

Nanoscale Morphology of Water in Silica Colloidal Crystals

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Supporting Information

ABSTRACT: We show a simple method to visualize the morphology of water adsorbed within the pore network of colloidal crystals made of submicrometer silica spheres. Water is replicated into silica by modified silicon tetrachloride hydrolysation under standard ambient conditions, making it visible to standard electronic microscopy and thus allowing one to discern the original water distribution. Different distribution patterns are identified depending on the water content, surface condition, and spheres arrangement. The dimension and shape of wetting layers (covering the submicrometer spheres) and capillary bridges (joining them) are measurable at the nanoscale. We finally use these findings to demonstrate proof-of-principle of fabrication of isolated and freestanding silica nanorings by using hydrophobic polymeric templates and selective etching.



SECTION: Physical Processes in Nanomaterials and Nanostructures

H ow water distributes between solid particles drastically affects the physical properties of many colloidal and granular systems present in nature.¹⁻³ Direct visualization is an ideal tool for exploring the liquid morphology in such environments, but it has revealed a very difficult task, especially in three-dimensional cases and at ever-smaller scales.⁴ Progress has been accomplished in at best submillimeter range using wetting liquids different than water or immersion fluids replacing the air to achieve enough contrast^{5,6} and demanding techniques such as X-ray microtomography.⁷ These critical drawbacks preclude the study of the most natural case: air and water between small particles. Here we demonstrate a straightforward method to visualize water distributed within the pore network between submicrometre spheres down to the nanoscale. Thereby, water is aimed to be faithfully replicated into silica by modified chemical vapor deposition (CVD) under standard ambient conditions, which can be then inspected by standard field emission scanning electron microscopy (FESEM), so the original water morphology can be discerned. To prove our method, we use colloidal crystals, a well-described system whose properties facilitate cross-checking, exploring the limits of the technique and expanding the available morphological description of such test systems. Specifically, colloidal silica is chosen because of its ability to adsorb water, versatile surface chemistry, and biocompatibility. Differences in the distribution pattern are explored under diverse spheres arrangements, silica surface hydrophilicity and ambient conditions. The morphology of the water structures (wetting layers on the spheres and capillary bridges between them) are quantifiable at the nanoscale. Calculation of the capillary forces, which depend on the accurate determination of these geometrical parameters,8 is provided. This will allow comparison with experimental measurements by other techniques and testing of theoretical aspects not entirely understood at this

scale. Finally, we use the one-pulse CVD technique on polymeric templates to demonstrate a simple way to fabricate freestanding silica nanorings.

Colloidal crystals (also referred to as artificial opals) are solid structures formed by self-assembly of monodisperse spheres with applicability in many research fields such as photonics, energy conversion, and sensing⁹ but also as model for other systems.^{10,11} In particular, submicrometre silica spheres easily build inexpensive and versatile high-quality face-centered-cubic (fcc) ensembles.¹² These silica opals can contain a significant amount of physisorbed molecular water within the network formed between particles (depending on the silica hydrophilicity, up to ~8 wt % under standard laboratory conditions^{13,14}). Thus, such an opal can be viewed as a sort of wet granular material with well-defined topology (spheres monodispersity and configuration), adjustable water content, and even controllable disorder degree, providing an excellent playground to study the water morphology in submicrometre environments. Furthermore, opals, as ordered arrangements, exhibit photonic crystal properties that are sensitive to any structural (lattice constant) or compositional (refractive index) change. This provides a useful probe tool to monitor every modification realized in them while one can profit from preceding opal research such as suitable simulation software (e.g., MPB-package¹⁵) or knowledge about water distribution between opal spheres. Regarding the latter, recent studies modeled the actual water pattern from the opal photonic properties,^{16,17} providing a useful reference to be compared with our results. There, the allocation of water, whether on the

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Figure 1. Silica-transformed water in artificial opals. (a) Ideal representation of water distribution in artificial opals after refs 16 and 17. Parameters were wetting layer thickness d = 0.02 D (D) is the sphere diameter), neck radius R = 0.19 D, and spheres separation of 0.04 *D*. Here, an internal (111) plane is shown. The wetting layer has been cut out from the central sphere for clarity. Every sphere has 12 water necks connecting its 12 neighbors (six in the same plane, three in the upper plane, and three in the lower plane). (b) FESEM images of 335 nm silica opals internal cleavage after exposure to one-pulse CVD. Silica necks connecting missing spheres (spheres belonging to the half cleaved sample) can be observed. (c) Azimuthal view of the opal spheres: silica necks resemble the water distribution modeled in panel a. (d) Detail of a 905 nm sphere opal, whereby both neck and wetting layer can be distinguished on each sphere. (e) Specular reflectance spectra of a 335 nm silica opal before (black line) and after (red line) one-pulse CVD. Shaded areas are the corresponding bandgaps calculated by MPB. (f) Redshift of the bandgap due to one-pulse CVD as function of the SiCl₄ pulse length. Scale bars are 2 μ m (b) and 500 nm (c,d).

silica spheres (water forming a wetting layer of thickness d) or around the contact points between adjacent spheres (water building a capillary neck of radius R), was distinguished (see Figure 1a). Quantitative estimations of d and R under different conditions were made for opals of ~330 nm spheres. Some of these results, in particular the prediction of several nanometersthick wetting layers and capillary neck menisci with radii larger than 20 nm at moderate humidities, conflict with classical theories regarding water adsorption and capillary condensation,^{8,18} so this work offers both a means to corroborate these findings and, indirectly, a simple way to test the validity of theory in such nanoconfinments.

Opals made of Stöber silica spheres with different diameter D and arrangement quality (see Experimental Section) are employed. Water is adsorbed from moisture within the opals, which are exposed to our laboratory normal conditions (NC)—relative humidity (RH) of 35% and room temperature (RT) of 24 °C—unless otherwise noted. To inspect the water distribution at the nanoscale, a commonly available means is electron microscopy, but it demands operational requirements far from ambient conditions (e.g., FESEM requires vacuum;

environmental SEM requires low temperature and high pressure).¹⁹ This precludes direct observation of the water morphology at NC by those means. We solve this problem by "stabilizing" the water pattern, whereby water is transformed into silica prior to the FESEM study, allowing one to infer the water morphology by direct visualization of the grown silica structures. The latter are aimed to be faithful replica of the original water pattern, and evidence supporting this assumption is presented along this work.

Typically, room-temperature CVD has been used in opals by alternating pulses of silicon tetrachloride (SiCl₄) and water vapor to grow silica in successive layers.²⁰ Here samples are subjected in a reactor at NC to "one-pulse CVD" with only a single SiCl₄ cycle and omitting any water cycle, so the precursor strictly reacts where the pre-existing (*native*) water in the opal is present.²¹ As a result, a silica replica of the original water pattern at NC is achieved, although a volume reduction of ~25% from the water structure to its replica must be considered according to the stoichiometric reaction 2 H₂O + SiCl₄ (vapor) = SiO₂ + 4 HCl (vapor) and a silica density of 2.2 g/cm³. FESEM images of opals subjected to one-pulse CVD

show a well-defined pattern on the spheres corresponding to the silica-transformed native water (Figure 1b). This pattern (Figure 1c), which clearly resembles the model of Figure 1a, demonstrates a significant accumulation of water in necks between the spheres, as predicted.^{16,17} The number of necks approaches 12 per sphere (i.e., three per quadrant in the images), as expected in an fcc arrangement. The absence of some necks denotes missing contacts to neighbors due to imperfect spheres or assembly. Coexisting with the necks, a homogeneous conformal film of silica is discernible (Figure 1d), which also confirms the modeled wetting layer covering the spheres in Figure 1a.

Spectral changes helped monitor the modifications due to the one-pulse CVD as the transformation of water into silica altered the opal optical properties, i.e., the bandgap wavelength red-shifted (Figure 1e). Such redshift depended on the amount of native water in the opal, being more pronounced in hydrophilic (as-synthesized) opals (20 nm) than in hydrophobic (annealed) ones (less than 10 nm). The expected spectral shifts were calculated with MPB by assuming the water pattern predicted in ref 17 to be completely transformed into silica, preserving the original dimensions and shape of water (only considering the above-mentioned volume contraction, which is assumed to occur isotropically), and accounting for the newly adsorbed water (see Supporting Information and Figure S1 for details). The calculated shifts excellently agree with the measured ones (Figure 1e), which strongly supports our hypothesis that the resulting silica structure after one-pulse CVD truly replicates the original water morphology. Importantly, the spectral changes were independent of the length of the SiCl₄ pulse above 40 s (Figure 1f –pulses of up to 120 s were tested). This proves, on the one hand, that the precursor reacts with the native water relatively fast (mostly within the first 30 s). Thus, although water transport through the opal structure can exist,¹⁷ this would occur in much longer times (several minutes 2,5) so any significant distortion of the water pattern during CVD can be excluded. Again, the agreement of the MPB simulation with the experiments (Figure 1e), whereby the shape of the water pattern was assumed to be maintained, supports this conclusion. On the other hand, the invariability of the spectral shift at longer pulses demonstrates that no silica growth occurred after the native water was consumed, so both any extraneous humidity source and any significant reaction with the vapor water from the reactor can be ruled out.

Examination of the FESEM images directly provides a wealth of quantitative information about the morphology of the water condensed between the spheres. As discussed above, we assume the 25% volume contraction due to the CVD transformation to be isotropic (hereafter, all quantities reported are referred to the original water pattern after correction of the volume reduction). Statistical analysis yields a mean value of the water neck radius $R = 67 \pm 5$ nm in as-synthesized 335 nm-sphere opals. This value is in excellent agreement with the estimates of $R \sim 64$ nm obtained in refs 16 and 17 from optical measurements. Similar neck/sphere size ratio is found in assynthesized opals of 905 nm spheres, where $R = 187 \pm 21$ nm. Given that an ideal fcc packing is the most compact arrangement (i.e., closest average distance between spheres), any degree of disorder must be directly reflected in the water morphology. Indeed, 335 nm-sphere opal samples with lower quality (reflectance below 50%; see spectra in Figure S2) had water necks with smaller radius but larger dispersion: $R = 61 \pm$

11 nm. This is evidence that disorder leads to lower packing density and larger average distance between spheres, so the same water content forms smaller and less regular (higher size distribution) capillary bridges.

Our approach enables direct inspection of nanometric features of the silica structures. For example, FESEM images allowed quantitative, although approximate, analysis of the wetting layer covering the spheres, yielding a water film thickness of d = 10-15 nm in the 905 nm-sphere opal (Figure 1d). Given that R scales with the spheres size, as mentioned above, one can assume as a rough approximation a film thickness of $d \sim 4-6$ nm in 335 nm-sphere opals, in close agreement with the estimates made in refs 16 and 17. (d = 5-7nm). Thus, FESEM images experimentally corroborate the existence of nanometer-thick wetting layers on colloidal silica spheres even at moderate humidities (~ 35% RH), although the theoretical thickness of a water film adsorbed on a flat surface is of molecular order at this RH.¹⁸ A possible explanation might be obtained by taking into account the surface roughness. Thus, the wetting layer should not be considered as resulting from water adsorption on a flat surface but from capillary condensation at narrow asperities of the surface, where water can condense at lower vapor pressure.¹⁸ The surface roughness of Stöber silica has been estimated to be about 4 nm or less,^{22,23} so part of the wetting layer thickness could be assigned to the rough sphere surface. Another factor to be considered is the possibility of multilayer adsorption, as water adsorption on previously adsorbed water molecules can be energetically favorable.²⁴ Indeed, multilayer water adsorption has been reported to lead to thick wetting films (of several nanometers) on hydrophilic silica surfaces at ~50% RH.^{25,26}

Factors such as the ambient conditions (temperature and humidity) or the silica hydrophilicity will drastically change the amount of water and its morphology in the opal.^{7,17} The influence of ambient conditions was readily demonstrated by subjecting the opal to different temperature and RH in the reactor and, subsequently, to one-pulse CVD. Water necks exhibit an obvious size rise at higher humidity (e.g., $R = 90 \pm 8$ nm at 60% RH; Figure 2a) as the water contained in the pore network increases. Necks approach contact to their nearestneighbors until coalescence, so the system enters in the funicular regime and the capillary cohesion may weaken.^{4,7} On the contrary, necks decreased with rising temperature as water was partially desorbed (e.g., $R = 54 \pm 6$ nm at 55 °C, at which temperature only half the original (at NC) physisorbed water remained;¹⁴ Figure 2b). Analogously, the influence of increasingly hydrophobic silica surface was verified by subjecting annealed opals to one-pulse CVD. A clear decrease of the water necks was observed ($R = 45 \pm 5$ nm in 560 °C, annealed opals at NC, which contain 4 times less physisorbed water than as-synthesized ones;¹⁴ Figure 2c).

It is worth remarking that the neck size is relatively insensitive to the strong decrease of the amount of water in the opal upon sample warming or silica pretreatment (Figure 2d). This is a simple proof that the water pattern does not scale with the water content. To account for the eliminated water, the wetting layer around the spheres must strongly diminish. This implies that the liquid in low contents tends to concentrate as capillary bridges and practically no wetting layer exists. FESEM images show that the wetting layer indeed appears to vanish by decreasing water content (Figure 2b,c) while the remaining water on the spheres surface accumulates in clusters of size up to ~40 nm. The formation of such water



Figure 2. Silica neck size. FESEM images of as-synthesized silica opals after one-pulse CVD performed at (a) 50% RH, 24 °C, (b) 35% RH, 55 °C, and (c) of 560 °C annealed (hydrophobic) silica opal at NC. (d) Water neck radii in as-synthesized and annealed (at 435, 510, and 560 °C) opals as a function of the amount of water contained in them.^{16,17} Radii estimated from FESEM images (solid symbols) and from optical measurements in refs 16 and 17 (open symbols) are represented. The solid line is a guide to the eye. Sphere diameter was 335 nm. Scale bars are 500 nm.

clusters on hydrophobic surfaces (like in Figure 2c) has been largely hypothesized, but only indirect evidence has been reported. In addition, we find indication that clusters appeared on the surface after partial evaporation of the originally homogeneous wetting layer (Figure 2b). These features are in accordance with the conclusions drawn from optical measurements, 16,17 and even fairly good quantitative agreement in R values is found (Figure 2d). Data projection unrealistically predicts a nonzero R value without water, so a drastic size decrease is expected at vanishing water contents.

The visualization of the water structure further allows an independent estimate of the amount of condensed water in the colloidal crystal. In the case of as-synthesized opals, by considering a water neck radius R = 67 nm in the fcc arrangement and water films of d = 6 nm on the spheres, an amount of water of 7.3 wt % contained in the opal interstices is obtained (4.4 wt.% if d = 0 nm is considered). This is in good agreement with thermogravimetric measurements^{13,14,16,17} and supports that the water contained in the opal is indeed mostly located outside the spheres (as assumed in the model of Figure 1a). Thus, only a small fraction of condensed water, if any, would be placed inside the spheres, i.e., in ultramicropores typically found in Stöber silica (these pores are supposed to be smaller than 2 nm—indiscernible by porosimetry—but accessible to water).^{27,28} Analogously, the amounts of water found outside the spheres in the case of as-synthesized opals at 55 °C (Figure 2b) and 560 °C-annealed opals at NC (Figure 2c) calculated from the measured neck sizes (and considering d= 0 nm) were 3.0 and 2.2 wt %, which again agrees well with thermogravimetric measurements of ref 14 (3.1 and 1.9 wt %). Once more, these experimental findings apparently contradict the theoretically expected amount of water at moderate RH. Indeed, the volume of condensed water between spheres at a given humidity can be calculated by considering the Kelvin equation and the form of a capillary bridge (see Supporting Information). Thus, the theoretical volume at 35% RH is \sim 4 × 10⁻²⁴ m³ per capillary neck, i.e., a water content of about 0.01



Figure 3. Geometry of the water necks. FESEM images of silica-transformed water necks between opal spheres and the substrate (a) or between isolated spheres having one (b), two (c), or six (d) neighbors. Spheres diameter is 905 nm. Scale bars are 500 nm.

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wt % in the opal, which is about 3 orders of magnitude below the measured values (the theoretical volume of the water layer adsorbed on the spheres is less significant at this RH, as the layer thickness would be of molecular order, as mentioned above).

Future research is needed to explain such discrepancies, but our technique may provide a valuable tool as it allows obtaining a rather precise geometrical description of the water menisci between the submicrometer spheres (Figure 3a exemplifies a water meniscus formed between a sphere and the flat substrate). The meniscus geometry is critical for, e.g., accurate calculation of the capillary force between two surfaces.8 The neck radius R, the filling angle β , and the meniscus radius r can be simply obtained from FESEM images (see Figure 3b). As an example to illustrate such potentiality, Figure 3b-d shows the (silica-transformed) water menisci formed between spheres having an increasing number of neighbors. The direct measurement of the parameters on the images reveals how the specific particles arrangement affected the water necks. Thus, their size decreased with the sphere coordination number: R = 229, 224, and 209 nm (statistical error obtained from analysis of up to 12 cases is below 8 nm) was measured at 905-nm spheres with one, two, and six neighbors, respectively. This progression is nearly linear with the number of neighbors and is consistent with the neck radius of 187 nm found in the opal (12 neighbors). β in Figure 3c,d was larger than 30°, so necks coalesced. Interestingly, the triangular openings between three adjacent spheres were, however, not completely filled with water. Meniscus radii r were measured to be about 30 nm, although the accuracy was insufficient to assess any trend with the arrangement. This is again a major divergence from theory (Kelvin equation predicts $r \sim 0.5$ nm for NC), which is actually connected to the fact that the measured water content is orders of magnitude over the theoretical one. Nevertheless, the relationship between r, β , and R approximately obeyed the circular approximation, i.e., assuming toroid-like necks⁸ (see Supporting Information). Notice that the water bridge formed between the sphere and the flat substrate (R = 267 nm; Figure 3a) was significantly larger than that between any two spheres. Explanation for these features is not available to date, and further experimental and theoretical investigation is required.

Knowing the geometry of the water bridges directly from FESEM images allows accurate calculation of the theoretical capillary force (F) by the circular approximation,⁸ which involves all the neck parameters r, β , and R (see Supporting Information). In all cases pictured in Figure 3, F induced by each capillary bridge was about 150 nN. This value can be readily compared to the one obtained from the more usual approximation¹⁸ $F = \pi \gamma D$ (where $\gamma = 0.072$ N/m is the surface tension for water), which yields F = 205 nN, i.e., about 1.4 times larger. Deviations from theoretical descriptions are predictable due to a number factors (including nonideal meniscus shape or surface roughness). Therefore, the fact that theoretical forces can be directly estimated from FESEM images gives the opportunity of straightforward assessment with experimental force measurements by, e.g., atomic force microscopy (AFM). For the sake of comparison, the expected normalized force (F divided by the sphere radius D/2) is ~0.3 N/m in Figure 3, which is in reasonable accord with the experimental ones between (sub)micrometer silica surfaces (sphere-sphere or sphere-plane) measured by AFM under similar ambient conditions.^{29,30} Regarding the cohesion of the assemblies, the sphere arrangements will gradually improve

their stability with the sphere coordination number on account of the increasing number of capillary bridges per particle.⁷ In the case of the opaline fcc arrangement, this figure is maximum. By increasing the disorder in the assembly, the number of water necks per sphere will decrease in average, so the cohesion of the arrangement is expected to diminish. Such correspondence can be investigated by, e.g., nanoindentation.³

As shown so far, the silica-transformed capillary bridges approach a ring shape, whether formed between two spheres or between a sphere and the substrate. The latter can be easily separated from the opal by detaching the spheres mechanically from the substrate. Bridges adhere more strongly to the flat surface and, as a result, a hexagonal pattern formed by welldefined silica nanorings is obtained on the substrate (Figure 4a). An important further step would be the gaining of



Figure 4. Isolated silica rings. (a) Silica nanorings resulting from transformed water necks between 335 nm silica spheres and glass substrate. Inset: between 905 nm silica spheres and silicon substrate. (b) PS opal (490 nm spheres) after one-pulse CVD at NC. (c) Isolated silica nanorings and clusters cast on a glass substrate after removing of the PS template. Inset: Morphological analysis by AFM. Scale bars are 500 nm, except in the inset of panel c (50 nm).

completely isolated silica rings, a kind of nano-object that has proved to be rather elusive and has only been achieved in a very few cases.³¹ This would succeed if the spheres that we use as template can be selectively removed without affecting the silica rings formed between them. For this purpose, we used opals made of 490 nm polystyrene (PS) spheres. The hydrophobic PS surface leads to very low water content (<0.3 wt %, as measured by thermogravimetry), which is consistent with the small spectral shift (6 nm) after one-pulse CVD (Figure S3). In spite of the low amount of water, silica necks were clearly formed (Figure 4b), indicating that water accumulated between the spheres (i.e., the wetting layer was negligible), so silica necks were mostly unconnected. After dissolving the polymeric template in organic solvents (toluene, in our case), a suspension of silica rings (six per opal sphere, i.e., half the fcc coordination number) is obtained, which were cleansed and cast on a silicon substrate for FESEM inspection (Figure 4c).

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Nanometer individual silica rings are attained, which are isolated from the original surface and not attached to each other. This confirms that the water pattern on the PS spheres was discontinuous, mainly comprised by necks between spheres and some clusters on the surfaces (the latter are visible in Figure 4b and, as small patches, in Figure 4c). AFM verified the ring morphology of the obtained silica structures, with an internal diameter of 105 ± 20 nm and a wall thickness of 30 ± 4 nm (Figure 4c, inset). Such rings are expected to be attainable in a wide range of sizes (controllable by the spheres diameter and water content) and materials (mainly oxides by hydrolysis).

In summary, these experiments demonstrate that our approach might be a relevant tool for future investigation on the morphology and interactions of water—solid interfaces at the nanoscale. In particular, this technique would allow a close comparison between actual features regarding water adsorption and capillary condensation in nanoconfinments and the corresponding theoretical descriptions. Additionally, although this study is focused on the water morphology in artificial opals, the method is readily applicable to any system just containing water and being liable to undergo CVD, including polydisperse and disordered ones made of any material. Its direct application therefore spans from colloidal systems to granular materials including nanopatterning and fabrication of novel isolated silica nanorings.

EXPERIMENTAL SECTION

Sample Preparation. Silica opals were prepared from dilute ethanol colloidal suspensions of monosized Stöber silica spheres³² (with diameter D of 335 or 905 nm, 3% polydispersity) and PS spheres (with diameter of 490 nm, 3% polydispersity) following the vertical deposition method on glass substrate under controlled temperature and humidity conditions.¹⁶ High-quality (maximum reflectance as high as 90%) colloidal crystals formed by ~30 monolayers were obtained. Compacts of inferior quality (reflectance of ~50%) were employed to test disorder effects. As-synthesized opals were optionally annealed at an annealing temperature of 560 °C to reduce the silica spheres hydrophilicity,14 and finally exposed to our laboratory NC for 1 day to ensure complete water adsorption from moisture. Before one-pulse CVD experiments, each sample was kept in the reactor chamber at the aimed humidity and temperature conditions for 5 h to reach equilibrium.

Optical Characterization. Reflectivity measurements were performed with an FTIR spectrometer (IFS 66S from Bruker) attached to an optical microscope. Spectra were collected at normal incidence before and after one-pulse CVD reaction to monitor both the samples quality and the water transformation into silica.

ASSOCIATED CONTENT

S Supporting Information

Reflectivity spectra before and after one-pulse CVD reaction, MPB simulation, and theoretical calculation of capillary forces. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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