

Columnar liquid crystals of gibbsite platelets as templates for the generation of ordered silica structures†‡

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In this paper we describe the use of columnar liquid crystals of silica coated colloidal gibbsite platelets as templates for the generation of ordered silica structures. The colloidal liquid crystal phases can be formed in a few hours by modest centrifugation forces (100–200g). Base catalysed hydrolysis of tetraethoxysilane (TEOS) is used to deposit silica in the space between the silica coated gibbsite particles. The size of the gibbsite platelets is varied between 200 and 500 nm and the thickness of the silica coating between 5 and 15 nm making the system a very versatile templating material. Acid leaching is used to selectively remove the gibbsite material.

Introduction

The use of surfactant liquid crystals for templated synthesis in the early 1990s led to the formation of ordered mesoporous silica structures.^{1–4} This new class of materials has boosted research in the application of catalytically active phases inside the mesopores of these materials.^{5–8} In the first reports on ordered mesoporous silica materials, cationic surfactants were used as structure-directing agents. Due to the very thin porous walls these materials display a rather large instability towards a number of aqueous catalyst precursor solutions, which hamper their application as support material. In 1995 Bagshaw *et al.*⁹ and later a group in Santa Barbara reported on the formation of mesoporous silica structures formed using block copolymers as templating materials [ref. 10, for a recent review see ref. 11]. Compared to the materials templated by cationic surfactants these mesoporous materials have the attractive properties of larger pore diameters, thicker walls and higher stability. This makes them attractive candidates as support materials.¹²

While interesting and versatile from a structural point of view, porous materials based on supra-molecular organic liquid crystal materials are limited in pore size (to 10 nm or less) by the size of the surfactant aggregates. The breakthrough to the macroporous range (50–1000 nm) came with the use of colloidal crystals as templating materials.^{13–15} In this method first a colloidal crystal of monodisperse spherical colloidal particles is produced. Subsequently sol–gel processing is used to deposit an inorganic material at the exterior of the colloidal particles. When the sol–gel process mixture has polymerised, the colloidal template is

removed by calcination or etching. This method leads to macroporous materials with spherical pores up to 1000 nm in diameter with fascinating photonic properties.^{15–17} Here we demonstrate that the colloidal crystal templating method can be taken one step further, towards the formation of materials with ordered uniform pores of *arbitrary* size and shape and *adjustable* thickness of the pore walls by colloidal liquid crystals as templates. For a colloidal liquid crystal to act as a template for the preparation of an ordered macroporous material it must satisfy three conditions:

- easy and fast formation of the colloidal liquid crystal;
- allowing adjustable thickness of the pore wall;
- possibility to remove the colloidal liquid crystal template.

We will show in this work that colloidal liquid crystals of gibbsite particles do fulfil these three conditions.

Over the last few years we have explored the liquid crystal phase behaviour of colloidal gibbsite platelets. In particular, we have observed that suspensions of both sterically¹⁸ and charge-stabilized gibbsite platelets^{19–21} at sufficiently high concentrations display beautiful iridescence. From high-resolution small-angle X-ray scattering^{22,23} measurements we have obtained unambiguous evidence that these iridescent phases have columnar structures with hexagonal inter-columnar ordering, which is quite remarkable as the platelets have a significant polydispersity of 19% (27%) in diameter (thickness). Under normal gravity, the gibbsite suspensions develop sediments on a timescale of years. These sediments show iridescence, due to Bragg reflections by the columnar arrangement. The slow growth rate of the sediment (1 Å s⁻¹) as well as its striking iridescence reminds one of the formation of natural opal. We have shown²⁴ that the formation process of the opal-like material can be sped up by three orders of magnitude (*i.e.*, 1 day instead of 3 years) by centrifugation. To prepare the system for silica polymerization we coat the gibbsite particles with a silica layer. These silica coated gibbsite particles also form a columnar sediment under centrifugation. This then forms the starting structure for fixation with silica through polymerisation starting from a Stöber mixture.²⁵ The gibbsite template inside the polymerised silica structure can be removed by acid leaching.

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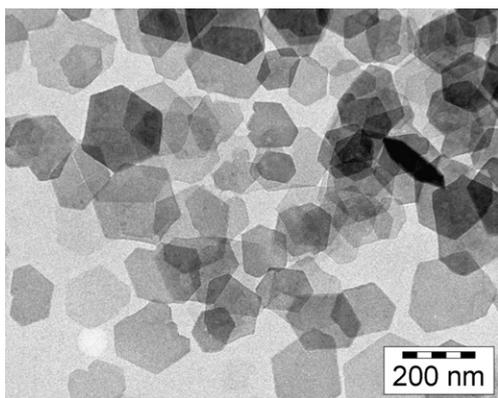


Fig. 1 Transmission electron micrograph of bare gibbsite platelets used in this study. The regular hexagonal gibbsite crystals have an average diameter $\langle d \rangle = 202$ nm, 19% and average thickness $\langle l \rangle = 13.2$ nm, 27%. Reprinted with permission from ref. 24: D. van der Beek, P. B. Radstake, A. V. Petukhov and H. N. W. Lekkerkerker, *Langmuir*, 2007, **23**, 11343. Copyright 2007 American Chemical Society.

Hexagonal columnar liquid crystal phases of colloidal gibbsite platelets at 1g

Colloidal gibbsite platelets were synthesized by crystallisation from an acidified aluminium alkoxide solution at 85 °C, following a procedure developed earlier at our laboratory^{26,19} and provided as ESI. ‡ The resulting suspension contained 6 g L⁻¹ gibbsite particles with a well-defined hexagonal shape, which can be observed in transmission electron micrographs (TEM), see Fig. 1. From such micrographs, the average particle diameter $\langle d \rangle$, defined as the average of the average corner-to-corner distances, and polydispersity σ_d defined as the standard deviation in the average, were obtained using image analysis software. The average thickness $\langle l \rangle$ of the platelets and the associated polydispersity σ_l were determined to within 0.1 nm using atomic force microscopy (AFM). The sample to be studied was prepared by filling a glass container with the gibbsite suspension. It was left undisturbed in a thermostatted dark room and inspected occasionally. From time to time, photographs were taken, three of which are shown in Fig. 2.

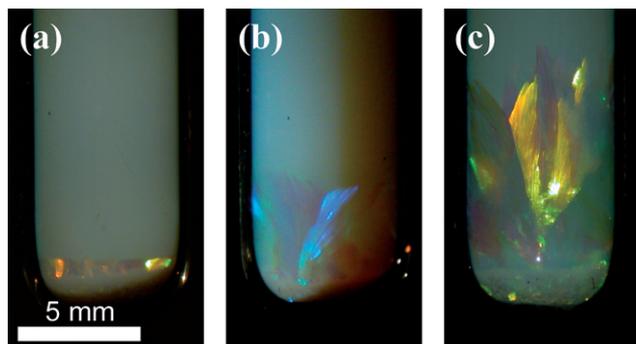


Fig. 2 Iridescent columnar phase of the colloidal gibbsite platelets, grown in the earth's gravitational field (1g). The sample has been standing for (a) 2 years, (b) 3.5 years, and (c) 6 years, and continues to grow. Image (a) was reprinted with permission from ref. 24: D. van der Beek, P. B. Radstake, A. V. Petukhov and H. N. W. Lekkerkerker, *Langmuir*, 2007, **23**, 11343. Copyright 2007 American Chemical Society.

Over 6 years the sample develops a sediment with strong Bragg reflections in the visible light that are due to the columnar liquid crystalline order. In earlier papers,^{18,22,24} we have employed small-angle X-ray scattering to confirm the existence of a columnar phase of these disk-like particles. From the photographs, two layers can be identified. The lower one has formed very quickly in the early stages of the experiment, *i.e.*, within a few months, and is composed of small columnar crystallites. The top layer grows much more slowly (about 1 Å s⁻¹), and as a result the columnar colloidal crystal formed consists of much larger single domains up to 5 mm. Still, the growth is not finished.

Apparently, it is relatively easy to grow large single domains of a columnar colloidal crystal of polydisperse gibbsite platelets, given enough patience. However, our observations invoke the question as to whether the formation of such a 'synthetic columnar opal' can be sped up. Indeed, this appears to be possible using centrifugation.

Hexagonal columnar liquid crystal phases of colloidal gibbsite platelets at 900g

From previous studies, it follows that the presence of Al₁₃ ions has a stabilizing effect on colloidal boehmite (AlO(OH)) and gibbsite particles.²⁷⁻²⁹ In order to enhance the colloidal stability of our gibbsite particles, we have treated them in the same fashion before starting the centrifugation experiments. To the gibbsite dispersion aluminium chlorohydrate was added, which hydrolyses to form Al₁₃ Keggin ions ([Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺). The treated batch of the suspension was contained in a glass flask of height 10 cm and centrifuged at 900g. After one day, all particles were sedimented and formed a viscous layer on the bottom of the flask. The supernatant liquid was removed and the sediment photographed, see Fig. 3. The sediment displays bright violet and green iridescent colours and consists of numerous

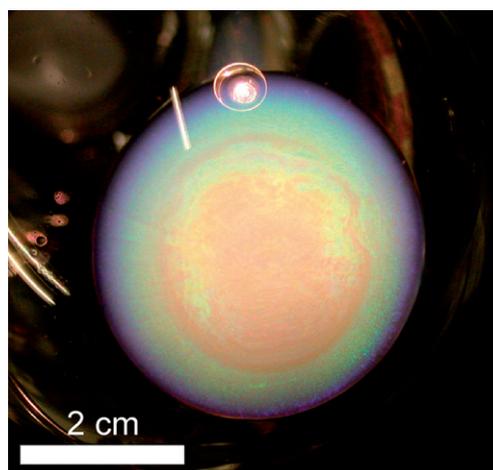


Fig. 3 Iridescent columnar phase of ACH-treated gibbsite particle, formed by centrifugation at 900g for one day. The columnar layer contains numerous small crystallites that show bright green and purple Bragg reflections due to the hexagonal lattice. Reprinted with permission from ref. 24: D. van der Beek, P. B. Radstake, A. V. Petukhov and H. N. W. Lekkerkerker, *Langmuir*, 2007, **23**, 11343. Copyright 2007 American Chemical Society.

small crystallites, which we attribute to the fast formation like in the early stage of the first sample (Fig. 2).

Thus, it is clear that the ‘synthetic columnar opal production’ can be accelerated by orders of magnitude using centrifugation at as much as 900g without arresting the system in a disordered glassy phase. It was found that samples in smaller tubes (diameter 1 mm) also developed these bright Bragg reflections, which remained present even after 4 years. Despite this stability, in order to obtain a hard opal-like material based on these colloidal liquid crystals, our next step is to prepare gibbsite particles with a discrete layer of silica.

Silica coated gibbsite

As mentioned in the Introduction we wish to obtain a templating colloidal liquid crystal that allows an adjustable thickness of the pore wall. In order to achieve this goal we first coat the gibbsite particles with layers of silica of different thickness. Then we produce a hexagonal columnar liquid crystal of these particles in a mixture of TEOS and ethanol, which is subsequently polymerised. This strategy is schematically illustrated in Fig. 4.

A batch of bare gibbsite particles with $\langle d \rangle = 210$ nm, *i.e.* very similar in size to the particles described above, was coated with silica using the method described by Wijnhoven.³⁰ For this purpose a dilute aqueous dispersion containing 0.5 g gibbsite particles was centrifuged (2 h, 1000g). Then, an aqueous solution of PVP [poly(vinylpyrrolidone), 100 g L⁻¹, MW 40000, Sigma] was used to replace the supernatant of the gibbsite. After 24 h of gentle stirring the excess of PVP was removed by centrifugation and redispersion in 0.5 L of a mixture of ethanol (Merck, p.a.) and 33 mL ammonia (Acros, p.a. 28–30%). While uncoated gibbsite particles flocculate upon dispersion in ethanol, PVP-coated gibbsite is able to form a stable dispersion. To this dispersion 1.0 mL of TEOS (tetraethoxysilane: Fluka, puris $\geq 99.0\%$) was added under vigorous stirring. A transmission electron micrograph of the resulting particles is shown in Fig. 5a. The thickness of the silica shell can be adjusted easily by the amount of TEOS that is added to the system of PVP coated gibbsite particles. Therefore, in some of the systems an additional amount of TEOS was added, to make the silica coating thicker.

In order to demonstrate the versatility of gibbsite particles as a templating agent we also explored the use of larger particles. For this purpose gibbsite particles with $\langle d \rangle = 207$ nm were redispersed in the acidic mixture of aluminium alkoxides in water for a seeded growth procedure similar to that described earlier.³¹ After such a procedure the particles had grown to an average diameter $\langle d \rangle = 493 \pm 59$ nm, as was determined from measurements of the corner-to-corner distance of 400 platelets from

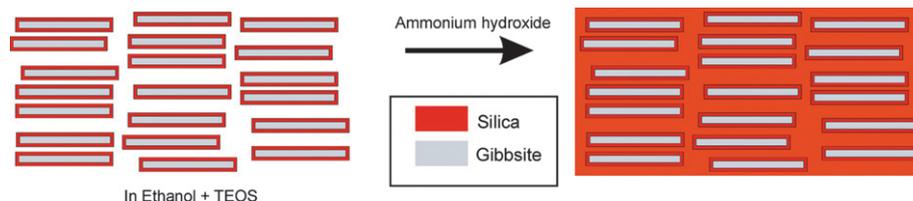


Fig. 4 Artist’s impression of the templating procedure of silica coated gibbsite in columnar liquid crystals within a solvent containing the silica precursor TEOS.

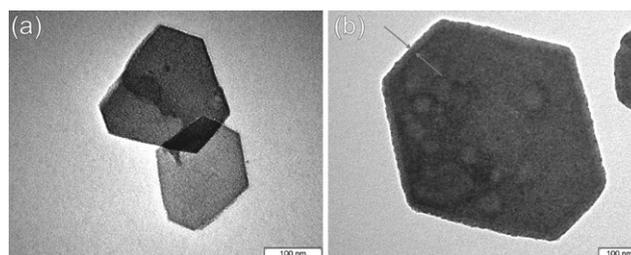


Fig. 5 Transmission electron micrograph of silica coated gibbsite particles used in this study. A system of small gibbsite particles ($\langle d \rangle_{\text{bare}} = 210$ nm) was coated with a silica layer (average thickness 5 nm) (a). Performance of a seeded growth procedure for gibbsite leads to a larger average diameter ($\langle d \rangle_{\text{bare}} = 493$, 12%) of the bare gibbsite platelets. Coating this larger system with silica (15 nm) leads to the system depicted in (b). The thickness of the silica coating is visible on the edges of the particles as indicated by the arrows.

transmission electron micrographs. These large particles were coated with a silica layer following the same procedure as described above for the smaller particles. The result is a very turbid dispersion of platelets that shows shear-induced alignment upon stirring.

In Fig. 5b a transmission electron micrograph of one of the resulting silica grafted gibbsite particles is shown. It is interesting to note that the gibbsite particle is coated with a silica layer that is slightly rougher than the gibbsite core. The average thickness of the silica layer in this system is determined by measuring more than 40 individual layers at the edges of the particles as visualized in Fig. 5b, yielding a thickness of 15 nm.

Hexagonal columnar liquid crystal phases of silica coated gibbsite

The silica coated gibbsite particles, prepared as described in the previous section, form stable suspensions in water, ethanol and mixtures of ethanol and TEOS. The latter is of crucial importance since in order to be able to deposit silica on the liquid crystal colloidal particles there is a need to work in an environment where a significant amount of precursor (*i.e.*, TEOS) is present. Solid material forming the pore walls is produced upon addition of an initiator.

In all of the solvents mentioned above, centrifugation leads to the formation of a columnar liquid crystal as evidenced by the appearance of Bragg reflections.

In Fig. 6 the results are shown for the system consisting of the small ($\langle d \rangle = 210$ nm) gibbsite particles coated with silica. Similarly in Fig. 7 the results are shown for the system containing the

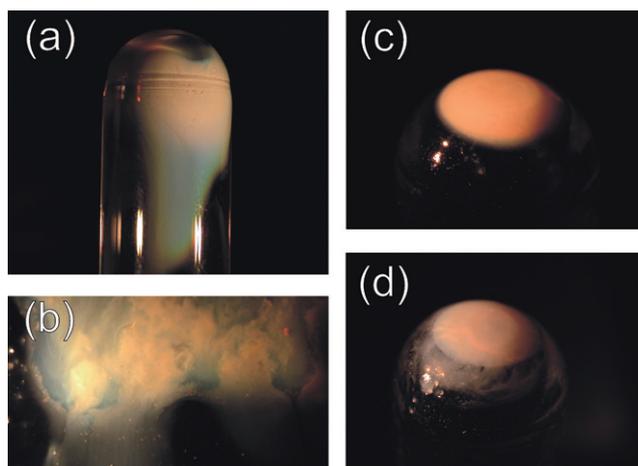


Fig. 6 Centrifugation of the system of silica coated small gibbsite particles leads to the formation of columnar phases in various solvents as is observed from iridescence. Right before observation the test tubes were turned upside down for practical purposes. The sediments shown are formed in (a) water (2 h, 185g), (b) ethanol (17 h, 185g) and (c) TEOS (20% v/v) + ethanol (80% v/v, 2 h, 447g). Replacement of the supernatant in (c) with ammonia and subsequent infiltration with TEOS-ethanol followed by ammonia leads to the formation of a solid system (d).

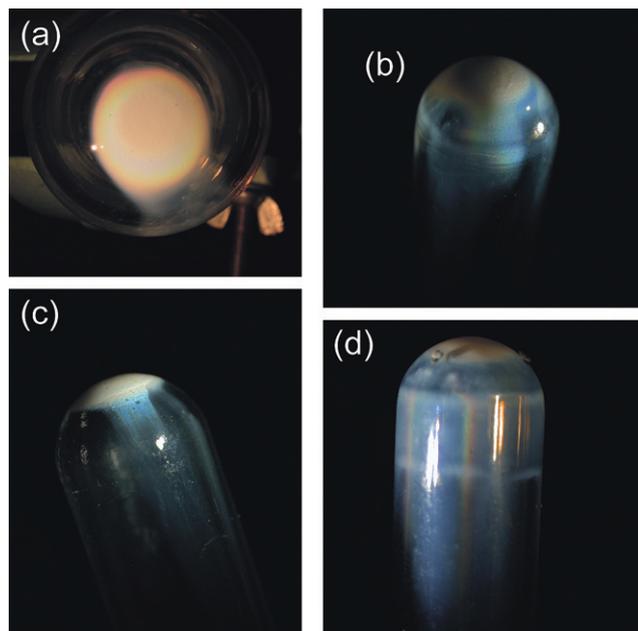


Fig. 7 Centrifugation of the system of silica coated large gibbsite particles leads to the formation of columnar phases in various solvents as is observed from iridescence. Right before observation the test tubes were turned upside down for practical purposes. The sediments after centrifugation in (a) water (3 h, 900g), (b) ethanol (30 min, 200g) and (c) TEOS (60% v/v) + ethanol (40% v/v) (30 min, 200g) are shown. After 4 days a columnar sediment is formed by normal gravity as is illustrated by the sample in 30% v/v TEOS + 70% v/v ethanol shown in (d).

larger particles ($d = 493$ nm). Dispersions of silica coated gibbsite particles in water were centrifuged and inspected under white illumination directly after stopping the centrifuge. Bright Bragg reflections became visible upon centrifugation of aqueous

silica in ring shaped layers at the bottom of the centrifuge tubes. When the tubes are inspected upside down, the sediment is perturbed by the tilt and becomes loose. A flow of previously sedimented material emerges along the walls of the tube. Even during flow, bright Bragg reflecting areas remain visible in the sediment. Similar phenomena were observed for dispersions in ethanol and mixtures of ethanol and TEOS. The centrifugal force and centrifugation time needed for the large particles was significantly smaller than for the smaller ones. Moreover, sedimentation of the large particles at 1g for 4 days in a mixture of ethanol (40% v/v) and TEOS (60% v/v) already leads to beautiful Bragg reflections (Fig. 7d).

Columnar liquid crystals of silica coated gibbsite particles as templates for directed growth of silica

To cast columnar liquid crystals in silica, first columnar pellets were obtained by sedimentation of silica coated gibbsite particles in a mixture of TEOS and ethanol as a solvent. After formation of such a sediment, the supernatant was removed and replaced by ammonium hydroxide (Acros p.a., 28–30% v/v) to start *in situ* polymerization of a silica network throughout the colloidal pellet. After addition of ammonia the colloidal crystals appeared fixated and no longer redispersed spontaneously. Optical Bragg reflections were still visible after this step. In order to prove the existence and characterize the columnar phase in more detail SAXS measurements were done on the solid system. So far, no conclusive results pertaining to the columnar phase could be extracted from these measurements.

For the small gibbsite particles coated with a 5 nm layer of silica 20% v/v TEOS (and 80% v/v ethanol) was the maximum amount of silica precursor that could be used while keeping the system stable. To increase the amount of silica deposited upon addition of ammonium hydroxide, the silica precipitation procedure was repeated two more times by addition of a fresh reaction mixture consisting of ethanol and TEOS followed by addition of ammonium hydroxide. The resulting solid system, shown in Fig. 6d, is quite rigid.

The large particles, with a silica layer of 15 nm, were stable in a mixture of 60% v/v TEOS (and 40% v/v ethanol). In this case a single precipitation reaction step produced sufficient silica to form a rigid structure. The resulting structure was dried in air to remove the remaining solvent over several days. Upon drying the sediment slightly shrank, cracked and released from the walls of the sample tube. Careful examination showed that the resulting flakes of material still show Bragg reflections (Fig. 8). Depending on the angle of illumination, different columnar crystal domains show coloured reflections. Note that whereas in Fig. 2 blue iridescence is visible, this not the case in Fig. 8. This could be related to the fact that the particles in Fig. 2 have a diameter of 210 nm and in Fig. 8 the diameter of the particles is 493 nm. To study the effect of particle size on the wavelength of the reflections experiments with carefully controlled angles of illumination and reflection must be performed.

Scanning electron microscopy (SEM) was performed on this material with a XLFEG30 (5 kV, Philips). Prior to SEM experiments samples were sputter-coated with a layer of approximately 5 nm thickness of Pt/Pd alloy. The micrographs reveal that despite the large TEOS content before addition of ammonia,

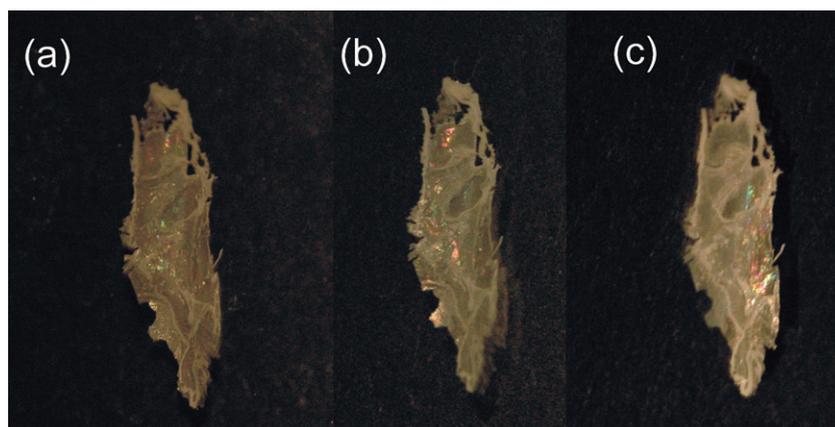


Fig. 8 Solid flake of columnar silica coated gibbsite in silica. A columnar liquid crystal of silica coated gibbsite particles dispersed in TEOS (60% v/v) + ethanol (40% v/v) was solidified by addition of ammonium hydroxide and dried. Illumination by white light under various angles leads to reflections of various domains and colors.

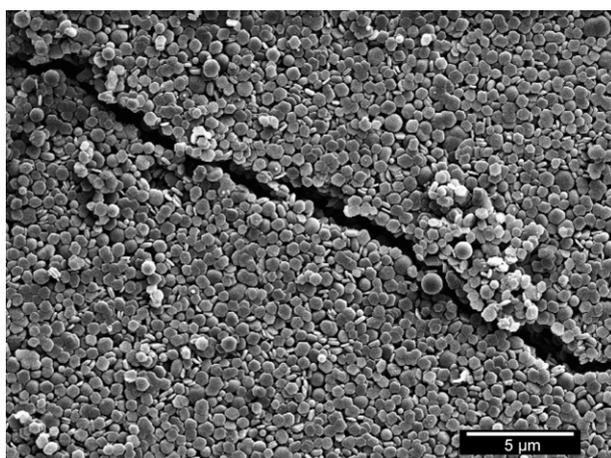


Fig. 9 SEM image of silica coated gibbsite particles in the columnar phase after deposition of silica from the solvent and subsequent drying.

separate silica coated particles can still be distinguished (Fig. 9). This does not imply that the structure is loose. It is known that in the Stöber synthesis originally separated particles may grow together at too high concentrations of ammonia or TEOS, an effect that is exploited in the production of silica dumbbells.³² A significant amount of silica has nucleated on the original silica coated gibbsite platelets making them appear much bulkier in SEM pictures. Although orientational order is clearly present and small stacks of platelets are visible, it is not obvious from SEM images that the platelets show hexagonal order. A possible explanation might be that whatever hexagonal order is present in Fig. 9 is masked by polydispersity. Moreover a limited amount of spherical particles is formed at the surface of the sediment. However, it is still unclear whether these spheres possess a gibbsite platelet as a core or if they are formed due to secondary nucleation.

Removal of the gibbsite cores

The gibbsite core of a composite silica–gibbsite particle can be removed through the silica coating in solution by acid leaching

the system in nitric acid, as was shown earlier by Wijnhoven.³⁰ Silica coated gibbsite particles were first transferred to water before concentrated nitric acid was added to the dispersion. After 4 days and 2 additions of a large excess of nitric acid, the system was investigated by TEM to see the result of the acid leaching on the particles. The leached particle displayed in Fig. 10a has an edge that is noticeably darker than the interior. Recall that the particles before leaching had the opposite contrast, being darker on the inside (Fig. 5b). From this we conclude that the gibbsite core has indeed been leached away. The dark edge has a thickness of approximately 17 nm, consistent with the thickness of the silica shell. The integrity of the silica coating seems unaffected by the leaching procedure.

Even more conclusive information is provided by STEM EDX (scanning transmission electron microscopy energy dispersive

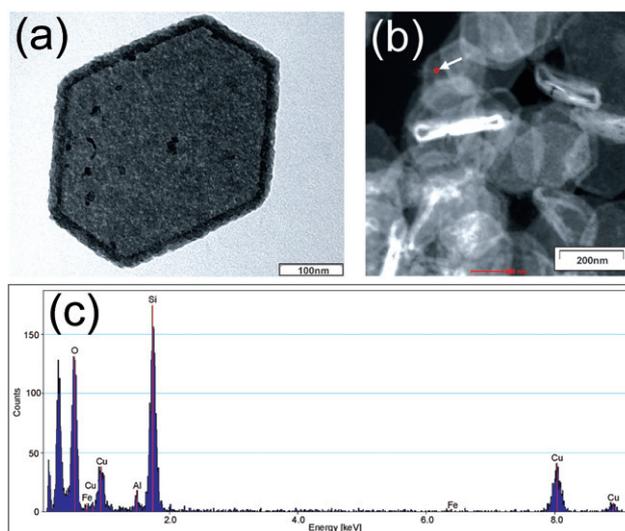


Fig. 10 Acid leaching of silica-coated gibbsite can remove the gibbsite core through the silica coating (a). In (b) an STEM image is displayed. The arrow indicates the location in the particle where an EDX measurement was done. (c) EDX spectrum of the location in the leached silica coated gibbsite particle indicated in (b).

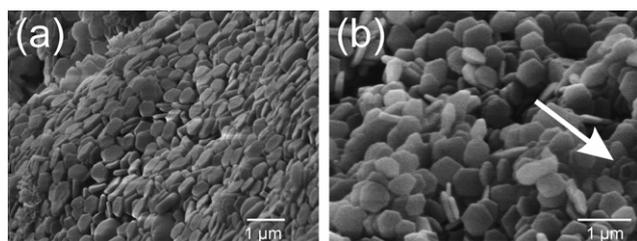


Fig. 11 The result of acid leaching on a flake of columnar silica coated gibbsite particles that were fixated by *in situ* deposition of silica as observed in SEM. (a) The global appearance of the flake is similar to that before acid leaching. (b) Hollow particle as observed in SEM (indicated by the arrow).

X-ray) measurements on silica covered gibbsite platelets that were leached. The dark-field STEM image displayed in Fig. 10b shows the location in a single particle where a spot EDX measurement was done. There is a large ratio between the signal attributed to Si and that attributed to Al in the corresponding EDX measurement that is displayed in Fig. 10c. This is in accordance with the removal of gibbsite. Since it is possible to leach out substantial amounts of aluminium from composite particles we have tried to use this acid leaching procedure for removal of the gibbsite cores in our dried, silica fixated columnar crystals. For this purpose flakes of Bragg reflecting material were immersed repeatedly for several days in concentrated nitric acid. SEM pictures reveal that the global appearance (Fig. 11a) of the system remains the same, but that individual platelets may show that they are hollow (Fig. 11b)

Conclusions

In this work we have shown that colloidal liquid crystals of gibbsite particles do fulfil the three conditions (easy and fast formation of the colloidal liquid crystal, allowing adjustable thickness of the pore wall, possibility to remove the colloidal liquid crystal template) to act as a template for the preparation of an ordered macroporous material.

Centrifugation appears to be a powerful tool to speed up the process of formation of liquid crystal phases from dilute suspensions of gibbsite particles. By coating the gibbsite particles with silica we have successfully used columnar liquid crystals as a template for the formation of inorganic composite materials with periodicity in the colloidal domain. The typical repeat distances of both components in the resulting material can be adapted. The original bare gibbsite particles can be grown to various sizes giving rise to different periodicities and the thickness of the silica shell can be adjusted before producing crystals. *In situ* growth of silica from alkoxides could stabilize and fixate the structure, such that the solvent could be removed. In this way synthetic opals of gibbsite in silica were produced. The resulting iridescent material can be treated with acid to leach out aluminium and therefore obtain macroporous silica with adjustable silica wall thickness.

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