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The Role of Charge-Matching in Nanoporous Materials Formation

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Abstract

Unravelling the molecular-level mechanisms that lead to the formation of mesoscale-ordered porous materials is a crucial step towards the goal of computational material design. For silica templated by alkylamine surfactants, a mechanism based on hydrogen-bond interactions between neutral amines and neutral silicates in solution has been widely accepted by the materials science community, despite the lack of conclusive evidence to support it. We demonstrate, through a combination of experimental measurements and multi-scale modelling, that the so-called “neutral templating route” does not represent a viable description of the synthesis mechanism of hexagonal mesoporous silica (HMS), the earliest example of amine-templated porous silica. Instead, the mesoscale structure of the material is defined by charge-matching of ionic interactions between amines and silicates. This has profound implications for the synthesis of a wide range of templated porous materials, and may shed new light on developing sustainable and economical routes to high value porous materials.

The discovery of templated periodic mesoporous silica (PMS) in the early 1990's, of which MCM-41 is the archetypal example [1], heralded a new era in material science research. This revolutionary approach, whereby the porous structure of the material is determined by cooperative self-assembly of silicates and surfactant molecules (originally cationic ammonium

compounds) in solution [2-4], allowed scientists to apply soft-matter physics principles to the synthesis of solid-state materials, enabling an unprecedented degree of control over the properties of the final material [5] and leading to a wide range of practical applications [6]. Despite these successes, PMS materials have an important shortcoming – their synthesis process requires rather harsh conditions (high temperature and pressure, very high or very low pH, toxic chemicals), resulting in unsustainable methods that cannot be adopted economically at industrial scales. This opened up a new area of research aiming to produce controlled nanoporous silica materials using environmentally friendly synthesis conditions [7, 8]. Shortly after the discovery of PMS, Tanev and Pinnavaia [9] made the first attempt towards this goal by synthesising Hexagonal Mesoporous Silica (HMS) materials using alkylamines as templates instead of ammonium surfactants, based on a hypothesised “neutral templating mechanism”. Interestingly, amine-rich peptides and long-chain polyamines have later been shown to play a crucial role in directing the porous structure formation in biosilicification by marine organisms like diatoms and sponges [10-12], a process that leads to the formation of hierarchical structures of amazing beauty and complexity at very mild conditions of pressure, temperature and pH. Currently, amine-based “additives” are at the core of the rapidly expanding field of bio-inspired silica synthesis, which aims to adapt the principles of biosilicification to produce synthetic silica materials of controlled porosity under mild conditions with a low environmental footprint [8, 13].

The main bottleneck hindering further progress in this field is the lack of in-depth understanding of the underlying mechanism of amine-templated silica synthesis [4, 8]. In this paper, we shed new light on this issue through a combination of experimental studies and multi-scale modelling, focussing on HMS [9] as the first example of synthetic amine-templated silica material. Tanev and Pinnavaia [14] originally hypothesised that the self-assembly of the templated mesostructure, which ultimately controls the material properties, was governed by non-ionic interactions between neutral amine surfactant head groups and neutral silicates in solution. According to those authors, hydrogen-bond interactions promoted the formation of rod-like micelles and their organisation into hexagonal mesophases, which led them to argue that this represented the first example of a “neutral templating route” to the synthesis of ordered mesoporous silica [9], in marked contrast with the “ionic” templating route of PMS materials [2]. The proposed neutral templating mechanism was considered revolutionary at the time, as it implied that ordered mesoporous silica could be synthesised at near-neutral pH. However, the pH of the synthesis solution was

never reported in the original papers or in subsequent studies of these systems, and the underlying assumptions of the mechanism remained untested. Despite this fact, the neutral templating route has been tacitly accepted by the material science community, as evidenced in several reviews of the topic [6, 7, 15].

Support for the proposed neutral mechanism was mostly indirect, based on the idea that weaker template-silica hydrogen-bond interactions, relative to the stronger ionic interactions present in PMS synthesis solutions, would lead to the observed thicker pore walls and lower degree of order [14]. Here, the nature of the interactions between silicates and amine templates during the self-assembly of these materials was investigated through a combination of titration measurements, NMR analysis and molecular dynamics (MD) simulations. Our results indicate that the majority of amine templates are positively charged at the conditions of synthesis, and provide evidence for a charge-matching mechanism at the origin of the self-assembly of HMS materials. This new insight has potentially profound implications for our understanding of amine-templated silica synthesis, including naturally occurring and bio-inspired hierarchical silica materials.

HMS was originally prepared by dissolving TEOS (tetraethylorthosilicate) and primary amine surfactants with variable alkyl chain lengths ($\text{NH}_2\text{C}_n\text{H}_{2n+1}$, where n was between 10 and 18 carbon atoms) in a mixture of water and ethanol at temperatures ranging from ambient to 80 °C, with a typical composition being reported as 1.0 TEOS : 0.27 DDA : 9.09 EtOH : 29.6 H_2O , where DDA is dodecylamine ($n=12$ in the above amine chemical formula) [14]. We first performed acid-base titrations of DDA in a 50% v/v water/ethanol solution (equivalent to the above molar ratios) using 1M HCl, shown in Figure 1a (see Supporting Information for details). The titration found the pKa to be 10.00, corresponding to 9.8 after correction for the non-aqueous composition [16]. This result is somewhat lower than the literature value of 10.63 [17], measured in aqueous solution, but this is likely due to the relatively high alcohol concentration; the same effect has been observed previously for alkylamine molecules in the presence of methanol [18].

We then proceeded to measure the pH of different solutions considered in the Tanev and Pinnavaia study: 1) initial reaction solvent with DDA but before the addition of any TEOS; 2) reaction mixture immediately after the addition of TEOS to the solution in 1); 3) deliberately acidified DDA solution obtained by adding HCl to the solution in 1). The solution conditions are precisely the same as reported in the original study, and we have confirmed that the

synthesis solution led to the formation of HMS material with porosity, morphology and adsorption characteristics that are very similar to the original materials reported by Tanev and Pinnavaia (see Figure S1 and associated discussion). The results of these measurements are overlaid on the titration curve of Figure 1a, showing that the addition of acidic TEOS significantly lowers the pH of the initial solution to 9.2, after correcting for the non-aqueous composition. This is in very good agreement with a theoretical estimate of 8.9, obtained using literature values for the pK_a of DDA (10.63 [17]) and of silicic acid (9.5 for the first deprotonation and 12.6 for the second deprotonation [19]). More importantly, it is sufficiently below the measured amine pK_a to indicate that a large majority of DDA molecules (at least 80%) will be positively charged at the start of the synthesis. Furthermore, we estimate, using the Henderson-Hasselbalch equation, that the charged amines will initially be in contact with approximately 77% neutral and 23% anionic silica monomers [20]. This is a far cry from the hypothesised “neutral” conditions in the original paper.

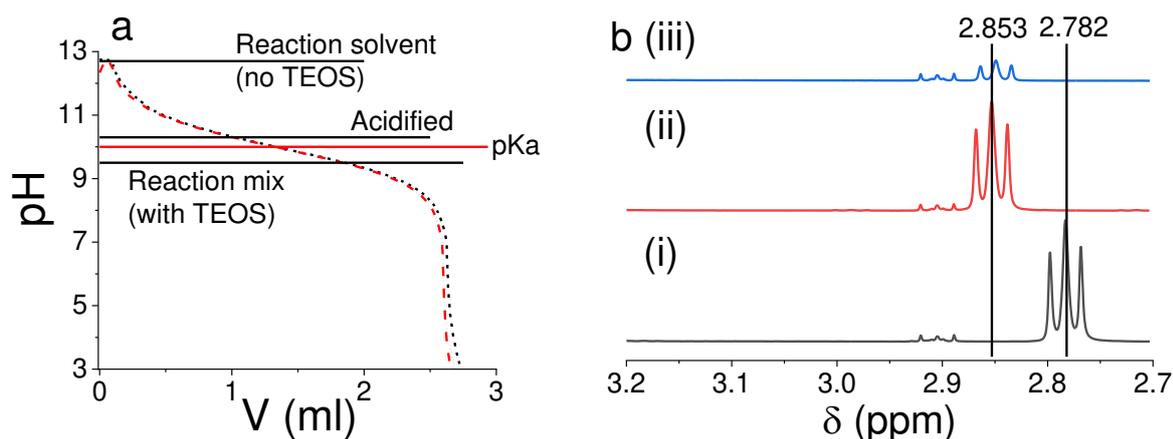


Figure 1 – (a) Titrimetric determination, in triplicate, of DDA pK_a in 50%v EtOH/H₂O mixture (initially 0.27 DDA: 9.09 EtOH: 29.6 H₂O by moles), overlaid with measured pH values from the reaction solvent (0.27 DDA: 9.09 EtOH: 29.6 H₂O by moles), acidified reaction solvent as described by Tanev and Pinnavaia [14] (0.27 DDA: 0.054 HCl: 9.09 EtOH: 29.6 H₂O by moles), and reaction mixture (1.0 TEOS: 0.27 DDA: 9.09 EtOH: 29.6 H₂O by moles). (b) (i) Comparison of ¹H NMR spectra for the reaction solvent, (ii) acidified reaction solvent, and (iii) reaction mixture solutions shown in figure (a). Overlay lines indicate the peak shift due to partial acidification of DDA relative to an external standard, which is similar for both the acidified reaction solvent and reaction mixture.

Tanev and Pinnavaia carried out ¹⁴N nuclear magnetic resonance (NMR) measurements on the synthesis solutions and on a deliberately acidified solution without silica. The fact that the acidified solution showed a strong NMR signal while no such signal was observed in any of the synthesis solutions led those authors to conclude that DDA was predominantly uncharged

during the synthesis of HMS, thus supporting the postulated neutral templating mechanism [14]. However, our titration results clearly show that the pH of the synthesis solution is lower than that of the “acidified” HCl-DDA mixture (see Figure 1a), a factor seemingly unaccounted for in the original paper. To support our titration measurements, we performed ^1H NMR measurements of DDA solutions under a range of conditions. Unlike the ^{14}N findings of Tanev and Pinnavaia, we were able to detect peaks corresponding to the C1 protons (linked to carbon atoms closest to the amine nitrogen; see SI for details) in all cases. These peaks were all shifted differently from an unmodified solution of DDA, indicating a different electronic environment in all cases (Figure 1b). Notably, this included a significant shift upon addition of TEOS to the DDA in EtOH/H₂O (and hence during HMS synthesis), similar to the shift observed upon partial acidification, and contrary to the conclusions of Tanev and Pinnavaia. Other modifications to the solution corresponding to changes in the ionic strength, DDA concentration or change in solvent composition during synthesis were then prepared and analysed to determine their effect on C1 peak shifting. Acidification was the only parameter that produced peak shifting of the magnitude seen in the reaction mixture (Figure S2).

Taken together, our results of acid-base titrimetry and ^1H NMR provide a clearer understanding of DDA chemistry during HMS synthesis than was previously possible. Whereas previous ^{14}N NMR experiments could only indicate the presence of protonated DDA, using ^1H NMR enables the estimation of the degree of protonation based on the amine moiety’s inductive effect. Using identical synthesis conditions to those previous studies, results from the ^1H NMR show that DDA molecules are predominantly in the protonated state during HMS synthesis, in marked contrast to the assertions of Tanev and Pinnavaia [9, 14]. The observed presence of large amounts of protonated DDA in both solutions strongly indicates that the origin of the different signals in their ^{14}N NMR measurements cannot be ascribed to different protonation states of the amine surfactants, as originally argued. A possible explanation is related to the pH-dependency of proton exchange rate and its peak-broadening effect. Rapid exchange of protons between protonated dodecylamine and water will lead to peak suppression, as the longevity of protonated dodecylamine species would be shorter than the ^{14}N chemical shift time scale. The pH-sensitivity of this phenomenon has been recently observed for the amine moiety in arginine over a narrow pH range [21], suggesting that the appearance of the ^{14}N peak in the previous work may have been due to the deceleration of exchange rate as the pH was lowered under acidified conditions, rather than

due to changes in the amine protonation state. It is also possible that the tetrahedral symmetry of the protonated amine group is distorted in the synthesis solution due to close interactions with silicates (see below), thus interfering with the ^{14}N NMR signal.

Our experimental measurements suggest that the system will be dominated by strong charge-charge interactions between silica and surfactants, and therefore the mechanism cannot occur on a neutral basis as originally assumed. To clarify the nature of the molecular-level interactions taking place in the synthesis solution, we carried out simulations using a multi-scale modelling approach. In brief, quantum-mechanical calculations [22] were used to obtain parameters for classical atomistic models of silicates in solution [23], which were then combined with atomistic models of water [24] and amine surfactants [25]. Parameters of a coarse-grained model of the system, based on the MARTINI approach [26], were then calibrated so that micelle density profiles and other structural properties matched those of the atomistic simulations. This approach has been successfully validated and applied to elucidate the self-assembly mechanism in the synthesis of PMS materials [23, 27-30] as well as of their organosilica derivatives [4, 31]. Details of the model parameterisation and validation procedure for HMS precursor solutions, including a diagram of the mapping scheme (Figure S5) and a table with the final set of parameters (Table S7), are provided in Supporting Information.

We began by carrying out simulations of a reference solution containing only water and DDA surfactants with a concentration of 0.22 M, which corresponds to the concentration used by Tanev and Pinnavaia, at different pH values. At a pH below 8, essentially all surfactants are charged (see Figure 1a), and they self-assemble into small micelles of nearly spherical shape (Figure 2a). The average aggregation number of these micelles (80) is quite close to that observed experimentally (68) [32], thus validating our coarse-grained model for the surfactant solutions. Conversely, when the pH is above 12, virtually all surfactants are neutral (Figure 1a). In this case, the system phase-separates into a pure solvent and a pure-surfactant phase, the latter being composed of a single completely disordered aggregate (Figure 2b). This also mirrors experimental observations, which show that DDA in the neutral form is insoluble in pure water at ambient conditions [33].

When TEOS is added to the DDA/water solution at the start of the HMS synthesis, the pH drops to 9.2, as described above. As such, the majority of DDA molecules will be protonated (Figure 1a) and the starting surfactant configuration will be similar to that shown in Figure

2a. The pH is also high enough that we can consider the hydrolysis of TEOS, yielding monosilicic acid and ethanol, to be rapid and complete [34]. Simulations of a solution of DDA and silica monomers with the speciation corresponding to the experimental pH (see SI for details) gives rise to the formation of rod-like micelles (Figure 2c). The sphere-to-rod transition upon addition of TEOS is caused by the strong electrostatic attraction between anionic silica and cationic surfactant heads. Indeed, a detailed analysis of the simulations leading to the structure shown in Figure 2c reveals that surfactant head groups interact predominantly with anionic silicates, while neutral silicates are practically absent from their immediate vicinity (Figure S16). As anionic silicates adsorb at the micelle surface, they screen the repulsion between positively charged head groups, reducing the equilibrium curvature of the aggregates [35]. A similar mechanism was observed in the early stages of the synthesis of PMS materials from permanently ionised ammonium surfactants [28]. Thus, the presence of anionic silica is shown to induce profound changes to the equilibrium surfactant structures, supporting a co-operative templating mechanism akin to that of PMS [3, 29].

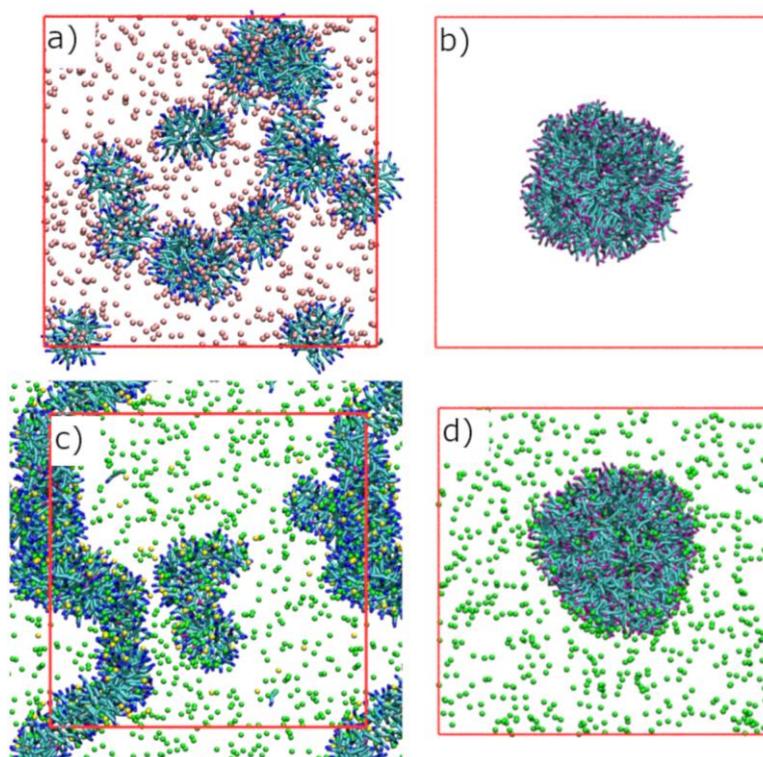


Figure 2 – Simulation snapshots obtained for aqueous DDA solutions at 0.22 M: (a) charged surfactants without silica ($pH < 8$); (b) neutral surfactants without silica ($pH > 12$); (c) charged (89%) and neutral (11%) surfactants with 23% anionic silica monomers and 77% neutral silica monomers ($pH \sim 9.2$); (d) neutral surfactants with 100% neutral silica monomers (hypothetical conditions). Water has been removed for clarity. Some of the

snapshots include part of their periodic images to aid visualisation. Colour code is: DDA+ heads, blue; DDA heads, purple; DDA+ and DDA tails, teal; chloride, pink; anionic silica monomers (SiO^-), yellow; neutral silica monomers (SiO^0), green. The red box represents the boundary of the simulation cell, which in all cases is close to 20 nm side (Table S8).

Interestingly, when neutral silica monomers were added to a solution containing only neutral surfactants, in an attempt to mimic the hypothesised neutral templating route, very little adsorption of silica at the surface of the surfactant aggregate was observed. Instead, silicates mostly remain in the aqueous phase and appear to have no effect on the phase separation of the insoluble surfactants (Figure 2d). Simulations of a smaller version of this system at the atomistic level of detail showed that neutral silicates do indeed form hydrogen bonds with neutral amine surfactants, but these are much weaker than bonds formed between either of those molecules with water (Figure S17). This explains why neutral silica monomers prefer to stay in the bulk solution, and further supports our argument that hydrogen-bond interactions between neutral species could not constitute a driving force for inducing mesophase formation in HMS synthesis.

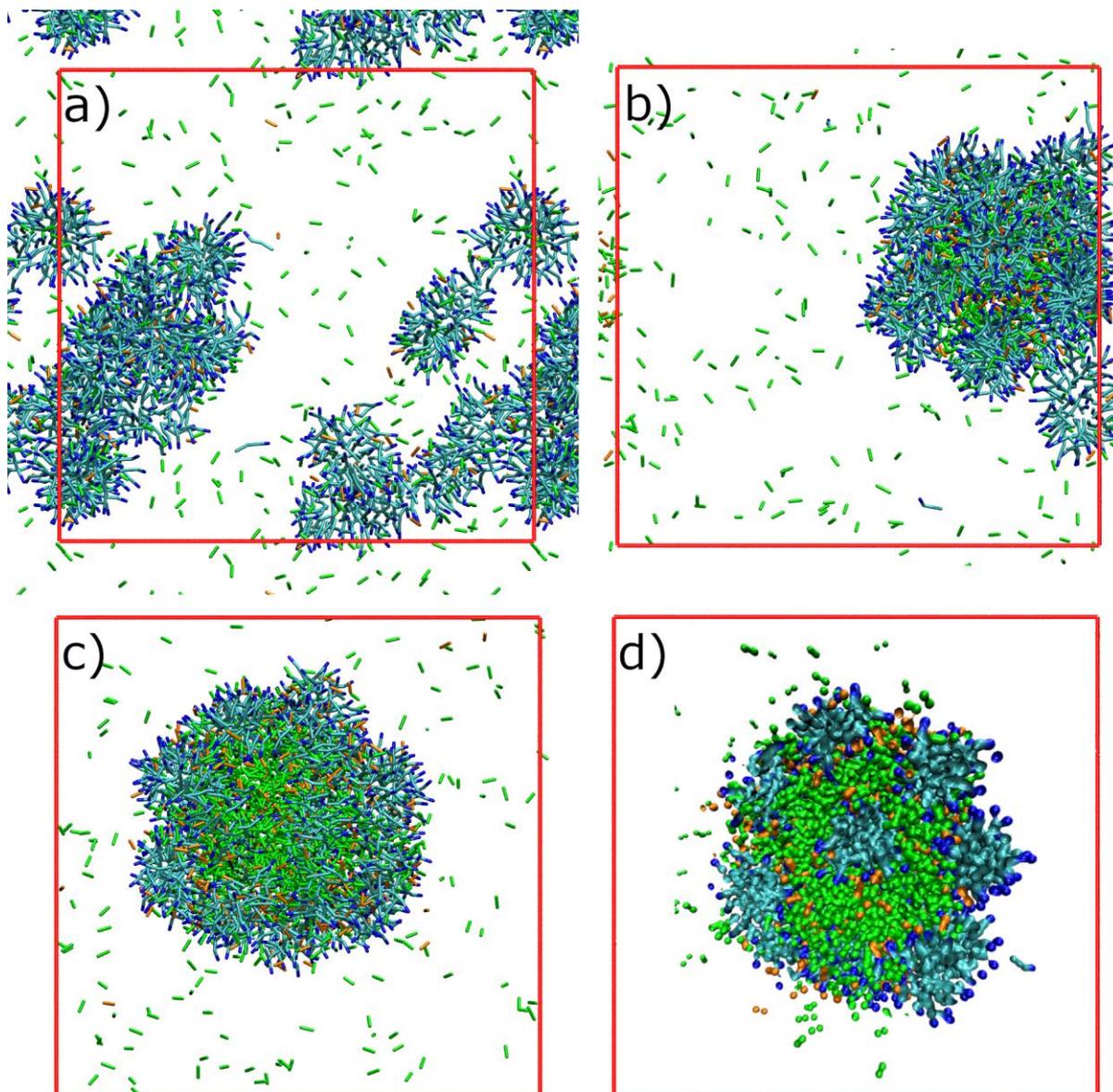


Figure 3 – Simulation snapshots obtained for surfactant/silica solutions with neutral and singly-charged silica dimers, at increasing silica:surfactant ratios: a) 1:1; b) 2:1; c) 4:1; d) cross-section of the aggregate obtained at a 4:1 ratio. Water and chloride ions have been removed for clarity. Some of the snapshots include part of their periodic images to aid visualisation. Colour code is: DDA+ heads, blue; DDA+ tails, teal; chloride, pink; anionic dimers, orange; neutral dimers, green. The red box represents the boundary of the simulation cell, which in all cases is close to 20 nm side (Table S8).

It has previously been shown that the presence of silica oligomers (at least 30% of dimers) was necessary to promote the formation of a hexagonal mesophase in the synthesis of PMS from cationic ammonium surfactants [29]. In the case of HMS, a similar conclusion can be drawn from our simulations. When silicates remain in the monomeric form, long rod-like micelles are formed (Figure 2c), but no evidence for the formation of an ordered array of

micelles is seen. In contrast, when the monomers are replaced by dimers, meant to represent a later stage of the synthesis after silica has been allowed to polymerise to some extent, the micelles begin to aggregate. This tendency for micelles to aggregate can already be seen at low silica/surfactant ratios (Figure 3a), and becomes increasingly dominant as the concentration of silica increases (Figures 3b).

In the original study of Tanev and Pinnavaia, using a silica/surfactant ratio of approximately 4:1 [14], the authors argued, through X-ray diffraction (XRD) and transmission electron microscopy (TEM) characterisation, that their materials possessed a long-range hexagonally ordered array of cylindrical pores, similar to that of PMS materials synthesised from alkylammonium surfactants, but with thicker and hence more stable pore walls. However, subsequent work by the same group [36] and by others [37, 38] showed that in fact the pore structure of HMS was more akin to a rather disordered packing of wormlike micelles, instead of the regular hexagonal packing of cylinders observed in PMS materials. Our simulations under similar conditions (Figure 3c) show the formation of a roughly hexagonal array of elongated micelles – Figure 3d shows the nearly spherical cross-section of each micelle (in blue) surrounded by a thick layer of silica (in orange and green). Interestingly, the degree of order of the HMS precursor mesophase is much lower than observed in the case of PMS [29], but the silica walls are significantly thicker. Both these observations are in strong qualitative agreement with available experimental information about the pore network structure of HMS materials [36, 37].

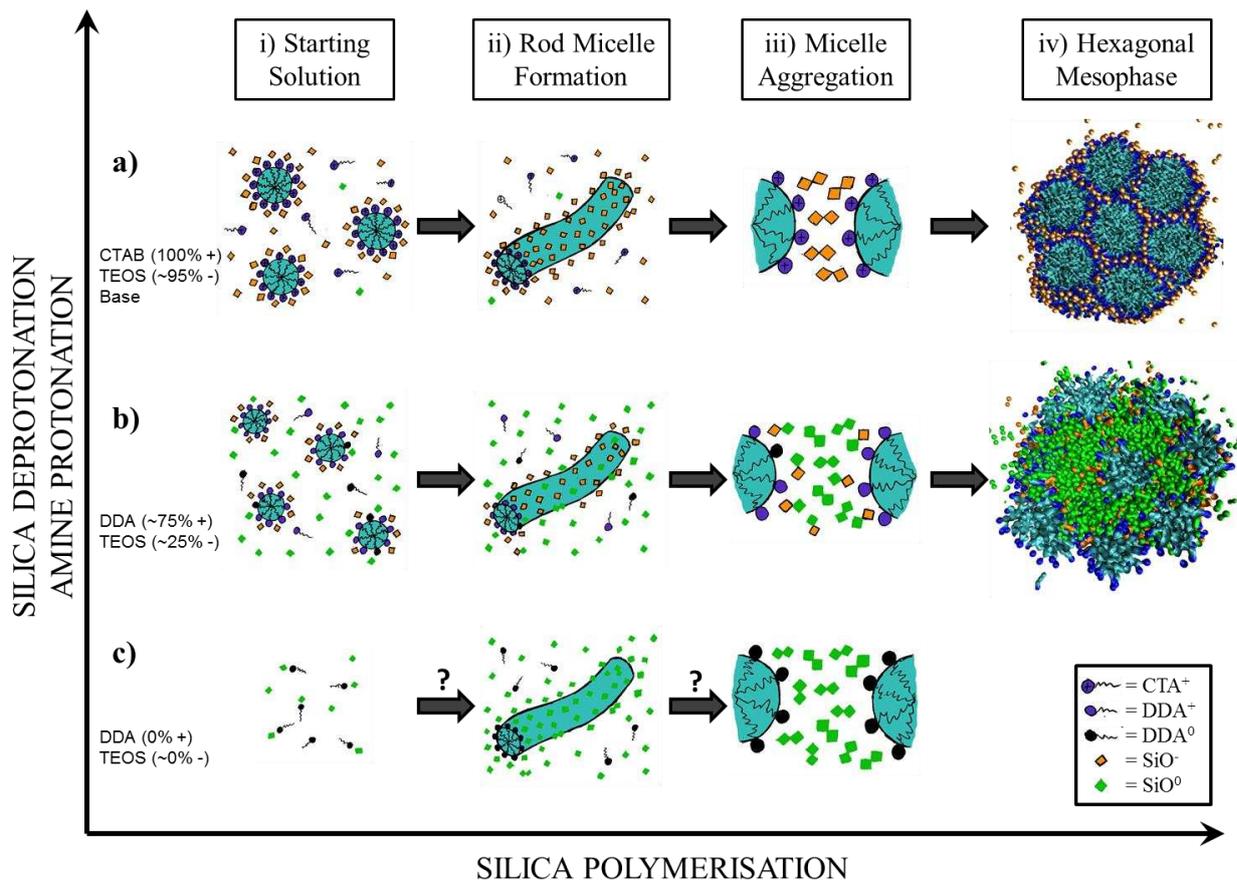


Figure 4 – Diagram depicting different mechanisms for the synthesis of mesostructured silica materials: a) PMS synthesis at high pH [29]; b) HMS synthesis (this paper); c) hypothetical neutral templating route to HMS [14]. The composition and approximate speciation of the initial solution is given at the start for each mechanism. Colour code is: surfactant heads, blue; surfactant tails, teal; anionic silicates, orange; neutral silicates, green. In the schematic drawings (see legend), cationic ammonium surfactants are represented by crossed circles, cationic amine surfactants by open circles, and neutral amines by black circles. The hexagonal mesophases are represented by snapshots obtained from our simulations.

In Figure 4, we also contrast our proposed mechanism for HMS synthesis, based on charge-matching (path b) with the hypothetical neutral templating mechanism (path c) proposed by Tanev and Pinnavaia [9, 14]. Those authors suggest that neutral silicates interact with neutral amines through hydrogen bonds in the initial synthesis solution (step i), leading to the formation of rod-like micelles. However, Tanev and Pinnavaia do not offer a conclusive explanation for how the weak hydrogen-bond interactions would lead to the formation of rod-like micelles (step ii) for a surfactant that, under normal circumstances, would form small spherical aggregates. As we have demonstrated above, such weak interactions are relatively rare in the synthesis solution and are highly unlikely to induce any changes in the amine aggregation state. Conversely, rod-like structures arise naturally in our mechanism due to the

effective reduction in charged amine head group size brought about by the adsorption of anionic silicates at the micelle surface. Similarly, Tanev and Pinnavaia do not explain in detail how the rod-like micelles are subsequently led to aggregate, stating merely that it arises due to “further silica condensation” [14]. Based on experimental and simulation results, we propose that such aggregation, leading to the formation of a loosely hexagonally-ordered mesophase, arises from a combination of strong charge-matching interactions and reduced silica solubility as the degree of condensation increases.

To summarize, our combined experimental and multi-scale modelling study has elucidated the synthesis mechanism of the earliest examples of mesoscale ordered silica materials in unprecedented molecular detail. Crucially, our results contradict the originally postulated, and widely accepted, neutral templating mechanism for HMS synthesis. Instead, acid-base titration and NMR measurements show that amine surfactants are mostly cationic when silica is added to the synthesis mixture, while the modelling shows that it is the charge-matching interactions between surfactants and anionic silicates that control the first stages of formation of HMS precursor mesophases. These interactions effectively screen the repulsion between initially spherical micelles, promoting a sphere-to-rod transition shortly after the addition of silica, when the latter is still in monomeric form. As silica polymerizes, hydrophobic interactions between neutral and anionic silicates begin to play a role, promoting the aggregation of worm-like micelles into a phase-separated mesophase with loosely hexagonal order. The higher concentration of silica necessary to aggregate the micelles leads to materials with relatively thick pore walls and relatively low degree of order, when compared to their PMS counterparts, in agreement with experimental characterisation.

Although our study focused on a particular example of porous silica, our conclusions regarding the importance of charged interactions are likely to be general for this class of materials, and beyond, given the widespread use of amine templating to produce a range of porous materials (TiO₂, ZrO₂, etc.) [40]. Indeed, our previous atomistic simulations of MSU-V [41], which is a similar material to HMS but synthesised from double-headed amine surfactants that form multi-layered vesicular structures [42], showed that its synthesis mechanism is also controlled by charge-matching interactions instead of the originally hypothesised weak hydrogen bonds. Furthermore, our results are relevant to the study of bioinspired silicas, which use amine molecules to control the reaction and product properties [13]. Our recent study of template removal in bioinspired silica synthesised from polyamine templates also demonstrated the key role played by ionic silica-amine interactions in the

synthesis process [43]. Taken together, this evidence indicates we should rethink the prevailing views about how these increasingly important materials are synthesised. Crucially, in all of the above examples, the synthesis is found to be heavily dependent on the pH of the precursor solution. This opens up interesting new routes to controlling the pore structure of industrial-grade silica. For example, it may be possible to synthesise a family of porous silicates and non-silicates with increasing degree of order by tuning the template self-assembly by slightly increasing the pH - i.e. operating somewhere between the two mechanisms depicted in Figure 4a-b. Also, adding a small percentage of permanently ionised surfactants, like quaternary alkylammonium, may increase the degree of order of the material. Further, by combining the findings reported herein with the recent developments on room temperature synthesis of porous silica [8] and eco-friendly removal of templates [43] has the potential to deliver commercially viable manufacturing routes to porous materials. Research along these lines is currently being explored in our laboratories.

Supporting Information:

Experimental details and additional results; technical details and force field parameters for atomistic simulations; technical details and force field parameters for coarse-grained simulations; parameterization procedure of the coarse-grained model; additional simulation results.

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Competing Interests: The authors declare no competing interests.

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