Immobilized Highly Charged Colloidal Crystals: A New Route to Three-Dimensional Mesoscale Structured Materials**

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Mesoscale-ordered macroporous materials have attracted great interest over the last few decades. With a three-dimensional periodic variation in the dielectric constant on a scale comparable to optical wavelengths, they have outstanding optical properties, in particular photonic bandgaps are possible which offer the possibility to manipulate and guide light.[1–5] Apart from their applications in optics, these materials can be designed for a variety of other applications, for instance for use in catalysis.[6, 7] Previous synthetic routes took advantage of the self-assembly of hard-sphere colloids or emulsions to prepare macroporous materials with spheroidal voids arranged in a three-dimensional periodic structure.[8–13]

Herein we present a new method for preparing metallic mesostructures that starts from highly charged polymer colloids. At low ionic strength these systems self-assemble to form liquidlike, glasslike, or crystalline structures,[14] which can be immobilized in a crosslinked polyacrylamide hydrogel.[15] These hydrogels can be applied as chemical sensors or as "entropic traps" for the separation of macromolecules.[16] Our experiments show that such hydrogels are also suitable templates for the preparation of mesoscale ordered metals.

Highly charged colloids allow, due to the repulsive interaction, interparticular distances that can easily be varied by the number density of colloidal particles. Accordingly, in highly charged colloidal crystals the lattice constant can simply be tuned by the concentration. According to DLVO theory (DLVO = Derjaguin – Landau – Vervey – Overbeek) charged colloids interact through a screened electrostatic or Yukawa potential that originates from charged surface groups.[17] The strength of the interaction is highly dependent on the ionic strength of the dispersion medium. Crystals formed by these colloids are therefore sensitive to ionic impurities in the dispersion medium. This and the fact that changes in temperature and mechanical stress can destroy the colloidal crystals limit the number of possible synthesis routes for the preparation of mesoscale ordered materials. The immobilization of highly charged polymer colloids provides a possibility to overcome these difficulties. In a crosslinked polyacrylamide hydrogel the particles are fixed in their positions, and crystals formed by charged spheres are no longer sensitive to impurities in the dispersion medium or to physical stress. Thus, further preparation steps with this system can be carried out in an aqueous solution with high ionic strength.

To synthesize immobilized colloidal crystals we prepared polymer colloids consisting of polybutylacrylate. The monomer butylacrylate is commercially available and its emulsion polymerization provides highly charged and monodisperse particles.[18] Dynamic light scattering (DLS) experiments on these particles show that they have an average diameter of 200.5 nm (Figure 1) and are monodisperse; the geometrical standard deviation of the logarithmic normal distribution of their sizes amounts to only $\sigma = 1.08$. The particles have a zeta potential of -50 mV in the pH range of 6 to 10 due to the dissociation of surface-bound acid groups. After removal of ions and other impurities from the dispersion, the spheres self-assemble into colloidal crystals and show opalescence when illuminated with light. The results of static light scattering experiments confirm the crystalline structure of the suspension, and by indexing the Bragg reflections a face-centered cubic (fcc) structure with a lattice constant of 1853 nm was determined.

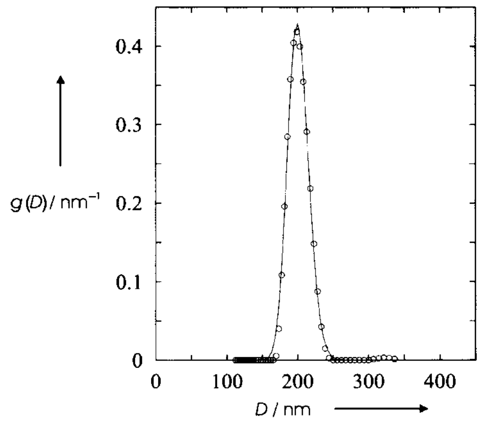

Figure 1. Size distribution $g(D)$ of polybutylacrylate colloids measured by DLS. The measured values are fitted with a logarithmic normal distribution function. The fit gave a mean particle diameter D of 200.5 nm with a geometrical standard deviation of $\sigma = 1.08$.

In a subsequent step a sample with a high volume fraction of particles ($\phi \approx 0.1$) was immobilized in a polyacrylamide hydrogel (Figure 2). The occurrence of Bragg reflections indicates that the order of the particles is maintained during the polymerization process. UV/Vis spectroscopy on these systems shows a shift of the absorption peak from 700 nm

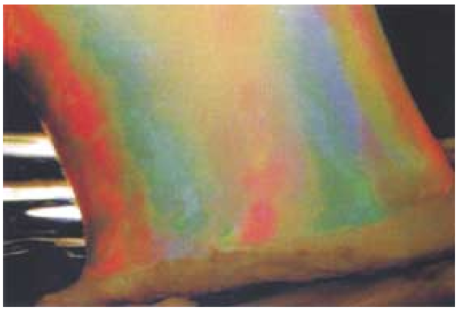

Figure 2. Photograph of a crosslinked polyacrylamide hydrogel in which polybutylacrylate colloids are immobilized. The occurrence of Bragg diffraction of the incident visible light indicates long-range order of the particles.

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[**] This work was supported by the DFG (SFB 277).

before to 830 nm after polymerization, which indicates an expansion of the lattice system during the polymerization process. These hydrogels with a periodic structure of the embedded polymer colloids then serve as a three-dimensional template for the synthesis of mesoscale structured silver.

Recently it has been shown that for hard-sphere systems the interspaces between colloidal particles can be filled electrochemically with another material.[19] To apply this technique to our systems, the hydrogel was polymerized directly onto the surface of a stainless steel electrode. By using this assembly as cathode, silver could be deposited into the interspaces by electrodeposition from an aqueous $AgNO_3$ solution. The resulting solid silver piece could easily be removed from the electrode surface; drying the sample at room temperature causes a slight shrinkage. The samples were then broken into pieces and were examined by scanning electron microscopy (SEM) without any further treatment.

The SEM images (Figures 3 and 4) reveal the three-dimensional structure of the silver/polybutylacrylate composite material. The latex spheres are arranged in hexagonal layers in which the particles do not touch each other but are separated by a silver layer with a well-defined thickness. The particles' diameter as determined from the SEM image is 160 nm, which differs from the value of 200 nm determined by dynamic light scattering due to shrinkage of the polymer spheres during drying. Although there are some defects in the structure, on the SEM image of larger regions of the sample (Figure 4) the long-range order in the material can clearly be seen. Monoparticular steps in the surface reveal the three-dimensional character of the periodic order.

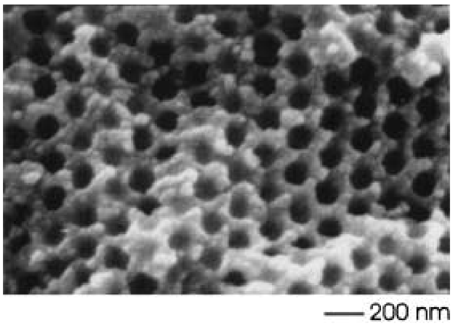

Figure 3. SEM image of the mesoscale structured silver sample. After the electrochemical silver deposition the periodic structure is maintained. The particle diameter of about 160 nm corresponds to the size determined by DLS if shrinkage of the particles during drying is considered.

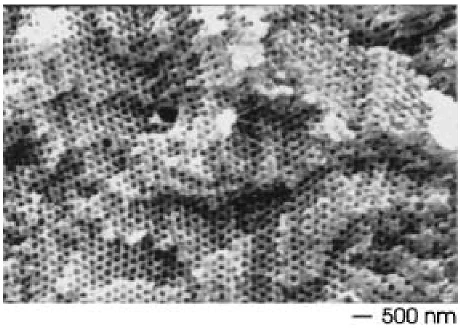

Figure 4. SEM image of larger areas of the silver sample shows the material's long-range ordered mesoscale structure. Monoparticular steps in the surface reveal the three-dimensional character of the periodic order (i.e. perpendicular to the plane of the picture).

Similar samples starting from colloidal suspensions with lower particle number densities have been prepared. In these samples the particles do not exhibit long-range order after immobilization but are randomly distributed in the material. Evidently, at lower volume fraction the mean interparticle distance is too large and the crystalline structure is destroyed during polymerization.

In summary by using suspensions with high volume fractions ($\phi \geq 0.1$) three-dimensional periodic structures have been prepared starting from highly charged colloidal crystals. This procedure is not limited to the electrodeposition of silver but can be extended to other materials, preferentially metals or alloys. For applications in optics the voids in these systems could be filled with semiconductor materials, which has been done already for hard-sphere systems.[19, 20] The adaption of this method to our systems is in progress. Thus, a novel route to photonic crystals is provided in which the lattice constant can be tuned by the volume fraction of colloidal particles. For use in catalysis a deposition of noble metals or other metals with catalytic activity can be considered. In this case the polymer spheres must be removed from the material after the deposition to create pores. As the size of the polymer colloidal particles can be adjusted over a wide range in the course of the emulsion polymerization, this procedure would lead to tailor-made catalyst surfaces with well-defined pore diameters and wall thicknesses.

Experimental Section

Colloidal suspension: The suspension was prepared by emulsion polymerization at 80 °C using butylacrylate and $K_2S_2O_8$ as initiator. The latex was purified by dialysis against distilled water and by subsequent treatment with ion-exchange resin.

Hydrogels: The hydrogels were prepared according to the method applied by Asher et al.[15] The colloidal suspension, acrylamide, crosslinker, and photoinitiator were mixed and shaken with ion-exchange resin. The mixture was injected into a cell between a quartz plate and a stainless steel electrode. The 1 mm thick layer was polymerized onto the electrode surface by using a UV lamp ($\lambda = 366$ nm, 4 W) for 5 h.

Electrodeposition: Using the assembly of hydrogel and electrode as cathode it was possible to deposit silver electrochemically from a 0.5 M $AgNO_3$ solution into the interspaces between the colloidal particles. The deposition was carried out for 24 h at a current density of $1.5\,mA\,cm^{-2}$.

Zeta potential: The zeta potential was measured with a Malvern Zetasizer model 3000 HSA.

Received: July 5, 2001 [Z17430]

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The Rational Design of Anion Host Compounds: An Exercise in Subtle Energetics[**]

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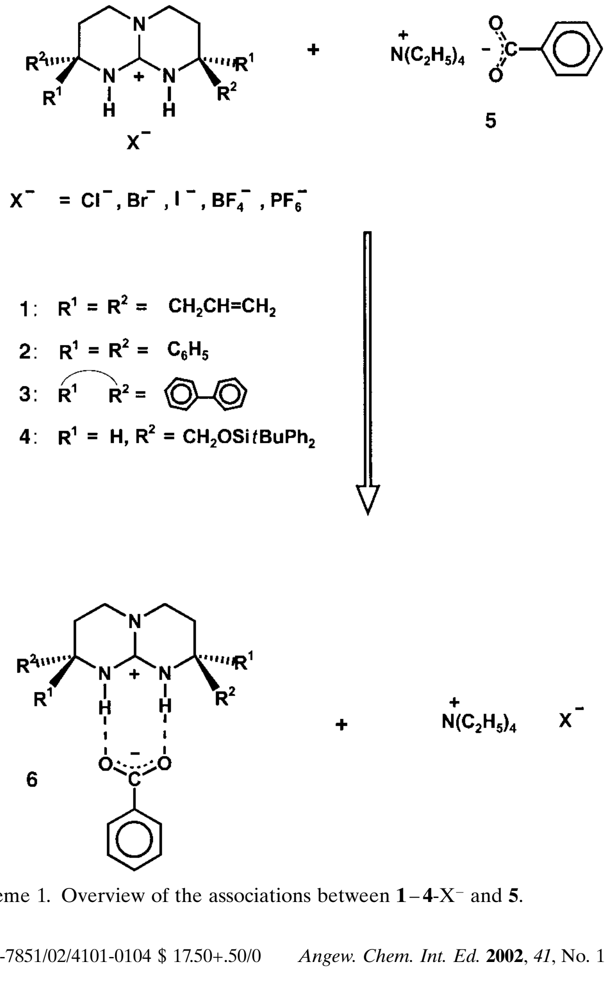
For more than 100 years the lock-and-key metaphor of Emil Fischer served as the fundamental concept to comprehend molecular recognition interactions.[1] The central idea rests on the assumption that the mutual geometric fit of a pair of supramolecular binding partners dominates their thermodynamic affinity.[2] Thus, generations of synthetic chemists have strived to optimize the direct interaction mode of hosts towards a given guest species by subtle modification of their covalent structures taking the Gibbs energy of complex formation ΔG° and the equilibrium constant for association (K_{ass}) as the ultimate judge. In many cases this approach did not live up to the expectations and met with only limited success. Here we describe an experimental attempt to evaluate the energetics of a simple host–guest system to develop more reliable guidelines for molecular recognition.

The failure of the lock-and-key model to rationalize general host–guest interactions can be traced to the premises of the concept which focuses exclusively on the enthalpic interactions of just two interaction partners, neglecting the entropic components as well as all solvent contributions. The latter point in particular gives rise to the phenomenon of enthalpy–entropy compensation[3, 4] that accompanies all weak interactions in solution. The enthalpic gain on binding of host and guest can thus be counteracted by an entropic influence. As a consequence, the free energy of association ΔG°_{ass}, which represents a combination of the state (enthalpic and entropic) functions ($\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$), may change only marginally and does not reflect the structural achievements. A remedy to connect the structural modification in a tailored host–guest relationship to the experimental energetics can be expected from isothermal titration calorimetry (ITC). This method allows the pertinent thermodynamic state functions to be obtained along with the stoichiometry of host–guest complex formation from a single experiment.[5] Since calorimetric measurements faithfully report on the cumulative heat response of the entire system it is mandatory to design a host–guest system simple enough to allow deconvolution of all the processes happening simultaneously in solution and ascribe the heat effect to just one association reaction. Studying a series of structurally related compounds should unfold the structure-affinity correlation, in addition, and the risk of misinterpretation is lowered by using trend analysis.

The association of bicyclic guanidinium cations (e.g. **1**) with carboxylates **5** (Scheme 1) may provide a suitable host–guest system. The interaction mode follows strict 1:1 stoichiometry



Scheme 1. Overview of the associations between **1**–**4**-X⁻ and **5**.

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[**] This work was supported by grants from Deutsche Forschungsgemeinschaft and the German Ministry of Science and Technology, BMBF project 13N7130/9.