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Photonic Crystals

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Towards Large-Scale Photonic Crystals with Tuneable Bandgaps

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colloids · gels · photonic crystals · polymers · self-healing

Naturally occurring materials such as nacre or opals, which modulate the flow of light, have fascinated mankind for several centuries. About 20 years ago, Yablonovitch coined the name "photonic crystals" for this class of material, which exhibits bandgaps in the visible region.[1] However, research dedicated to these materials is a long-standing field, which had already started in the 19th century.

At present, the search for pathways for the production of artificial photonic crystals is a major issue in colloid science, and studies of the properties of these materials are also numerous.[2] Despite all these efforts, the large-scale preparation of these materials is still a difficult task and usually only rather small photonic crystals (in the μm range) can be obtained. In this context, a recent publication by St. John Iyer and Lyon is of great relevance.[3] In this work, the self-healing capacity of poly(*N*-isopropylacrylamide) (PNIPAM) microgel-based colloidal crystals was studied by microscopy. PNIPAM microgels are colloids that exhibit a so-called volume phase transition (VPT). This transition between the swollen and the shrunken state of the colloids is fully reversible, which is why microgels are called "smart materials".[4]

Figure 1 shows examples of colloidal crystals obtained from microgels. The crystallization of these colloids was studied as early as 10 years ago.[6] At the time it was speculated that these materials might be well-suited to the creation of artificial opals that have fewer defects than hard-sphere colloids based on SiO_2, polystyrene beads, or polymethylmethacrylate (PMMA) lattices. This hypothesis was based on the unique VPT behavior of these particles: firstly, PNIPAM microgels have a rather soft outer shell and secondly, they shrink close to the VPT temperature to lead to a "melting" of the colloidal crystal. The soft compressible character of the particles was already shown by Richtering and co-workers by using small-angle neutron scattering.[7] In concentrated microgel dispersions at higher effective volume fractions ϕ_{eff} greater than 0.35, strong deviations from true hard-sphere behavior is observed. Interpenetration of the outer regions of the soft microgel particles, which have fewer cross-links, also occurs, as well as particle compression. The small-angle neutron scattering (SANS) data for different concentrations of microgels are shown in Figure 2. The apparent shift in the scattering curves with increasing concentration is in agreement with the observation that both the equilibrium colloidal phase behavior and rheology exhibit some features of soft-sphere systems.

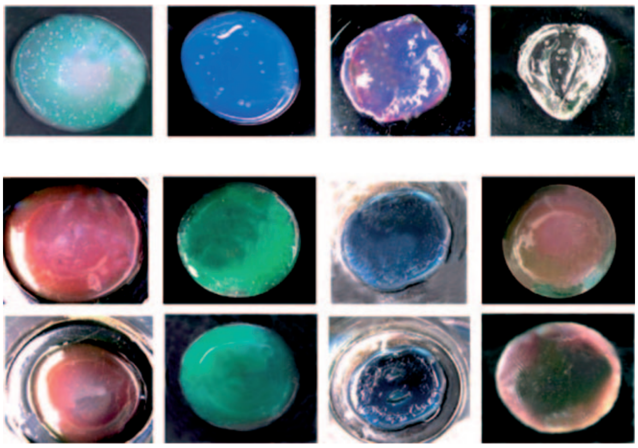

Figure 1. Colloidal crystals of PNIPAM-co-AA and PNIPAM microgels obtained at different temperatures and sedimentation times. The color arises from Bragg diffraction in the visible region.[5]

In their article, St. John Iyer and Lyon exploit the softness of the particles and show that the obtained colloidal crystals are tolerant with regard to perturbations of the structure that

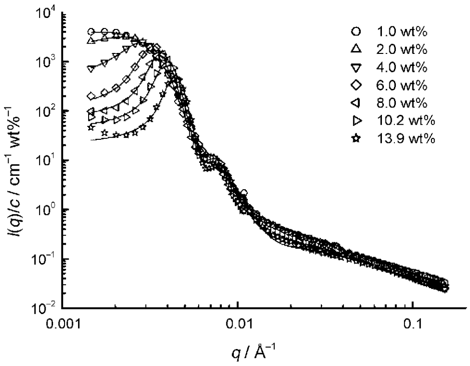

Figure 2. SANS curves for different microgel concentrations. The shift of the structure factor peak toward higher values of the momentum transfer *q* indicates a compression of the particles. Reproduced from Ref. [7]. Copyright American Chemical Society 2004.

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stem from incorporation of a particle with a different size. Such a particle does not normally fit into the grid, thus leading to packing defects. This work clearly shows that the PNIPAM microgels are indeed very "tolerant" with respect to defects, are not prone to polydispersity, and hence can accommodate even strong deviations in particle size. The dopant particle shown in Figure 3 is practically indistinguishable from the major component that surrounds it, even though the original size difference between the microgel and the dopant was very large. The soft character of the dopant means that it can be compressed, and it adapts to the lattice constant dictated by the major component that forms the colloidal crystal. This tolerance makes soft microgel spheres promising candidates for the fabrication of large arrays of colloidal crystals. Together with recent results related to the synthesis of core–shell microgels with inorganic cores, the problem of the rather low refractive index of these polymer-based materials can be overcome.[8] Incorporation of Au@SiO_2 into the core of the microgels forming colloidal crystals will probably lead to materials that have a full band gap in the visible range of the electromagnetic spectrum. The work by St. John Iyer and Lyon, together with other work on microgels, presents a route to the large-scale production of photonic crystals. At present, it seems that the only unresolved problem is the three-dimensional fixing of the structure by permanent cross-linking of the assemblies. Moreover, if the particles can be fixed in a responsive polymer matrix, materials with a tuneable band gap can be accessed.

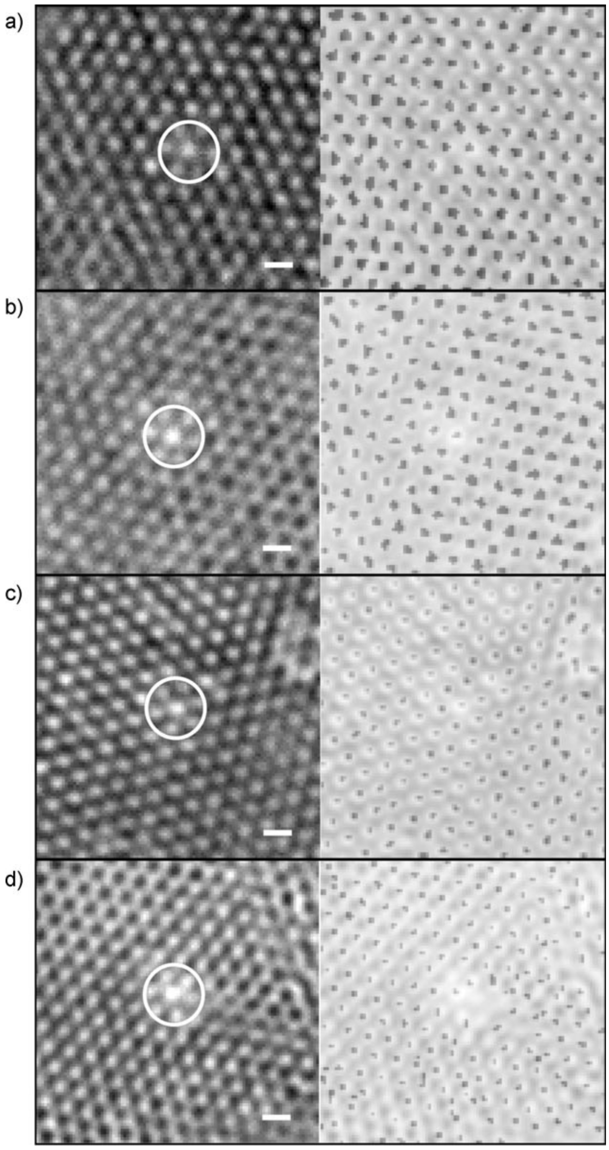

Figure 3. Micrographs (left) and particle trajectory maps (right) for crystals with a single central PNIPAM–AAc microgel dopant (circled; AAc = acrylic acid) over a range of different PNIPAM microgel concentrations. As the overall microgel concentration is increased, there is a small but observable decrease in the apparent cage size available to each microgel. This decrease is in good agreement with the SANS results.[7] It is remarkable that there is no observable difference in the volume available for the dopant particles that have a bigger diameter than the average bulk particles. The structure and dynamics are preserved in the vicinity of the defect and no perturbations were observed in the lattice. The scale bar is 1 μm. Reproduced from Ref. [3].

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