

From the de Broglie to Visible Wavelengths: Manipulating Electrons and Photons With Colloids

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Introduction

Because of their size and ability to self-organize, colloidal particles are ideal building blocks for the creation of three-dimensional (3D) structures that can have feature sizes of the order of the wavelength of electrons, photons, or both. This article is too short to provide an extensive literature survey but instead will give some illustrative examples, based on work of the author and co-workers, of how specially developed core-shell particles might be organized on a 3D lattice. These examples are only intended to give an impression of how colloidal-particle systems can be used in the design of new materials with interesting photonic properties.

Generally particles are considered colloidal if their size is between several nm and several μm .¹ This range is more or less defined by the importance of Brownian motion—that is, the irregular, overdamped, random displacements the particles make as a result of the not completely averaged-out bombardment of solvent (or gas) molecules.¹ Consequently the lower size range is determined by the size of the solvent molecules. Compared to the particle size, the solvent molecules need to be so small that the time scales of the solvent molecules and particles are so far apart that the solvent molecules can

be “integrated out” in a description of the particles. If such a description holds, the solvent can be approximated well by a continuum. The upper size limit is determined by the size at which external fields, like gravity, start to overshadow the effects of Brownian motion. In the absence of such disturbing fields, the Brownian displacements may simply become too small on a human time scale. Brownian motion is not only important in defining a colloid, it also allows these particles to travel through “phase space” of statistical mechanics. Consequently colloids have a well-defined thermodynamic temperature and strive to reach equilibrium structures with the lowest free energy. It is quite important to realize that this sets a dispersion of colloidal spheres apart from the “macroscopic” world of, for example, granular materials. For instance if granular material consisting of two sizes of spheres is shaken in a gravitational field, the larger spheres end up on top. This experiment, which can be performed at breakfast with muesli enriched by nuts, clearly demonstrates that granular materials do not behave in a “thermodynamic” sense seeking the lowest free-energy state. On the contrary, binary dispersions of colloids do form

equilibrium structures. This is the reason that colloidal dispersions are used as a model system in the study of condensed-matter problems like glass transition, crystallization, and melting (see, e.g., References 1–4 and references cited).

The size of colloids not only leads to experimentally accessible time scales for processes like crystallization but also makes it possible to study such processes quantitatively in 3D real space.^{3,4} The knowledge obtained through these model studies is increasingly being used to design new materials based on colloidal building blocks. There are several reasons for this trend. One has to do with the development of better synthetic routes to make monodisperse particles, especially of the smallest size colloids. Such particles of several-nm size are called nanoparticles or quantum dots. Quantum dots are semiconductor or metal particles with highly size-dependent properties determined by quantum mechanics.^{5,6} The size of these particles is of the same order as the free-electron wavelength, which results in an increase of the electronic bandgap and tunability of—for instance—absorption and luminescence. In addition nonlinear effects may become important.⁶

Another impetus for new materials made from colloids was the realization some 10 years ago that, for sufficiently strong interactions with photons, a regular dielectric material would modulate the propagation of light in a similar way as a semiconductor modulates the propagation of electrons. Inside such a photonic crystal with a complete photonic bandgap, the propagation of photons with any polarization is forbidden in any direction.⁷ These periodic dielectric structures can be doped dielectrically to open up transmission paths for specific wavelengths inside the bandgap.⁷ With such regular dielectric materials, both the propagation and spontaneous emission of photons can be manipulated leading potentially to many (electro)optical applications such as—for example—a thresholdless laser. However as will be shown in the article by Asher in this issue, even for colloidal crystals that only scatter photons once, the resulting Bragg condition can be used in very interesting “smart” materials.⁸

The terminology in this relatively new field of materials made from colloidal crystals, glasses, or gels—for short, *colloidal matter*—is still diverse and mostly reflects the background of the researcher. For instance the already mentioned smallest *colloidal particles* are called *quantum dots*, *nanocrystals*, or *artificial atoms*

and the corresponding *colloidal crystals* of these colloids are referred to as *regular arrays* or *superlattices*, whereas colloidal crystals used to manipulate photons are referred to as *photonic crystals*, *lattices*, or (*artificial*) *opals of dielectric microparticles* or *nanospheres*.

Tuning the Properties of Colloidal Particles

The range of interactions between colloids can be varied over lengths such that it includes hard-sphere-like to essentially unscreened coulomb-like (as in a one-component plasma) potentials.^{1,2} Control over the interactions comes from chemical or physical modification of the surface and bulk properties of the colloidal particles and the solvent in which they are dispersed. For instance by changing the number of dissociable groups on the particle surface or by changing the ionic strength of the solvent, the range of the charge repulsion between the spheres can be varied in water from several nm to hundreds of nm. For charged colloidal particles, this results in a volume-fraction range from well below 0.1% for body-centered-cubic (bcc) colloidal crystals to 74% for close-packed crystals. In addition to charge stabilization, colloidal particles can also be stabilized against the always-present van der Waals forces by so-called steric stabilizing chains grafted to the particle surface. The stabilizing chains can be very short—for example like octadecyl alkane chains—or quite large molecular-weight polymer brushes.

In the synthesis of nanocrystals, the variability of the particle interactions with particle size is used to selectively destabilize either larger particles through use of a marginal solvent of the stabilizing chains and/or increasing van der Waals forces through a change in the solvent refractive index. Through this process of selective aggregation and separation, it has become possible to synthesize nanocrystals with polydispersities within the limit of atomic roughness. Such accuracy leads to polydispersities small enough that colloidal crystals can be obtained even in this size range.⁹ In addition to particle stabilization, surface coverage is also important for electronic passivation, enabling—for instance—room-temperature photoluminescence with high quantum yields >10%.^{5,10} Changing the length of the stabilizer molecules can also provide almost atomic-scale control over the spacing of the nanocrystals in a colloidal crystal.⁹ Passivation can also be achieved through an additional layer of semiconductor around the nanocrystal with a larger electronic bandgap. An ex-

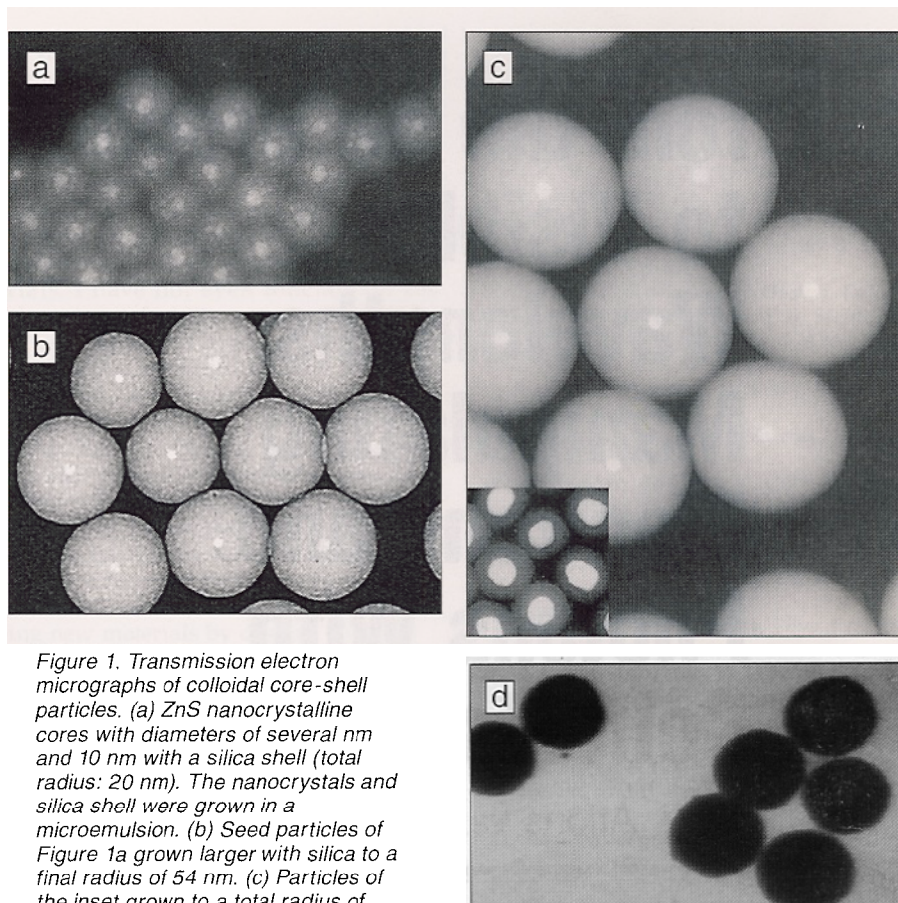


Figure 1. Transmission electron micrographs of colloidal core-shell particles. (a) ZnS nanocrystalline cores with diameters of several nm and 10 nm with a silica shell (total radius: 20 nm). The nanocrystals and silica shell were grown in a microemulsion. (b) Seed particles of Figure 1a grown larger with silica to a final radius of 54 nm. (c) Particles of the inset grown to a total radius of 150 nm. Inset: gold core (radius 15 nm) with thin (several nm) silica shell. (d) ZnS colloidal spheres with a radius of 135 nm.

ample appears in Figure 1a where ZnS cores inside a silica shell are shown.¹¹ The nanocrystals were made by precipitation of ZnS through the mixture of two water-in-oil microemulsions containing the Zn^{2+} and S^{2-} ions, respectively; the silica shell was grown in the same microemulsion. In this example, the precipitation was performed in two steps leading to 10-nm-diameter nanocrystals surrounded by hardly visible particles with a diameter of a few nm. This example further demonstrates that the silica shell can make this complex arrangement of nanocrystals quite monodisperse with just a ~4% relative width of the size distribution. Further growth of these particles with additional silica leads to a reduction in the polydispersity proportional to the inverse of the particle radius (Figure 1b). The ZnS nanocrystals can be doped in the electronic bandgap with, for example, manganese that can be coprecipitated. The luminescence of such particles has been reported to be as high

as 18% at room temperature with a luminescent decay at least five orders of magnitude faster than is the case with bulk crystals.¹⁰

Silane coupling agents also can be used to grow silica shells around metal cores such as gold (Figure 1c). Gold particles have an interesting size-dependent plasmon absorption in the visible wavelengths.⁶ These core-shell particles were made by a modification of the procedure developed by Liz-Marzan et al.¹²

Colloids used for photonic crystals with photon interactions strong enough to have a complete bandgap need to have an index contrast higher than 2. Titanium dioxide with its large refractive index would be a good candidate. However it is quite hard to produce particles that are sufficiently monodisperse. Therefore we have chosen ZnS with refractive index 2.35 as the high-index cores. The first results are shown in Figure 1d. Again these particles can be coated with a silica shell of any thickness.

The silica-shell morphology has, in addition to the possible higher monodispersity, two other advantages in the design of new materials. First, silica is the material for which the widest range of surface coatings have been documented in the literature. Second we developed a procedure to place fluorescent organic groups inside the silica shell with nm control over the radial position.¹³ These kinds of fluorescent spheres are not only useful in quantitative real-space studies with confocal microscopy^{3,4} but are also good candidates for the characterization and design of applications for photonic crystals (see the section on Quantum-Dot and Photonic Crystals).

Manipulating Colloidal Crystallization

Monodisperse colloidal particles with spherical symmetric interaction potentials are known to crystallize in several crystal structures depending for the most part on the range of the interaction potential.^{1,2} For particles with an (almost) hard-sphere-like potential, the crystals formed are usually not the face-centered-cubic (fcc) equilibrium phase but instead—because of kinetic reasons—a more random stacking of close-packed hexagonal layers, generally referred to as random hexagonal stacking (RHS). An example of such a crystal (consisting of silica coated with octadecyl chains in cyclohexane) formed under the influence of gravity appears in Figure 2. If the test tube would not have been disturbed, the “columns” of RHS “crystal” with a diameter of about 1 mm would have extended for the full 20-cm length of the tube. If the potential is softer, for example, because of overlapping double layers for charged spheres (Figure 3) or overlap of steric stabilizing polymers, pure fcc crystals can be obtained. The silica particles shown in the transmission electron micrograph in Figure 3 have been made in the already-mentioned microemulsion and have a polydispersity below 1%, which is exceptionally low for particles with a radius under 100 nm.¹¹ For interactions with a long repulsion, bcc crystals are formed (Figure 4). At this moment, the following types of binary colloidal crystals have been experimentally realized: AB, AB₂, AB₄, AB₁₃. See for instance the references cited in Reference 14.

More crystal structures are possible if the interaction forces are made anisotropic. For instance dipolar interactions can be induced between the colloids by a MHz alternating-current electric field of sufficient strength. In 1991 the zero tem-

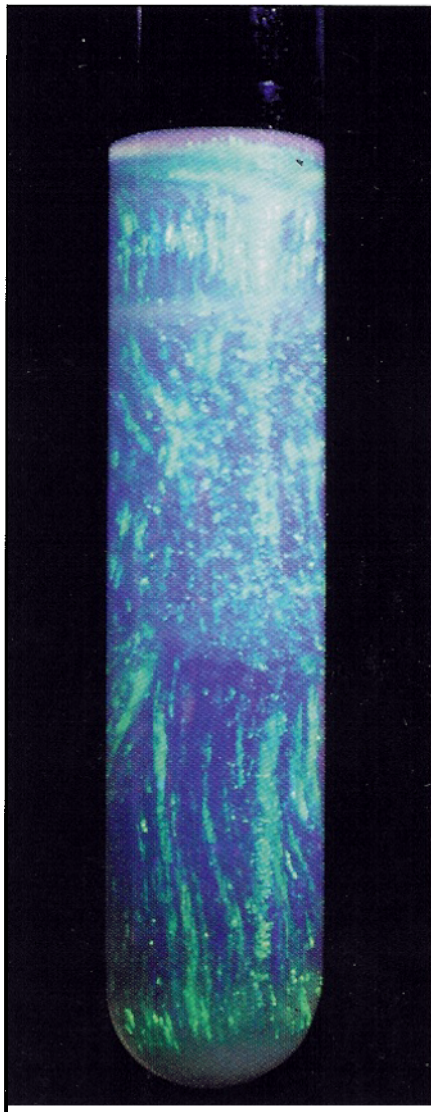


Figure 2. Bragg reflections of colloidal random-hexagonal-stacked crystals of hard-sphere-like octadecyl-coated silica spheres (radius: 130 nm) in cyclohexane.

perature phase was predicted to be a body-centered-tetragonal (bct) crystal.¹⁵ As far as we know, this structure has not yet been reported for a colloidal system. Furthermore in this first example, shown in Figure 5a, it is demonstrated that bct crystals also form at finite temperatures because—for the crystal shown in Figure 5a—the strength of the interaction forces at room temperature was such that Brownian motion was still important.

Another direct consequence of the size of colloidal particles is that the crystalline structures they form have very low

elastic moduli compared to molecular crystals. (For this reason, colloid science—together with other fields—is sometimes referred to as soft condensed matter.) The influence of external fields like gravity, shear flow, or an electric field is therefore relatively large and can be used to manipulate the crystallization process. We will briefly discuss here only one of these manipulation methods, template-directed crystallization in a gravitational field, and refer for other interesting methods such as electrophoretic deposition or shear alignment of colloidal crystals to a recent review paper.¹⁴

We termed the process “template-directed crystal-growth colloidal epitaxy” because of its resemblance to the growth of molecular crystals on a well-defined single-crystal plane of a substrate. The substrate in the colloidal case was not a colloidal crystal but instead a lithographically designed pattern of holes in a polymer film.⁴ This template can be recognized in the fluorescence confocal micrograph of Figure 5b because a fluorescent dye was added to the polymer. Heterogeneous crystal growth was the only crystal-growth mode because the overall volume fraction was kept low and sedimentation took care of slow addition of spheres to the growing crystal on the bottom of the container. In this way, fcc crystals consisting of thousands of layers could be grown in the (100) and (110) crystallographic directions with the size of the crystals perpendicular to the growth direction only determined by the size of the template. Furthermore it was shown that two fcc crystals could be grown next to each other with just a thin slab of RHS “crystal” in between. These kinds of structures are important for the design of waveguides. Quantitative real-space measurements of these structures are possible through exploitation of the high resolution and sectioning power of confocal microscopy with fluorescent core-shell particles (Figure 5). Defect structures resulting from a lattice mismatch can also be studied quantitatively in 3D. At present we are trying to grow nonequilibrium hexagonal-close-packed crystals and to determine if colloidal epitaxy can be extended to softer interactions and binary structures.

In regard to two-dimensional (2D) structures or thin crystals, several “controlled-drying” processes have been developed.¹⁶ For instance in the study of photonic crystals, it would be useful if one could probe the buildup of a band-gap as a function of crystal size. It turns out that manipulation of the growth by a template also works for this nonequi-

librium drying process as is demonstrated by the 2D crystal depicted in Figure 5c. Measured with atomic force microscopy, the thickness of the polymer template was less than 100 nm—much thinner than the sphere size of 1 micron. The drying process was not well-controlled in this example, resulting in an incomplete crystal. Still the holes of the template imposed the placement of colloids on the square lattice even for regions where the number of direct neighbors was less than four.

In some sense, two confining walls can also be seen as a “field” influencing the possible regular structures that can form between them. (See the contribution of Murray in this issue.) Preliminary measurements have also shown that the templated wall can be used to guide crystal orientation and in certain instances can compete with the packing geometries dictated by the wall separation.

Quantum-Dot and Photonic Crystals

Colloidal crystals of quantum dots could form interesting electrophotonic materials if the capping agents could be made to be conducting, enabling charge transfer between different dots. This could for instance be realized through the use of conducting polymers as capping agents. In the case of binary crystals of (semi-) conducting spheres, the electrical properties of the material could even be made anisotropic. In such structures, the nanocrystals would truly be used as “artificial atoms.” At present such conducting colloidal crystals have not yet been realized, but efficient excited-state energy transfer through the near fields of the electronic transition dipoles has been observed.⁹

The core-shell morphology shown in Figure 1 will make it possible to place the quantum dots on a lattice with a lattice parameter of the same size as the wavelength of the optical transition of the dots. A nanosecond optical switch as demonstrated by Asher and co-workers is just one example of the colloidal crystalline material that could be improved significantly with these types of particles.⁸

Three-dimensional photonic crystals with a complete bandgap in the visible region have not yet been realized. For photons with a wavelength in the visible part of the spectrum, the feature size needs to be around half this wavelength or smaller—which makes the design of 3D dielectric structures with conventional means very difficult. Clearly, colloidal crystallization is quite powerful in the creation of such a lattice. However with

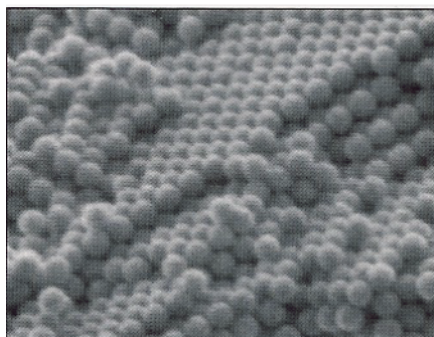


Figure 3. Scanning electron micrograph of a face-centered-cubic (fcc) colloidal crystal of particles with a radius of 75 nm and a polydispersity below 1%.

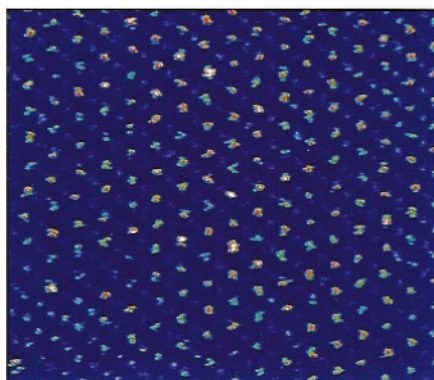


Figure 4. Reflection confocal micrograph ($25\ \mu\text{m} \times 25\ \mu\text{m}$, $20\ \mu\text{m}$ from the glass wall) of a body-centered-cubic crystal consisting of highly deionized silica spheres with a radius of 64 nm (polydispersity: 1.5%) in water. Interparticle separation is $1.15\ \mu\text{m}$, giving a volume fraction of 0.9%.

colloids, the problem is not so much in the size of the building blocks but in the high contrast (above ~ 2) and crystal symmetry needed to make a truly 3D structure with a complete bandgap. Calculations have shown that, for symmetry reasons, an fcc crystal made from dielectric spheres does not have a complete bandgap. Further the optimal filling fraction is below 50%.⁷ Quite nice procedures have been developed to make the colloidal crystals formed at lower volume fractions from particles with soft potentials less sensitive to shear melting and vibrations. For instance it is possible to

crystallize the colloids in a sea of monomers that can subsequently be polymerized (see Reference 8 and references cited therein). Crystals with a low volume fraction of particles can be “frozen-in” effectively with this procedure. However the contrast of the particles with the surrounding medium is much reduced. With touching spheres and mild sintering as shown in Figure 3, the contrast is against air and thus much higher. The necessary lower filling fractions in this case can be achieved through the use of particles with a core-shell geometry. The lower index shells are touching in the sintered dielectric materials, whereas the filling fraction of the high-index cores can be tuned. Theoretical work has shown that in order to have a complete bandgap, it is important that the dielectric material is connected. Recent calculations show that the core-shell approach offers important improvements over homogeneous spheres.¹⁷ Also, breaking the symmetry in the unit cell through the use of binary crystals such as AB_2 seems very promising.¹⁷ The theoretical understanding at the moment is such that structures really need to be calculated numerically in order to see if a complete bandgap can be expected or not. At the moment, there are only a few general guidelines in the design of the optimal structures.

One other approach to generate connected dielectric structures is to fill the regions between the spheres with a dielectric material and to remove the spheres in order to create so-called air-sphere structures (i.e., the negative of dielectric spheres in air). Here the high-index material is in between spheres of air. Such a structure can be made through the use of a colloidal crystal as a template for the deposition of high-index material and subsequently to remove the spheres by dissolution or combustion. Recently the creation of crystalline air spheres in a TiO_2 matrix with a volume fraction of high-index material around 15% has been worked out;¹⁸ see a review (Reference 14) for earlier work.

Even for structures with an incomplete bandgap, there can be strong deviations from Bragg’s law.¹⁹ Calculations show regions inside the dielectric structure where spontaneous emission is significantly altered.^{7,17} The ability to probe these regions with controlled placement of fluorescent centers either in the form of organic molecules or quantum dots will be very important both from a characterization as from an application point of view. For applications the ability to dope the photonic structures through the

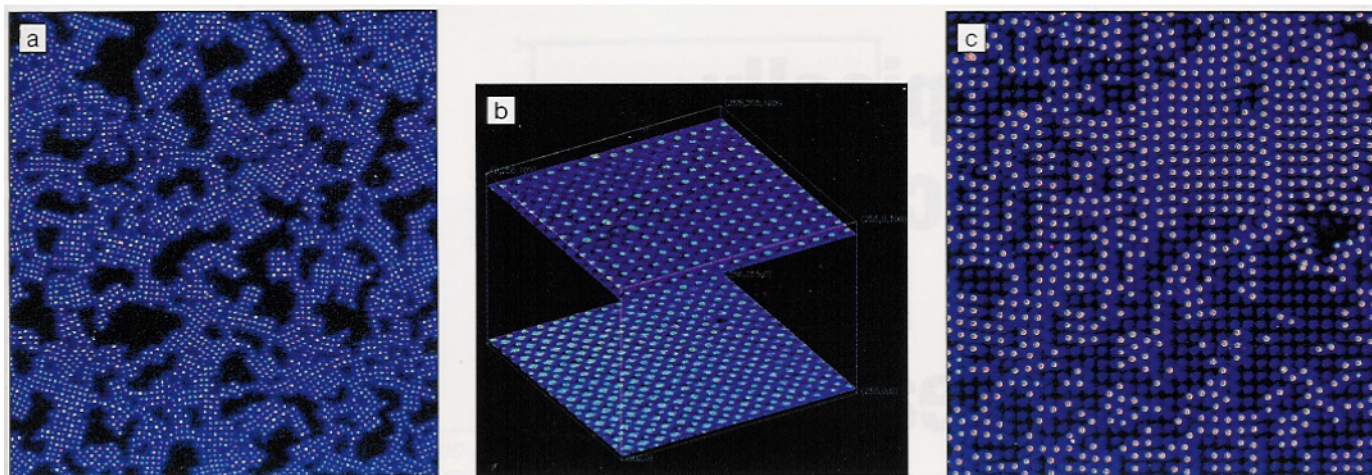


Figure 5. Confocal micrographs of fluorescent core-shell particles (core radius: 200 nm, total radius: 525 nm) in index-matched solvent mixtures. (a) Optical section ($100\ \mu\text{m} \times 100\ \mu\text{m}$, $40\ \mu\text{m}$ from the transparent electrode) of body-centered-tetragonal crystals created with an alternating-current electric field (1 MHz, $0.4\ \text{V}/\mu\text{m}$). (b) Template-directed fcc crystal growth in the (100) direction. The dyed polymer template with holes is visible in the lower section; the upper section shows the tenth layer above the template. (c) Template-directed crystal growth by drying of a dispersion on top of a two-dimensional template with a thickness less than 100 nm ($50\ \mu\text{m} \times 50\ \mu\text{m}$).

placement of high- or low-index material inside the crystals, for instance to open up pathways in the bandgap, is important as well. Here the core-shell morphology will be beneficial as well because it is relatively easy to make a homogeneous low-index silica sphere of the same radius as the core-shell particles. Similarly a high-index core and a polymer-shell particle could be used to dope the air-sphere crystals.

Outlook

The development of procedures to make new materials based on colloidal building blocks with special optical properties is only just starting. Although already interesting materials have been made, much more is possible. For instance just by combining a few of the examples shown in this article (Figures 1 and 5), a 3D structure with unique features can be imagined: A lasing photonic colloidal crystal with no threshold in which the spontaneous emission of an optical transition of quantum mechanically confined electrons in a nanocrystal is switched by an electric field that changes the photonic crystal symmetry. Such combinations of control over the electronic environment by quantum dots, control over the energy-momentum relationship for photons by a photonic crystal, and control over the 3D dielectric structure by an external field will no doubt give rise to more applications.

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1998 MRS FALL MEETING PREVIEW • PAGE 51