Colloidal Crystals

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Observation of Nano-Dewetting in Colloidal Crystal Drying**

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Dedicated to the MPI für Kohlenforschung on the occasion of its centenary

Abstract: *The drying of colloidal crystals is connected with a continuous shrinkage process. However, several minutes after starting the drying, the system seems to take a breath before it shrinks monotonously until its final state after about one day. This short period we call "v"-event because of the shape of the curve characterizing the lattice constant: a decrease followed by a counter-intuitive increase which ends after one hour. This event is found in time-dependent optical spectra. It is assigned to the start of a nano-dewetting process occurring at the colloidal particles.*

Self-assembly of colloidal particles is a promising approach for fabrication of three-dimensional periodic structures. This approach is simple, cheap, and applicable for a large range of lattice constants. However, these big advantages are accompanied by some drawbacks, namely the imperfectly controllable fabrication process and the inevitable existence of the intrinsic defects. The type and amount of defects inside opal films are unknown and difficult to obtain from measurements.[1,2] The efforts to improve the self-assembly process have led to many proposed deposition methods with a different degree of controllability and special limitations.[3,4] Furthermore, many studies have been devoted to understand opal formation.[5] The actual understanding, however, is still limited to qualitative explanations of the preferential ordering of the opal lattice or of the dependence of opal thickness on deposition parameters.[6–8] The formation mechanism itself has rarely been discussed.[9]

Furthermore, opal fabrication does not end with a wet opal, which is only an important intermediate state. The final product is in the most cases a dried opal where interstitial spaces contain air. Contrary to a widespread belief, drying is not simply removing the water or other liquids occupying interstitial spaces in more or less fixed lattice of particles. During drying, the water acts back to the opal. Water evaporation may even induce structural changes, such as particle re-ordering.[4] Besides, cracks and other defects are formed or removed in this stage. The drying process will determine the final quality of opals to a large degree.

The drying process is difficult to investigate because in most of deposition methods drying occurs simultaneously with crystal formation.[5,10–12] In this respect, the capillary deposition method (Supporting Information, Figure S1) has a clear advantage; the drying process starts only after particle assembly is completed. Nevertheless, the remaining water has attracted attention because it affects the optical properties of opals significantly.[13] Also post-deposition opal drying was investigated[14] and led to a distinction of different stages in drying opals. Now we concentrate on the water redistribution in drying crystals. This process may have implications on defect formation or removing.

After detachment of the capillary cell from the suspension, the opal starts to dry and the coloration of the opal films changes within minutes. In our experiments, the appearance changed from transparent red-metallic to opaque, starting from the open edges of the capillary cell. A color change follows the drying front separating the transparent and the opaque area. Within 2 h, opal films sandwiched between two glass slides of $20 \times 25\ \text{mm}^2$ became completely opaque. The opals remained opaque for a few hours before becoming transparent again. This clearing process also starts from the open edges and moves towards the center of the capillary cell.

With an optical microscope it can be observed that the opaque area corresponds to a region containing cracks. The drying front is identical with the crack front. The crack formation, propagation, and spacing have been described before extensively.[15,16] Along with these investigations we observed, however, that a later re-clearing process occurs when the content of water is already very low and no change in the crack pattern occurs anymore. Therefore, this re-clearing must be connected to a change inside the non-interrupted opal parts at the final stage of drying.

Measured extinction spectra are shown as a "drying map" in Figure 1a. The map shows a continuous blue-shift and sharpening in the Bragg peak region as a function of time. Figure 1b displays spectra at selected times, that is, cuts through the drying map. The position, intensity, width, and shape of the Bragg peak undergo significant and reproducible changes. The Bragg peak experiences a blue-shift and grows in intensity. Furthermore, the shape of the Bragg peak develops from nearly Lorentzian to Gaussian. At intermediate times (such as at 6 h), the Bragg peak is very asymmetric.

The water content of the opal (Figure 1c) shows the main decrease within the first 50 min of drying with a nearly

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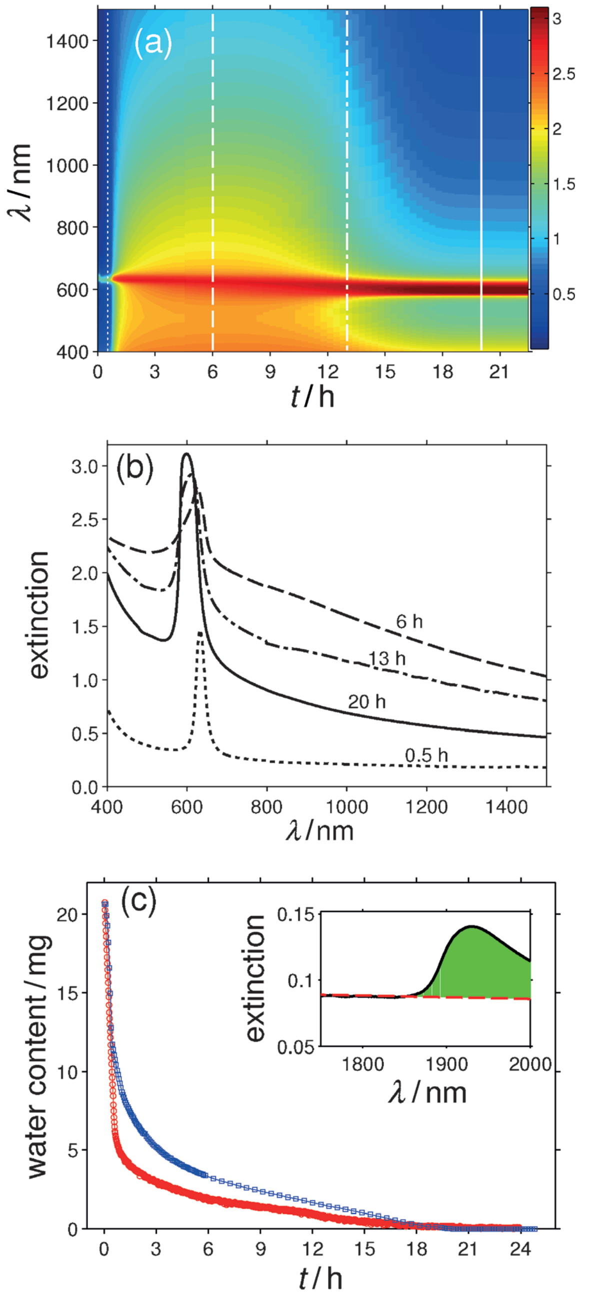

Figure 1. a) Contour plot of the extinction $E = -\log T$ over time and wavelength (drying map). b) Cuts of the map for some selected times indicated with the line style in (a). c) Water content in an opal during solvent evaporation obtained by an integral (weight, blue) and a local (spectroscopic, red) measurement. Inset: Water peak used for the content determination.

constant loss rate of (0.43 ± 0.03) mg min^{-1}. In this period, more than 75 % of the water evaporates. After that, the water content decays with a strongly decreased rate of about 0.02 mg min^{-1} till the pore water is completely evaporated. The fast decay of the total water content within the first 50 min must be ascribed as elimination of water from the volume of the interstitial voids between particles. The slower decrease of water content is likely related to evaporation of water from the particle surfaces or from narrow slits near to the contact points between particles.

To gain more insight into the opal drying process, the temporal behavior of selected spectral features was analyzed. Figure 2 a shows the maximum extinction, which decreases slightly within the first hour before it suddenly increases up to a temporary saturation. The reached value weakly depends on the thickness of the opal film and remains constant until a slight increase after 10 h. The background ($E_{bg} = E$-(1400 nm), Figure 2 b) hardly changes in the first few minutes before it increases abruptly within the first hour. After a broad maximum it decreases monotonously to its final value. At the end of drying, the background is always higher than its initial value. The Bragg peak (Figure 2 c) shows a pronounced blue-shift with a surprising interruption between 0.2 and 1 h. This phenomenon, which will be called "v-event", is characterized by the red-shift following the fast blue-shift. The v-event is followed by a further monotonous decrease of the Bragg wavelength. The rate of this decrease is enhanced up to 3 nm h^{-1} between 10 and 17 h. The Bragg peak width ($\Delta\lambda/\lambda_B$, Figure 2 d) shows an initial narrowing followed by an increase. In comparison to the other spectral features, this broadening of Bragg peak is less pronounced. After reaching its maximum, the width decays to its final value.

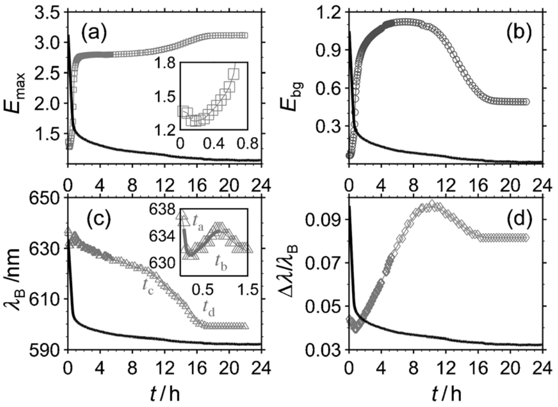

Figure 2. The behavior of selected spectral features during the drying process for the same sample as in Figure 1. a) Maximum extinction, b) background, c) Bragg wavelength, and d) normalized FWHM. The solid black curves are the local water content (without scale). Some details are shown as insets. The particular remarkable shape of λ_B at about 0.2 h is highlighted ("v-event").

The behavior of the spectral features is repeatable upon re-infiltration of dry opals with water. All temporal features for secondary and ternary drying are very similar to the primary drying. They only differ slightly in the duration of saturation stage of the maximum extinction and of the background (see the Supporting Information).

The time dependence of the spectral features has obvious characteristic points. The first already occurs at $t_a = 0.2$ h, when a surprising re-increase of the Bragg-peak position starts. After $t_b = 1$ h this increase has stopped and the system is back to the normal expected behavior. At $t_c = 10$ h, an acceleration of shrinkage starts, and it ends at $t_d = 17$ h. The question arises as to how these characteristic times and the stages of opal evolution defined by them be understood.

During $0 < t < t_a$ (stage **a**), most of the water leaves the interstitial space of the opal, leading to the formation of voids. The additional surface of the voids generates a strong pressure in the opal causing a compression of the lattice. This compression is manifested in the strong blue-shift of the Bragg peak. The second influence on the Bragg wavelength is by the effective refractive index n_{eff} appearing in the Bragg equation $\lambda_B = 2\,d_{hkl} n_{\mathrm{eff}}$. The evaporation replaces water by air and, therefore, n_{eff} should decrease in this period (optical dilution). This also decreases λ_B, so this influence points in the same direction as the compression influence.

Stage **b** ($t_a < t < t_b$) is a surprise, considering the compression and the dilution influence mentioned before. The re-increase of λ_B at about 0.2 h has no explanation by both influences. Re-densification of the opal is unlikely in this period and, therefore, we ascribe the effect to a temporal interruption of the compression. This can be caused by a re-structuring of residual water in the opal. The drying stage **a** leaves back a thin water layer surrounding the particles. The water system is still interconnected, but experiences a large surface tension. However, a re-construction of this system to separated water necks between the particles could reduce this surface tension drastically. This is what is very likely happened in the *v*-event. The resulting pressure on the opal is suddenly reduced by shifting the water from the shell into the necks and by a changed curvature of the meniscus. This increases interparticle distance within this stage. As a consequence, the Bragg peak undergoes a fast red-shift.

In stage **c** ($t_b < t < t_c$), the system has returned to normal behavior. The Bragg wavelength slowly decreases, whereas $\Delta\lambda/\lambda_B$ increases. Moreover, slight increases of $E_{\max}$ and E_{bg} can be seen. As expected, the evaporation in this period reduces the interparticle distance that in combination with the lowering of n_{eff} results in the blue-shift. $\Delta\lambda/\lambda_B$ should increase owing to the increase of refractive index modulation as water is replaced by air. However, it needs to be discussed separately if the whole effect of the peak width increase can be explained by the changing refractive index distribution only.

In stage **d** ($t_c < t < t_d$), an accelerated decrease of λ_B is observed. $E_{\max}$ slightly increases while all of the other spectral feature parameters decrease. These changes cannot be explained based on water loss only. They must be related to a compression of the spheres in the opal.[14] On the other hand, these changes are reversible. Therefore, the term "physical sintering" was introduced for this compression, differing it from normal sintering processes leading to chemically connected spheres (see also the Supporting Information).[14] However, up to now the event initializing the sintering process was not clear. The present data show that the relevant time period ($t_c < t < t_d$) is connected with the complete expulsion of water from the opal. Thus, the water necks between the particles disappear in this time. This means that the dielectric double layers at the particle surfaces vanish as well as the capillary pressure. These liquid-mediated interactions are replaced by the direct van-der-Waals interaction. After t_d, the final stage of the opal is reached. This dry state has shown no spectral change after one week or even after one year.

The values for the characteristic times depend on film thickness, particle size, and particle composition. These parameters indeed influence the drying kinetics, but the occurrence of the characteristic points in the spectral features remains very similar. The drying process becomes slower for thicker films and larger particles (Supporting Information). First experiments with PMMA-based crystals delivered shorter times for t_a and t_b, but longer times for t_c and t_d.

Figure 3 shows our picture of the drying path schematically. Especially interesting is the transformation of water from shells to a neck-type distribution (v-event).

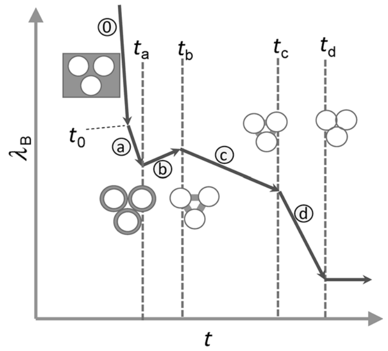

Figure 3. Representation of the drying stages. The drying starts at $t_0 = 0$. The discussed water distribution around the particles is indicated in gray.

In conclusion, opal drying is more than simple water disappearance from interstitial voids. The evaporation induces noticeable changes in the lattice. A sudden re-distribution of water is manifested in a counter-intuitive red-shift of the Bragg peak. As the underlying physical process we propose a dewetting process at the nanometer scale. The event is shock-like and might be used for opal healing experiments. These experiments should involve tuning of surface tensions and van der Waals interactions in the drying system.

Physical sintering[14] occurs in the last stage of the drying, starting with the complete expulsion of water from the contact points between particles. This sintering is connected with a significant crystal clearing effect. Here, the intensity of the Bragg peak increases while the background is reduced.

The understanding of both nano-dewetting and physical sintering may lead to strategies for the reduction of intrinsic opal defects. This is a task for future works, but present work shows already that the drying stages influence the photonic properties and the unfavorable scattering of the intrinsic defects significantly.

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