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Title: Reversible structuring of photosensitive polymer films by surface plasmon near field radiation

The metal nano-antennas confine optical energy to a scale smaller than the exciting wavelength. The interaction between the photosensitive polymer material placed above and the localized near field leads to a mass transport resulting in reversible topography changes on a nanometer length scale.
Cubic crystals from cubic colloids†

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We have studied the crystallization behavior of colloidal cubes by means of tunable depletion interactions. The colloidal system consists of novel micron-sized cubic particles prepared by silica deposition on hematite templates and various non-adsorbing water-soluble polymers as depletion agents. We have found that under certain conditions the cubes self-organize into crystals with a simple cubic symmetry, which is set by the size of the depletant. The dynamic of crystal nucleation and growth is investigated, monitoring the samples in time by optical microscopy. Furthermore, by using temperature sensitive microgel particles as depletant it is possible to tune depletion interactions to induce crystal melting. Assisting crystallization with an alternating electric field improves the uniformity of the cubic pattern allowing the preparation of macroscopic (almost defect-free) crystals that show visible Bragg colors.

The relation between particle shape and crystal symmetry and structure remains a fundamental issue in condensed matter science. The simplest and most symmetric crystal is cubic and its natural building block is the cube. Simple cubic crystals are quite rare: the lethally toxic α-emitter polonium is the only element which forms a simple cubic (SC) structure.1,2 Here we present the first observations by optical microscopy of simple cubic crystals, close-packed colloidal structures, that have self-assembled in aqueous dispersions of novel hollow silica cubes. There are important reasons to investigate the uncommon simple cubic structure employing colloids rather than atoms. SC-crystals of colloidal cubes may fill space, in marked contrast to the very open atomic SC-patterns. On the other hand cubic particles can fill space with non-registered planes which lack shear rigidity, sliding phases, and also constitute a promising experimental system for theories4 of cube fluids. In our system cubic crystal nucleation and growth, directly observed with an optical microscope, is driven by anisotropic depletion forces that cannot be generated in conventional sphere fluids. This allows additional control of the condensed phase where for example decreasing the size of the depletant locks neighboring sliding planes in registry and produces a true simple cubic crystal. Essential for time- and space-resolved imaging is that cubes are large enough for optical microscopy but still small enough to exhibit Brownian motion such that equilibrium thermodynamics of the cubes is probed on the time scale (typically minutes to hours) of optical microscopy. We synthesized micron-sized hollow cubic colloids suitable for such studies in three steps. First, iron-oxide template cubes (Fig. 1) are prepared following ref. 9, which are then covered with an amorphous silica shell to form what will become the hollow cube. Finally the iron oxide templates are dissolved by hydrochloric acid to iron chloride which diffuses away through the nano-porous silica shell (see Materials and Methods for synthesis details). The synthesis yields particles with uniform size and shape with a typical side of 1338 nm and

![Image](https://example.com/image.png)

**Fig. 1** Left: transmission electron micrograph (TEM) images of bare hematite (α-Fe2O3) cubes (a), covered with amorphous silica (b) and dissolved by acid yielding hollow silica cubes (c), with a total cube length of 1338 nm and a silica shell thickness of 100 nm. Cubes are very uniform in shape and size, with a typical size polydispersity of 3%. Scale bars are 1 μm. Right: cubes have rounded edges and can be modelled as super-ellipsoids with semi-major axis lengths $a = b = c$ and shape parameter $m \sim 3.5$ (see ref. 3 and ESI†).
polydispersity of 3%. The detailed shape of our particles is actually well approximated by a superellipsoid (superball): \((x/\alpha)^p + (y/\beta)^p + (z/\gamma)^p = 1\), a shape that smoothly interpolates between a cube and a sphere by varying a single parameter \(p\) that characterizes the roundedness of the corners (\(\alpha\) is the parameter representing the size of the particles, see ESI for details†). For their ability to interpolate between spheres and cubes, superballs are of significant interest in the study of packings of anisotropic particles.68 Our particles are the first experimental realization of a colloidal system of superballs. While the hollow cubes are stable in water over a wide pH range, our experiments were performed on aqueous dispersions at pH = 9 to increase the repulsion between the silica cubes and the glass wall of the capillaries used for the microscopy experiments. All aqueous cube dispersions discussed here contain 10 mM NaCl, which reduces the Debye length to \(\kappa^{-1} = 3\) nm; this is small enough for interacting colloids to fully experience their anisotropic shape. Despite the anisotropic shape of the colloids, we never observed crystallization of silica cubes dispersed in pure 10 mM NaCl aqueous solutions.

However, when a non-adsorbing polymer is added, within minutes (see Movie 1 in ESI†) simple cubic crystals nucleate that subsequently grow via coalescence with other nuclei to beautiful cubic mosaics as can be seen in Fig. 2, 3 and ESI Fig. 1†. Responsible for this crystal formation is the depletion effect of the polymers that drives cube faces together. When colloids are dispersed in the presence of a non-adsorbing polymer, each particle is surrounded by an exclusion zone depleted of polymers with a thickness corresponding to the radius of gyration \(R_g\) of the polymer. When the surface of two particles approach to a distance closer than \(2R_g\) the two exclusion zones overlap by \(\Delta V\) resulting in an osmotic pressure imbalance that drives the cubes together as illustrated in Fig. 2a. The contact attraction energy between two cubes due to a number density \(n\) of the depletant can be estimated from:

\[
U(n) = -\Delta V n k_B T, \tag{1}
\]

where, for two cubes, the overlap volume \(\Delta V\) is approximated by:

\[
\Delta V \approx (L - 2\delta + 2R_g)^2 2R_g, \tag{2}
\]

where \(L\) is the total length of the cube’s side and \((L - 2\delta)\) is the length of the flat faces (see Fig. 2) such that \(\delta\) is a measure of the roundedness of the cubes. The depleting polymers force the cubes together into close-packed structures that maximize the overlap volume mentioned above. Surprisingly, this close-pack occurs in the form of a simple cubic lattice. It should be noted that cubes may form close-packed mosaics that are not simple cubic: linear rows of touching cubes centred on a straight line fill a 2D plane but the rows may be shifted along their main axis over arbitrary distances without changing the close-packing condition. Similarly, if such close-packed 2D planes are stacked to a 3D structure, the planes may also be randomly translated (and rotated) without changing the packing fraction. Nevertheless, Fig. 2 clearly illustrates the marked preference of cubes to form simple cubic structures in which particles are quite precisely in register, in the plane as well as in 3D. Experiments were performed by allowing the cubes to sediment in a capillary which was imaged from below with an inverse optical microscope (for details see Materials and Methods). Due to their small gravitational height\(^{16}\) (~300 nm) the cubes assemble in a quasi 2D fashion growing only 2 or 3 particles in height. Larger gravitational heights can be reached by dispersing the particles in a density matching solvent (for instance a mixture of ethanol and bromoform) to retard sedimentation for the assembly of 3D crystals.

The cubes crystallization in register is an unexpected consequence of the shape of the cubes which have slightly rounded corners (Fig. 1). When four cube corners meet, they form a pore with a radius of about 160 nm, which is large enough to accommodate depletant polymers. Thus there is a free-energy penalty for a cube to cover such a pore, because when the cube shifts its position to be precisely on top of a neighbour the volume accessible for polymers increases. We demonstrate this preference for the silica cubes to form simple cubic crystals in dispersion using two different kinds of depletant with radius smaller than the size of the pore: poly(ethylene oxide) (PEO) with molecular weight of 600 000 which corresponds to a radius of 57 nm\(^{11}\) (see Fig. 2b) and poly(N-isopropylacrylamide) (pNIPAM) microgel particles with a radius of 65 nm (see Fig. 2c and 3). The size of cubic crystals, as shown in Fig. 2b, is limited in the presence of PEO depletant because of this polymer’s tendency to adsorb on silica.

**Fig. 2**  a. Schematic of depletion effect responsible for the self-assembly of colloidal cubes to crystals with a simple cubic symmetry. The osmotic pressure exerted by the polymer when two cubes approach each other closer than \(2R_g\) drives the particles together, with a contact energy proportional to the polymer number density \(n\) and the overlapping excluded volume \(\Delta V\) (see eqn (2)). b. Typical snapshots of optical microscopy movies of hollow silica cubes readily crystallizing into close packed, simple cubic (SC) arrays. The cubes diffuse in an aqueous solution of salt and the depletant poly-ethyleneoxide. Surprisingly, cubes in a second layer (b, right) fit precisely on top of cubes from the first layer (b, left), for reasons explained in the text. c. Particle tracking (right) of confocal images of cubes labelled with rhodamine-B isothyocyanate (left) clearly confirms the SC order in crystallites separated by grain boundaries. Cubes with the same (false) color differ in orientation as indicated by the color scale in the insert. Scale bars are 10 \(\mu\)m.
defect dynamics in 2D SC lattices. Time resolved studies of simple cubic structures, for example, on face-to-face packing of the cubes as the peculiar consequence of dispersing rhodamine-labelled silica cubes in an index matching quality of confocal microscopy images can be further improved by a template or by identifying its nearest neighbours (see ESI†). The formation and dynamics. Fig. 2c shows a confocal image of a single layer of dyed cubes resting on a glass slide. Using an algorithm based on circular Hough transforms, each cube can be easily identified and tracking for quantitative studies of phase behaviour, structure formation and dynamics. Fig. 2c shows a confocal image of a single layer of dyed cubes resting on a glass slide. Using an algorithm based on circular Hough transforms, each cube can be easily identified and its orientation (Fig. 2c) determined either by comparison with a template or by identifying its nearest neighbours (see ESI†). The quality of confocal microscopy images can be further improved by dispersing rhodamine-labelled silica cubes in an index matching solvent such as dimethyl sulfoxide which also allows the imaging of 3D crystals. In conclusion, we report the first optical microscopy imaging of the nucleation, growth and melting of simple close-packed cubic crystals (in some cases almost defect-free) in colloidal fluids of specially designed hollow silica cubes. Depolymerizing drives the crystallization, for sufficiently small depletant molecules, to a precise face-to-face packing of the cubes as the peculiar consequence of rounded cube edges. Our system provides a new tool for space-and-time resolved studies of simple cubic structures, for example, on defect dynamics in 2D SC lattices near or far away from the melting point, set by temperature and pNIPAM concentration. In addition, the cubes offer unique possibilities to study on a microscopic scale the mechanism of formation and melting of SC crystals in two dimensions, which is not possible for cubic crystals from (magnetic) nanocubes. Extensive close-packed SC mosaics are also interesting for ceramic membrane layers with controlled density and pore diameters (set here by four adjacent cubes). An interesting further option is to load the porous silica cubes with in situ precipitated functional substances to achieve mosaics of controlled-release or catalytically active cubes.

Materials and methods

Particles
Template iron-oxide (hematite) cubes were prepared from condensed ferric hydroxide gel following ref. 9. Typically 90 mL of aqueous 6.0 M NaOH solution was slowly added under stirring to 100 mL aqueous solution of 2.0 M FeCl3·6H2O. The resulting gel was stirred for another 10 min after adding 10 mL water and left undisturbed in a Pyrex bottle at 100 °C for 8 days. Next the particles were washed by centrifugation and dispersed in water. To minimize aggregation of hematite cubes during the silica coating procedure, the cubes were sterically stabilized via adsorbed polyvinylpyrrolidone (PVP, average Mw = 10 000) following the procedure in ref. 19. For later dyeing of the silica coating, 0.01428 mmol rhodamine-B isothiocyanate and 3.61 mmol 3-aminopropyltriethoxysilane (APTES) were mixed with 10 mL ethanol. This dye solution was stirred overnight in the dark and stored in a refrigerator. For the silica coating first a mixture of 913 mL absolute ethanol, 66 mL water, 10 mL tetramethylammonium hydroxide (TMAH, 1 %wt in water) and 9.41 g of PVP-stabilized hematite cubes (conc. 13.22 %wt in ethanol) was mechanically stirred and sonicated in a 2 L round bottom flask at 20 °C. The silica deposition was started by adding a mixture of 5 mL tetraethyl orthosilicate (TEOS), 4 mL of dye solution and 1 mL ethanol to the flask in portions of 2 mL every 15 min, followed by 2 mL portions of a mixture of 5 mL TEOS and 5 mL ethanol. Next a solution of 20 g PVP in 200 mL ethanol was added to the flask to prevent aggregation induced by dye molecules at the silica surface. Finally the flask was sonicated for at least 2 more hours and stirred overnight. To remove unreacted molecules the dispersion was washed several times via centrifugation in ethanol. After centrifugal transfer of the silica coated particles to water, the hematite cores were dissolved by adding hydrochloric acid (37 %wt) to a final concentration of 5 M. The complete hematite dissolution, taking typically 6 h, then manifests itself by a color change from the red hematite to bright yellow iron chloride solution. The dispersion was then washed several times, first...
with water and finally with ethanol. Poly(N-isopropylacrylamide) (pNIPAM) microgel particles were prepared following ref. 13.

**Optical microscopy**

Cube dispersions were imaged on a single-particle level with a Nikon inverse optical microscope, equipped with a 100× Nikon oil objective and a CoolSNAP EZ Photometrics CCD camera. Dispersions were kept in flat optical VitroCom capillaries, sealed to a microscopy slide with epoxy glue.

**Depletants concentration**

Typical depletant number densities used in the experiments are \(8.1 \times 10^{20}\) molecules/m³ for PEO polymers and \(6.9 \times 10^{20}\) particles/m³ for pNipam particles.

**Melting experiments**

Crystal melting experiments were performed by gluing capillaries on microscope slides coated with a thin layer of indium tin oxide, heated to the desired temperature by an electrical resistance.

**Electric field experiments**

Electric field experiments were performed by introducing two parallel platinum electrodes in the capillaries at a distance of about 2 mm with a typical alternating current electric potential of 6 V at 35 kHz for several hours.

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**References**


![Fig. 4](image)

**Fig. 4** Demonstration of the reversibility of cube crystallization: upon increasing the water temperature as indicated, cubic crystals gradually melt to an unbound state, whereas the simple cubic structures re-appear upon cooling to the initial temperature. This remarkable temperature effect is due to the shrinkage of the depleting microgel pNIPAM particles with increasing temperature, as illustrated by the cartoon. Typical snapshots are shown from an optical microscopy movie, see ESI Movie 2.†