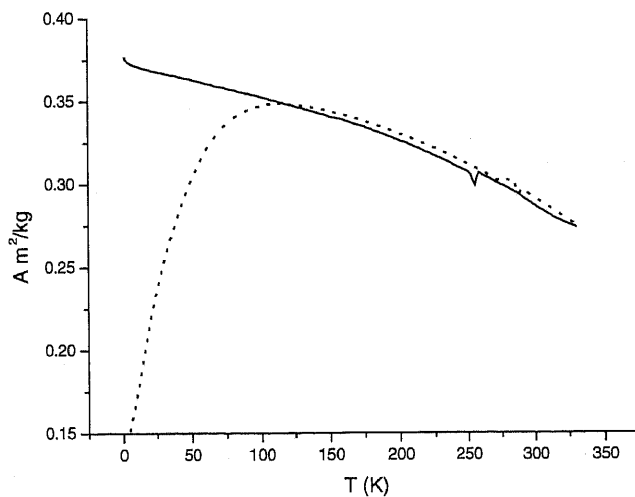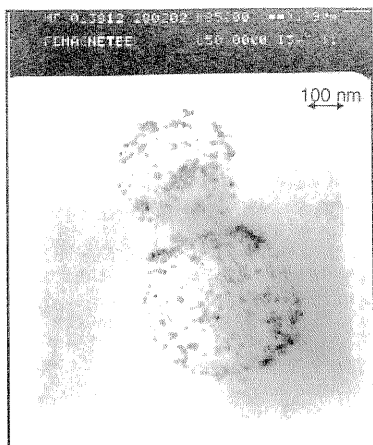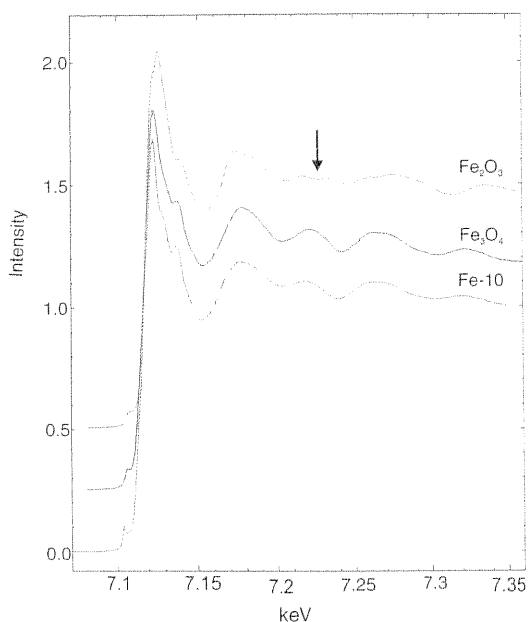

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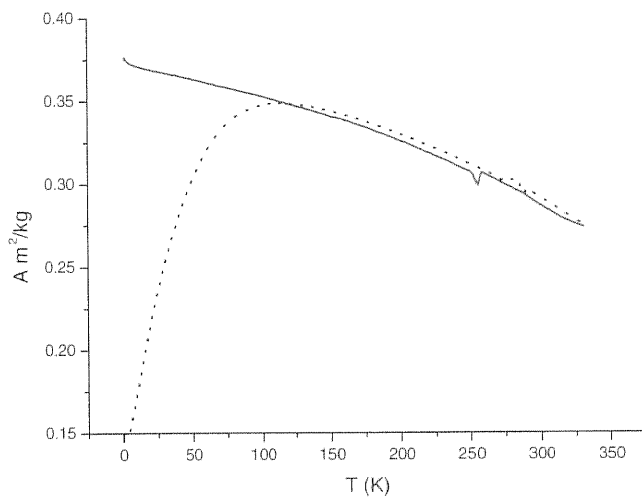

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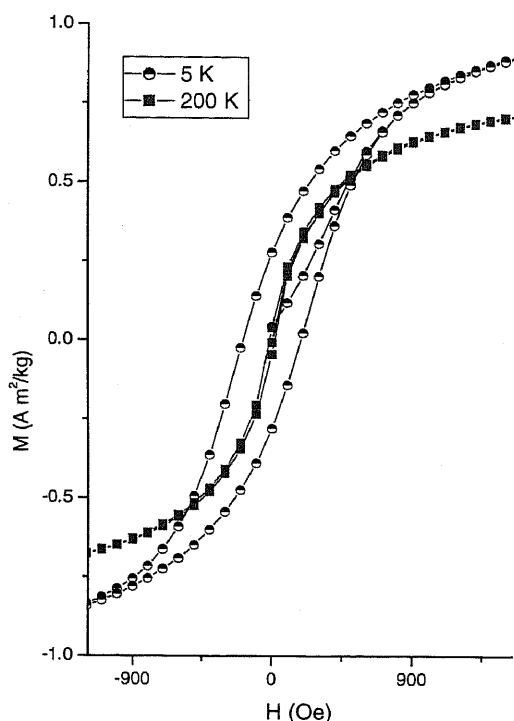
Experimental

Fig. 6. Hysteresis loop at 5 and 200 K in a plot of magnetization versus applied magnetic field.

(Millipore), and 50.0 mg potassium peroxodisulfate (p.A., Merck). Depending on the desired particle size between 400 and 700 nm, the amount of monomer in the reaction mixture was varied within the range mentioned above.

The monomers and the water were stirred for 1 h at ambient temperature under nitrogen flow in a 250 mL flask, equipped with condenser, bubbling valve, and magnetic stirrer. Subsequently, the peroxodisulfate radical initiator was added and the whole mixture was stirred for another 5–10 min. The flask was then placed in a preheated oil bath and stirred at 75 °C for a further 15 h under nitrogen. The resulting white dispersion was cooled to ambient temperature and dialyzed for 4–5 days in order to remove remaining monomer and initiator.

Reaction with Ethylenediamine: In order to attach anchor groups inside the particles for the final iron ion impregnation, ethylenediamine was added to the polymer dispersion. For this purpose, a mixture of 50 mL of the PMA dispersion, 75 mL water (Millipore), and 50 mL ethylenediamine (p.A., Merck) was prepared in a 250 mL flask and stirred at 80 °C for 4.5 h. The product mixture was dialyzed for 4 days to afford the final dispersion of the amino group-containing PMA particles (PMA-EDA).

Magnetite Impregnation: A 250 mL flask with 100 mL of a PMA-EDA dispersion (containing 2.5 g solid material) was cooled in an ice bath under nitrogen atmosphere. Two solutions, namely of 0.490 g iron(III) chloride (3.0 mM) and 0.340 g iron(II) chloride (1.7 mM), each in 10 mL water, were also cooled before they were combined and added to the dispersion. A light brown dispersion formed. The ice bath was removed and the flask was continuously evacuated while the dispersion was stirred until no further foaming was observed (30–45 min). Evacuation was stopped, and 10 mL of an ice-cooled ammonia solution (25 %) was added, causing the color of the reaction mixture to turn first to dark brown and then to black. This mixture was stirred for another 30 min at 80 °C, then cooled to ambient temperature, and purified by dialysis for 4 days.

Characterization: The products of all synthesis steps were examined by SEM using a Philips XL40 microscope. Additionally, the magnetic colloids were investigated by optical microscopy using a Zeiss Axiovert 100 inverted microscope with a special sample table equipped with a permanent magnet to generate a tunable magnetic field up to 125 mT. TEM was performed on a Zeiss EM 900 in order to determine particle size and size distribution. For this the particles were embedded in a Spurr polymer matrix and cut to 100 nm thick sections. The amount of inorganic material was determined by TGA using a STA 429 thermal balance (Netzsch). The samples were heated to a maximum temperature of 800 °C at a rate of 5 K/min under an oxygen atmosphere. The type of iron oxide species formed was determined by EXAFS at studio A1 of

the Hasylab in Hamburg. Data analysis was performed with *WinXAS* from Thorsten Ressler. SQUID measurements were performed with Quantum design MPMS XL.

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Controlled Hydrothermal Synthesis of Thin Single-Crystal Tellurium Nanobelts and Nanotubes**

By *Maosong Mo, Jinghui Zeng, Xianming Liu, Weichao Yu, Shuyuan Zhang*, and *Yitai Qian**

Since the discovery of carbon nanotubes in 1991,[1] the one-dimensional nanostructure has been the focus of considerable interest due to its great potential for addressing some basic issues about dimensionality and space-confined transport phenomena, as well as for applications in nanodevices.[2] The key to preparing a one-dimensional nanostructure is the way in which atoms or other building blocks are rationally assembled into a structure with nanometer size but a much larger length.[3] Many methods have been used for the preparation of one-dimensional nanostructures including arc discharge,[1,4] laser ablation,[3,5] template-assisted synthesis,[6–8] and other methods.[9–14] Recently, a family of long semiconducting oxide nanobelts, a new group of quasi-one-dimensional nanostructures with a rectangular cross section, were successfully synthesized simply by evaporating metal oxide powders at high temperatures.[15] By means of an organogel template, novel helical ribbon and double-layered nanotube TiO_2 structures were also created at 500 °C.[16] More recently, by using spherical selenium droplets as spools at 740 °C in an evacuated quartz tube, Tanda et al. successfully created a novel Möbius strip of single $NbSe_3$ crystals,[17] which offers a new route for exploring topological effects in quantum mechanics, as well as the potential for constructing new devices. To date,

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