The role of curvature in silica mesoporous crystals

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Silica mesoporous crystals (SMCs) offer a unique opportunity to study micellar mesophases. Replication of non-equilibrium mesophases into porous silica structures allows the characterization of surfactant phases under a variety of chemical and physical perturbations, through methods not typically accessible to liquid crystal chemists. A poignant example is the use of electron microscopy and crystallography, as discussed herein, for the purpose of determining the fundamental role of amphiphile curvature, namely mean curvature and Gaussian curvature, which have been extensively studied in various fields such as polymer, liquid crystal, biological membrane, etc. The present work aims to highlight some current studies devoted to the interface curvature on SMCs, in which electron microscopy and electron crystallography (EC) are used to understand the geometry of silica wall surface in bicontinuous and cage-type mesostructures through the investigation of electrostatic potential maps. Additionally, we show that by altering the synthesis conditions during the preparation of SMCs, it is possible to isolate particles during micellar mesophase transformations in the cubic bicontinuous system, allowing us to view and study epitaxial relations under the specific synthesis conditions. By studying the relationship between mesoporous structure, interface curvature and micellar mesophases using electron microscopy and EC, we hope to bring new insights into the formation mechanism of these unique materials but also contribute a new way of understanding periodic liquid crystal systems.

Keywords: silica mesoporous crystals; mean curvature; Gaussian curvature; surfactant packing parameter; electron crystallography

1. INTRODUCTION

Silica mesoporous materials have been recognized as a novel class of porous solids since the first reports of their synthesis [1]. Besides their importance in industry and chemical engineering owing to their various potential applications, silica mesoporous materials have shown intriguing geometrical aspects that have been discussed prominently in the liquid crystal community [2]. Among various types of silica and other inorganic mesoporous materials, ordered mesoporous silicas are of particular interest because of the well-defined degree of pore periodicity and the readily tuneable pore sizes along with the pore geometries; those structural parameters are essential to control properties useful for catalysis, separation, drug delivery and medical engineering. We call such ‘ordered’ ones silica mesoporous crystals (SMCs) where geometrically...
characteristic mesopores (sphere, cylinder and ramified multi-continuous pores) are arranged fulfilling the translation symmetry, and thus amenable to structural analyses using crystallography.

In a typical synthesis of SMCs, the mesostructure is formed through cooperative self-assembly of inorganic species and amphiphilic molecules or copolymers in the presence of water (and additive organic solvents). Therefore, although the system is more complicated and not necessarily at thermodynamic equilibrium, SMC structures are considered to be the solidified version of the associated lyotropic mesophases, where the surfactant and water domains are replaced by the mesoporous voids and the amorphous silica matrix, respectively. This solidified replication enables, compared with liquid crystals, more detailed investigation of the specific structure of SMCs using electron microscopic techniques with relative ease. A distinct feature of SMCs is that, in contrast to ordinary atomistic crystals, mesostructure, including pore position, pore shape, pore size and silica wall density, fluctuates remarkably from place to place [3]. This originates from the associated micellar mesophases that is a typical soft matter system, as well as some perturbation during the synthesis.

Pore geometries of SMCs originate from the associated micellar mesophases which can be concisely summarized using a simplified value, $g$, a surfactant packing parameter defined as $g = V/a_0$, where $V$ is the surfactant chain volume, $a_0$ is the effective hydrophobic/hydrophilic interfacial area and $l$ is the chain length [4]. The $g$ parameter relates the micellar global geometry to the averaged molecular shape of surfactants, which facilitates the understanding of the mesostructural formation. Based on this scheme, ideal mesophases such as globular, cylindrical, bicontinuous and bilayer geometries must possess respective values of $g = \frac{1}{3}$, $\frac{1}{2}$, $2/3$ and 1, owing to the simple geometrical constraints. Correspondingly, various mesostructures on SMCs have been formed according to the packing behaviour of the surfactants. Local properties of a surface can be described by two useful measures: the mean curvature $H$ and the Gaussian curvature $K$. $H$ is related to the surface bending while $K$ to the local shape of the surface and the global structural topology [5].

Among various geometries, infinitely periodic minimal surfaces have been of particular interest as they can be studied using crystallography combined with the fundamental knowledge of the differential geometry; they are three-dimensionally periodic and simultaneously realize the complex structures constructed by curved patches on which translation symmetry is preserved. However, unlike minimal surfaces, the curvature is related to the surface bending while $K$ to the local shape of the surface and the global structural topology [5].

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2. CURVATURES ON ELECTRON CRYSTALLOGRAPHY

The determination of pore structures, such as the pore location, size, shape, connectivity and their deviation, is essential to understand further properties (related to gas adsorption, separation, functionalization, diffusibility, etc.) of SMCs. Among various experimental techniques for characterizing structures, electron tomography (ET) and EC are the only methods that can generate a direct reconstruction of their detailed mesostructures three-dimensionally without any geometrical assumptions [13]. When an object satisfies the translation symmetry as SMCs do, EC is the method of choice owing to the finer spatial resolution than ET. We have developed an application of EC to directly reconstruct ordered mesoporous materials, which has approached a spatial resolution of 1.5 nm [14, 15].

A number of synthesized SMCs have been visualized by EC as three-dimensional electrostatic potential maps (hereafter the ‘potential map’) [11, 16, 17]. In the following, a potential map is arbitrarily expressed as $p(r)$ that is reconstructed by the Fourier synthesis [18] of the Fourier components obtained from TEM image data through EC.

Determination of the wall boundary structure from the reconstructed potential map is important to determine pore structure in detail. As already mentioned, SMC pore wall structures, including pore position, shape, size and the wall density, fluctuate remarkably [3]. This fact limits the Fourier components of $p(r)$ within small scattering vectors up to approximately 0.6 nm\(^{-1}\), and consequently a reconstructed potential map is visualized by only a broad distribution in three-dimensional real space (figure 1). A rough sketch of the silica wall structure can be perceived by the gradual variation of the potential levels. However, for quantitative discussion of the pore properties, it is necessary to determine the wall structure in detail. The pore wall structure of SMCs can be described by an iso-potential surface (IS), $p(r) = c$, which partitions the potential map into the wall and the mesopore zones by a certain potential level $c$ [15]. Determination of an appropriate potential level $c_T$ is difficult using the vague potential map (i.e. the most probable wall picture among the deviating mesopore structures).
One way to obtain the value of \( c_T \) is by combining the EC data and the pore volume information from gas adsorption measurements, for which an assumption of the silica wall density is required [15]. This combined method is amenable only to very high crystalline samples because the adsorption measurements use the bulk amount of samples while TEM data are to be detected from a few single nanocrystals. Also, the samples must be calcined to create void pores for the gas adsorption measurement. To overcome these limitations, we have explored an approach to obtain a self-consistent structural solution of SMCs within EC data [19]. This attempt has been realized by minimizing the Helfrich energy density on the boundary surface between inorganic and organic components. We rely on an evaluation of curvatures along ISs defined at every potential level \( c \). From a set of the evaluation, we select the value of \( c_T \) giving the IS closest to the constant mean curvature (CMC) realm as the best solution for the mean wall position. It is worth noting that the structural solution for mesoporous crystals should be described by a representative unit cell reflecting the averaged picture among highly deviating mesopore structures. Respective ISs at different potential levels are candidates for such an averaged picture. The curvature assessment and the minimization of the Helfrich energy density are used to find the best IS representing the typical silica wall as the realistic structural solution of the underlying SMC.

During syntheses of SMCs, the polymerization of the silica precursor takes place at the boundary between water and the amphiphile sheet. The amphiphile sheet can be approximated as an elastic continuum, where the Helfrich energy is a good description for a factor governing the micellar geometry [20]. We would like to note here that this regime is generally applicable to structures emerging in material and life sciences where the interface boundary energy drives the formation [21]. The Helfrich energy per unit area is expressed as

\[
2\kappa_1 (H(r) - H_0)^2 + \kappa_2 K(r)
\]

where \( H_0 \) represents the spontaneous curvature, and \( \kappa_1 \) and \( \kappa_2 \) are the bending and the saddle-splay elastic moduli, respectively [5]. Local values of \( H \) and \( K \) are calculated from the surface normal \( n = \nabla p/|\nabla p| \) as follows:

\[
H(r) = \frac{\text{div} n}{2}
\]

and

\[
K(r) = \frac{1}{2} \left\{ (\text{div} n)^2 + (\text{rot} n)^2 - \sum_{i,j} (\partial n_i n_j)^2 \right\}.
\]

Here \( n \) is defined as it directs from the silica wall to the surfactant or mesopore zone. Owing to the Gauss–Bonnet theorem, the integral of \( K(r) \) over the surface

\[
\int K(r) \text{d}A = 2\pi \chi
\]

keeps constant, where \( \chi \) is the Euler characteristic and is related only to the global topology of the structure. Thus, a term of the Gaussian curvature is dropped within an identical topology. The dimensionless Helfrich energy is then given by

\[
F = \int \left( H(r) - H_0 \right)^2 \text{d}A.
\]

On the basis of this \( F \), the energy minimization leads us to a scheme of CMC. A validity of CMC description for SMCs has also been discussed by Anderson et al. [22, 23]. By comparing models of several cage-type SMCs reconstructed by EC with mathematical CMC surfaces made by a Surface Evolver program [24], they established that the ISs of SMCs are consistent with the CMC regime within experimental error, and the value of the mean curvature depends on the surfactant employed and as a result the structural topologies. Our attempt here concentrates on a self-consistent derivation of an appropriate IS within EC reconstruction. It should be noted that we do not incorporate the bending elastic module since its dependence on a material is unknown, which restricts the evaluation to be valid within respective EC data. The weighted average of \( (H(r) - H_0)^2 \) is given by \( F/A \), where \( A \) denotes the area over the surface. The formulation of \( F/A \) is equivalent to the variance of the mean curvature distribution from \( H_0 \), which gives rise to the dependence on the frequency distribution of \( H(r) \) over the surface. To determine the prescribed value of \( H_0 \), we adopt the weighted average of \( H(r) \) over the surface so that the most probable value is obtained. Thereby, \( H_0 \) is expressed as

\[
H_0 = \frac{1}{A} \int H(r) \text{d}A.
\]

Although \( H_0 \) is generally non-uniform as a function of position and curvature, we however assume \( H_0 \) to be uniform for simplicity. The present approach has a closure within EC data, and thus it allows the evaluation of properties of the mesopore geometry regardless of remnant of surfactants. This point is advantageous for cases where surfactants are designed to remain...
within the pores on purpose to stabilize the molecules, drugs and peptides. Moreover, the fundamental mesopore information (the mesoscopic surface area and mesoporosity) can be obtained along with the curvature distribution on the determined IS. Knowledge of local curvatures is also useful, especially for functional properties of ramified porous structures.

This analysis is applied to the most known bicontinuous SMC MCM-48 (analogous to the G-surface) of as-synthesized (as-syn-, the lattice constant \(a = 8.8\) nm) and calcined (cal-, \(a = 8.5\) nm) materials with space group \(Ia\bar{3}d\) having a certain wall thickness. First of all, the mesopore ramification is characterized by \(x = 16\). As can be seen in figure 2a, \(F/A\) of as-syn-MCM-48 and cal-MCM-48 are minimized at \(c_T = 59.5\%\) and \(c_T = 78.3\%\), respectively. This determined wall offers the IS closest to the CMC realm among imaginable ISs within EC data, which is considered to be the most reliable mean wall position. In figure 2b, a comparison of the experimental and simulated TEM images is made to verify the validity of the determined wall structure; a good agreement has been obtained. The cal-MCM-48 accommodates a larger subspace volume \((393\) nm\(^2\)) than that of as-syn-MCM-48 \((316\) nm\(^2\)) despite shrinkage of the unit cell, which results from the contraction of the silica wall. On those ISs, the distribution of both \(\Delta H\) (deviation from the surface-averaged mean curvature, \(\Delta H = H - H_0\)) and \(K\) are examined as depicted in figure 3a, b. \(H\) of the as-syn-MCM-48 surface varies around \(H_0 = 0.20\) nm\(^{-1}\) from 0.11 to 0.34 nm\(^{-1}\), while \(H\) of cal-MCM-48 around \(H_0 = 0.13\) nm\(^{-1}\) from 0.09 to 0.17 nm\(^{-1}\). The wall structure of cal-MCM-48 remains closer to the CMC surface; its \(\Delta H\) is roughly half of the value of as-syn-MCM-48. \(K\) is mostly negative for both of the structures (up to \(-0.50\) nm\(^{-2}\)) over nearly the entire surface; however, the as-syn-MCM-48 shows positive \(K\) around the ‘flat point’ (0 < \(K\) < 0.07 nm\(^{-2}\)). This indicates that the shape of the surface around the flat point on \(<111>\) is concave. The concave surface area of the cal-MCM-48 is negligible, and thus the surface irregularity around the flat point appears to be reduced by the calcination process. It is stressed here that using EC data one may evaluate the porosity of SMCs whose mesopores are filled by surfactants, and thus able to show the structural change from as-synthesized to calcined crystal forming a more homogeneous surface.

Similar analysis is also applied to cage-type SMCs, although there is some debate as to whether the Helfrich regime is still appropriate for mesocaged structures. Figure 4 shows \(K\) distributions for four
mesocaged SMCs: bimodal types (AMS-8 and SBA-1) and unimodal types (SBA-12 and SBA-16). At first glance, it is readily noticed that there is a distinct difference between unimodal and bimodal mesopore walls; the ISs of bimodal types tend to be saddle-shape (\( K < 0 \)) and in contrast, those of unimodal are mostly concave (\( K > 0 \)). This is related to the difference in \( \chi \), where the bimodal mesocaged SMCs possess highly negative \( \chi \) originated from more complex mesopore linkage compared with the unimodal structures. When a look is focused on large cages and their connections, this bunch of mesopores can be considered as a sort of ‘unlevel cylinder’ rather than a view of sphere-to-sphere. As expected by the above result, the mean curvature on the wall of bimodal SMCs is lower and closer to zero, which would give an inference that the curvature contribution is of more significance in bimodal SMC structures with a low value of \( \chi \).

On the basis of the parallel surface concept [5], local curvatures of \( H \) and \( K \) may be interconnected with the local values of packing parameter \( g \) and surfactant chain length \( l \). When a local IS and its wrapping mesopore zone are considered simultaneously, the parallel surface away from the IS must vanish at the mesopore centre

\[
1 + 2H(r)l + K(r)l^2 = 0
\]

and the volume wrapped by the IS has to be \( V \) (used in the definition of \( g \)), leading to

\[
1 + H(r)l + K(r)l^2/3 = g.
\]

Solving the above simultaneous equations gives the local values of \( g \) and \( l \). In addition to understanding the global geometry for various mesostructures through the \( g \) parameter, it would also be useful to consider the \( g \) distribution at each point on the pore wall structure of SMCs. In the next section, the packing parameter \( g \) is employed to elucidate the geometrical relationships of the structural transformation among SMCs synthesized using anionic surfactant templating methods.

3. STRUCTURAL TRANSITION IN THE ANIONIC SURFACANT-TEMPLATED MESOPOROUS SILICA (AMS) SYSTEM

A large number of novel mesoporous structures have been yielded over recent years using anionic surfactants for their preparation, which gives a valuable insight into the synthesis mechanism of SMCs as well as the role of micellar curvature on the structural formation. It is important to note that the use of anionic surfactants for the preparation of SMCs posed an interesting charge matching problem owing to the nature of the
carboxyl group, common in fatty acid surfactants (e.g. palmitic acid, acid dissociation constant \( pK_a \) 4.78), which forms charged carboxylate ions typically above the isoelectric point of silica (typically between 1.5 and 3.5). Thus, there is no means of direct charge matching possible between solubilized silica ions and the charged headgroup of the surfactant, in contrast with other approaches such as the use of cationic surfactants under alkaline conditions. Another key problem is that the solubility of anionic surfactants is subsequently dramatically changed with pH. Che et al. [25] first reported an elegant solution to this problem through the use of so-called CSDAs. Examples include 3-aminopropyltriethoxysilane (APES) and \( N \)-trimethoxysilylpropyl-\( N \),\( N \),\( N \)-trimethylammonium chloride, which form an electrostatic interaction between negatively charged headgroups of the anionic surfactants, providing a silica shell surrounding the micelle for further silica condensation to occur.

This intuitive approach opened up the surfactant chemistry of the rich structural diversity of amino acid-derived surfactants [26]. Two of these, \( N \)-lauroyl-glutamic acid and \( N \)-lauroyl-alanine, adequately represent the group. The glutamic acid group possesses two carboxyl groups spaced out by a propyl chain with approximate \( pK_a \) 2.1 and 4.1, in contrast to that for alanine which has a single group (\( pK_a \) 2.35). Hence, one is a bulky headgroup, which is more likely to lead to spherical micelles with low packing parameter \( g \), while the other has a smaller headgroup area, and is more likely to lead to cylindrical micelles with higher \( g \). Indeed initial results suggest as much. A variety of mesocaged structures based on cubic and hexagonal close-packing of spherical micelles were produced and characterized with \( N \)-lauroyl-glutamic acid [26,27], and likewise, cylindrical hexagonal and bicontinuous cubic mesophases were prepared with \( N \)-lauroyl-alanine [28].

Of specific interest in these early studies were structural transformations driven by reaction kinetics, where it was found that one could vary the outcome of the final mesostructure produced by varying the time of addition of the tetraethyl orthosilicate (TEOS) source versus the addition of the CSDA [29]. With small time changes in the range of a few minutes, the structure transforms from \( Fd\bar{3}m \) to \( Pm\bar{3}n \) and tetragonal \( P4_2/mnm \). It was later shown through in situ conductivity measurements (figure 5) that the
The transition spans four structures from order: with increasing chain volume fraction occurs in the different cubic bicontinuous phases. The transition of the amphiphilic molecule, including apolar chain volume fraction (defined as the total apolar fraction of low g). At a given packing parameter, small variations in the external volume of low g may cause structural transformations between the CSDA and the carboxyl headgroup of N-lauroyl-glutamic acid. TEOS addition (t = 600 s) drastically changed the ionic environment of the synthesis gel [30]. Two reasons surfaced as candidates to explain the micellar changes observed, namely: neutralization of the headgroup carboxylate ions by the amino group of APES, and condensation of the latter dates to explain the micellar changes observed, namely: neutralization of the headgroup carboxylate ions by the amino group of APES, and condensation of the latter neutralization of the headgroup carboxylate ions was successfully employed by Gao et al. [17] to induce structural transformations in N-myristoyl-L-glutamic acid, leading to the formation of the cubic bicontinuous SMC AMS-10 with space group $Pn\bar{3}m$. The transition spans four structures from $P4_1/mnm$ of low g to $Pn\bar{3}m$ of high g. This is understood to be caused by a reduction in charge density surrounding the anionic headgroup, contributing to a partial decrease in the electrostatic repulsion between the charged surfactant headgroups and a decrease in the effective surfactant headgroup area of the surfactant, and ultimately in an increase in the g value. It is interesting to note that there is no observation in the N-myristoyl-L-glutamic acid system studied of another cubic bicontinuous structure (known as AMS-6, $Ia\overline{3}d$), which should lie in close proximity. The bicontinuous cubic phases are extremely close in terms of the packing parameter. At a given packing parameter, small variations in the chain volume fraction (defined as the total apolar fraction of the amphiphilic molecule, including apolar solvents) may cause structural transformations between the different cubic bicontinuous phases. The transition with increasing chain volume fraction occurs in the order: $Im\bar{3}m$, $Pn\bar{3}m$ to $Ia\overline{3}d$ (P- to D-, D- to G-surface topology). According to differential geometry, the Bonnet transformation between the associated minimal surfaces will not change the surface area, but change the pore volume. This suggests that the pore volume per fixed surface, which may roughly correspond to the chain volume fraction, should increase in the order of G-, D- and P-surfaces. The contradictory observation requires further detailed studies linked with those three Bonnet-related topologies.

Figure 6. (b) SEM images of trapezoidal icositetrahedron particles, observed in mesoporous material synthesis using the N-lauroyl-alanine anionic surfactant, using P123 as a dispersant. Also shown are particles deviating from the expected $m\bar{3}m$ (a). A particle along the indexed facets is also shown.

conductance immediately increased with the addition of CSDA (t = 0 s) owing to the creation of charged moieties and reached the maximum after 65 s, followed by the gradual decay associated with the neutralizing interaction between the CSDA and the carboxyl headgroup of N-lauroyl-glutamic acid. TEOS addition (t = 600 s) drastically changed the ionic environment of the synthesis gel [30]. Two reasons surfaced as candidates to explain the micellar changes observed, namely: neutralization of the headgroup carboxylate ions by the amino group of APES, and condensation of the latter neutralization of the headgroup carboxylate ions was successfully employed by Gao et al. [17] to induce structural transformations in N-myristoyl-L-glutamic acid, leading to the formation of the cubic bicontinuous SMC AMS-10 with space group $Pn\bar{3}m$. The transition spans four structures from $P4_1/mnm$ of low g to $Pn\bar{3}m$ of high g. This is understood to be caused by a reduction in charge density surrounding the anionic headgroup, contributing to a partial decrease in the electrostatic repulsion between the charged surfactant headgroups and a decrease in the effective surfactant headgroup area of the surfactant, and ultimately in an increase in the g value. It is interesting to note that there is no observation in the N-myristoyl-L-glutamic acid system studied of another cubic bicontinuous structure (known as AMS-6, $Ia\overline{3}d$), which should lie in close proximity. The bicontinuous cubic phases are extremely close in terms of the packing parameter. At a given packing parameter, small variations in the chain volume fraction (defined as the total apolar fraction of the amphiphilic molecule, including apolar solvents) may cause structural transformations between the different cubic bicontinuous phases. The transition with increasing chain volume fraction occurs in the order: $Im\bar{3}m$, $Pn\bar{3}m$ to $Ia\overline{3}d$ (P- to D-, D- to G-surface topology). According to differential geometry, the Bonnet transformation between the associated minimal surfaces will not change the surface area, but change the pore volume. This suggests that the pore volume per fixed surface, which may roughly correspond to the chain volume fraction, should increase in the order of G-, D- and P-surfaces. The contradictory observation requires further detailed studies linked with those three Bonnet-related topologies.

Bicontinuous SMCs with $Ia\overline{3}d$ symmetry have in contrast been observed in the N-lauroyl-alanine system extensively. Small variations in reactant concentration and temperature lead to the hexagonal $p6mm$ phase [26]. In order to elucidate this transition, the synthesis was conducted with the addition of a non-interacting dispersant, namely the block co-polymer P123, which under the alkaline conditions used for the synthesis behaves as a retardant of crystal growth [31]. Under these conditions, monodispersity and trapezoidal icositetrahedron particles with the corresponding point group symmetry $m\bar{3}m$ were obtained (figure 6). It is interesting to note that a small proportion of these particles showed skewed trapezoidal icositetrahedron shapes, and elongated ’coffin-like faceted particles. The latter are in disagreement with the expected point group symmetry for the $Ia\overline{3}d$ space group [31]. Preliminary TEM investigations did not directly show any defect characteristics that could explain the deviation from the expected morphology (figure 7). Irrespective of the formation of unexpected faceted morphologies, the formation of SMCs with bicontinuous cubic $Ia\overline{3}d$ or $Pn\bar{3}m$ symmetry, and their relationship and transformations, remains a subject of great intellectual interest. Further synthetic studies have demonstrated that the formation of cubic $Ia\overline{3}d$ SMCs with N-lauroyl-alanine is not a thermally stable phase. Prolonged hydrothermal treatments (from 1 to 6 days) performed on an SMC AMS-6 with spherical...

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morphologies at 100°C showed interesting fluctuations in structural properties, with \( Ia\overline{3}d \) and \( p6mm \) symmetries. These transitions are good evidence that SMCs are not equilibrium structures. Small perturbations to the synthesis conditions lead to large variations in the structural and morphological features of the resulting material.

As mentioned above, the bicontinuous gyroidal \( Ia\overline{3}d \) structure has not been formed with glutamic acid-derived surfactants by solely changing the micelle curvature through varying the surface area. However, in our recent study, both \( Ia\overline{3}d \) and \( Pn\overline{3}m \) structures were found to form within the same synthesis system with the addition of hydrophobic molecules, such as trimethyl benzene (TMB), and the non-ionic surfactant \( C_{16}(EO)_{10} \) (termed Brij-56), into the synthesis systems.

As shown in figure 8, the structural transitions between \( p6mm \) to \( Ia\overline{3}d \), and \( Ia\overline{3}d \) to \( Pn\overline{3}m \) have been observed with a clear relationship in the presence of TMB [32]. The synthesis of bicontinuous cubic SMC with \( Pn\overline{3}m \) (known as AMS-10) symmetry has been achieved in this study through micellar swelling of the \( N \)-lauroyl-alanine surfactant under alkaline conditions.

TEM images confirm the formation of AMS-10 at the TMB/surfactant ratio of 64, where the coexistence of the \( Pn\overline{3}m \) and \( Ia\overline{3}d \) structures is observed (figure 8b). The transformation is primarily governed by kinetics, where addition of TMB promotes the formation of a \( Pn\overline{3}m \) mesophase that is stable only at low temperatures. An epitaxial relation has been observed between \( [111] \) and \( [110] \) orientations of the \( Ia\overline{3}d \) and \( Pn\overline{3}m \) symmetry structures, respectively. Kinetic studies suggest that the transition occurs via the initial formation of a hexagonal structure, which slowly restructures during the first 18 h of synthesis to the \( Ia\overline{3}d \) structure. An epitaxial relation between the hexagonal and \( Ia\overline{3}d \) mesostructures has additionally been observed involving the \( [001] \) and \( [111] \) orientations of the \( Ia\overline{3}d \) and \( Pn\overline{3}m \) symmetry structures, respectively. The formation of the minor helical hexagonal mesostructure has been identified during the transition between the hexagonal and cubic I phase structures, and these may be representative of intermediate phase structures during the transition. The formation of the AMS-10 structure initially occurs at the expense of the hexagonal phase structure and is delayed by several hours if the samples are hydrothermally treated. With prolonged synthesis...
and without hydrothermal treatment, the cubic \( \text{Pn}\overline{3}m \) phase structure is the more kinetically favourable phase.

It has been found that the non-ionic surfactant Brij-56 can be associated with the anionic surfactant \( \text{N-stearoyl-L-glutamic acid} \). As the Brij-56 molecules become more hydrophobic at higher temperature, the organic/inorganic interface curvatures can be tuned by addition of Brij-56 and varying the reaction temperature [33]. On the basis of this concept, a series of SMCs have been obtained and an unusual structural change was observed with the following sequence: cage-type \( \rightarrow \) two-dimensional cylindrical hexagonal \( p6mm \) \( \rightarrow \) epitaxial intergrowth of \( p6mm \) and \( \text{Pn}\overline{3}m \) \( \rightarrow \) epitaxial intergrowth of \( p6mm \) and \( \text{Ia\overline{3}d} \) \( \rightarrow \) \( \text{Pn}\overline{3}m \) \( \rightarrow \) \( \text{Ia\overline{3}d} \) \( \rightarrow \) one-dimensional lamellar structures. TEM observations of the intergrowth samples suggest that the cylinders of \( p6mm \) are parallel to the \( <110> \) of \( \text{Pn}\overline{3}m \), showing a ‘side by side’ epitaxial relationship with \( p6mm\{11\} \leftrightarrow \text{Pn}\overline{3}m\{221\} \) transition (figure 9a), while in the other intergrowth structure, the cylinders of \( p6mm \) are parallel...
to <111> axes of \(\text{Ia}3d\) with both \(p6\text{mm}\{10\} \leftrightarrow \text{Ia}3d\{220\}\) transitions (figure 9b,c). Interestingly, the \(P63\text{m}\) sample showed spherical morphology with inner polyhedral hollows (figure 9d) [34]. It has been found that the vesicle with a low-curvature lamellar structure was first formed, followed by a structural transformation to a highly ordered \(P63\text{m}\) shell-like structure with retaining the hollow. It is worth noting that during the transition, the [111] direction of the cubic domains is perpendicular to the lamellar layer, facing the centre of the sphere, and the boundaries were relaxed by forming twinning structures before the completion of silica condensation. This mechanism leads to the reversed multiply twinned structures with icosahedral or decagonal hollow. Besides, the local \(g\) parameter was obtained from EC reconstruction by calculating mean curvatures and Gaussian curvatures from the IJs (figure 9e).

4. CONCLUSION

In this paper, a role of curvatures for structural studies on SMCs has been overviewed based on experimental observations, principally by TEM. Within the data obtained through EC image processing from TEM, we established that assessing the curvature on reconstructed electrostatic potential maps of SMCs was useful both for a self-consistent determination of the pore wall structure, and for an access to an insight into the detailed silica surface geometries. The synthesis of SMCs using anionic surfactants along with CSDA has yielded a versatile library of mesostructures with both high and low packing parameters. Those structures can readily be tailored to cause interesting mesostructural transformations and control morphological features of the resulting mesoporous products. Detailed TEM observations revealed the structural relation among transforming and coexisting mesophases as a function of the synthesis parameters.

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