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Phase evolution in the alkane–P123–water–TEOS quadru-component system: a feasible route to different complex mesostructured materials

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Directed by the temperature-induced phase transformation in the alkane (from heptane to dodecane)–P123–water–TEOS quadru-component system, *i.e.*, from a swollen inverse hexagonal phase (H_2) to a swollen lamellar phase (L_α) and then to a swollen normal micelles phase (L_1), complex silica materials, such as mesoporous nanofibres, multilamellar vesicles (MLVs) and mesocellular foams (MCFs), are constructed.

Since the discovery of highly ordered mesoporous silicas,[1] a new era of supermolecular self-assembly of mesoporous materials has begun. Due to their potential industrial applications, the controlled construction of ordered porous silica materials has always been one of the focused issues in this field. Generally, controlling the self-assembly of organic (*i.e.*, surfactant)–inorganic composites was considered to be the key factor in the construction of mesoporous materials. Up to now, various routes have been explored to get structural/morphological variations. Specifically, different reaction compositions and conditions can remarkably alter the self-assembly of inorganic–organic composites, and various mesostructures can then be constructed.[2–6]

The oil–water–surfactant emulsion systems have been widely studied for their potential applications in oil refineries.[7] Emulsion morphology transformation in the oil–water–triblock copolymer systems has been well documented,[8] *e.g.*, different lyotropic liquid crystalline or solution phases have been observed.[8*a,b*] For oil–water–surfactant systems, although various mesoporous silica materials have been obtained, most of these works were focused on pore size expansion and other aspects of the mesoporous materials.[9–11] For instance, a small amount of TMB, acting as a swelling agent, was proven to be effective in the synthesis of ordered large-pore SBA-15.[1*c*] However, when a large amount of TMB was used, due to the relatively strong interaction between aromatics and the copolymer surfactants,[8*d*] highly organized/ordered structures were difficult to maintain, instead, mesocellular foam (MCF) structures often resulted.[11] Thus, it seems that a proper interaction between an additional component (besides water and surfactant) and the copolymer surfactant is crucial in constructing highly ordered structures. In our previous studies, it was demonstrated that alkanes with different chain lengths interact differently with the P123 surfactant.[10] Only those of suitable chain length, *i.e.*, ranging from hexane to decane, are good matches to P123 copolymers, and can thus be used to build highly ordered large-pore SBA-15. It is well known that the amphiphilic behavior of triblock copolymers is sensitive to temperature changes, which has been used to control the wall thickness of SBA-15.[1*c*] Therefore, by altering the initial reaction temperature, it is possible to tune the relative affinity of the P123 surfactant, and the phase behavior of the alkane–water–surfactant–TEOS emulsion system. Based on our recent studies,[10*b*] herein, by finely tuning the reaction compositions of the alkane–water–P123–TEOS quadruple emulsion system,[12] a temperature-induced phase transformation, from a swollen inverse hexagonal phase (H_2) to a swollen lamellar phase (L_α) and then to a swollen normal micelle phase (L_1), is set up in the current alkane (from heptane to dodecane)–P123–water–TEOS quadru-component system, directed by which, corresponding complex silica materials (such as mesoporous nanofibres, MLVs and MCFs) are obtained.

Alkanes from heptane to dodecane have been tried in the current studies. It was found that a temperature-induced phase transformation, from a swollen inverse hexagonal phase (H_2) to a swollen lamellar phase

(L_{α}) and then to a swollen normal micelles phase (L_1), happened, and the corresponding inorganic mesoporous silicas could be obtained in all emulsion systems. However, the initial reaction temperature where phase transformation took place is different, depending on the alkane used. This temperature increased with the increase of the alkane chain length. In this Communication, we choose decane as an example to demonstrate the feasibility of the strategy in constructing the different complex mesostructures.

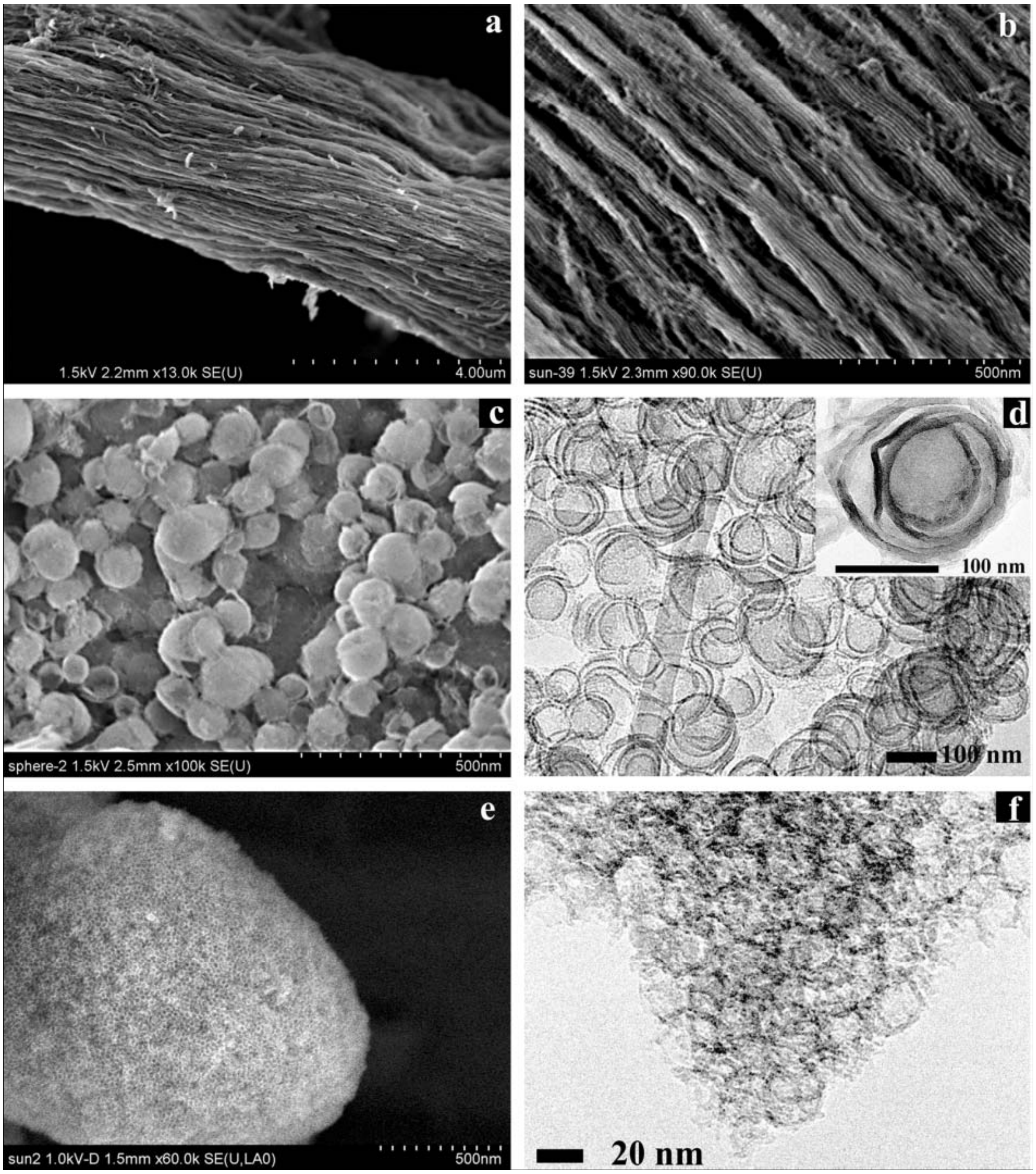
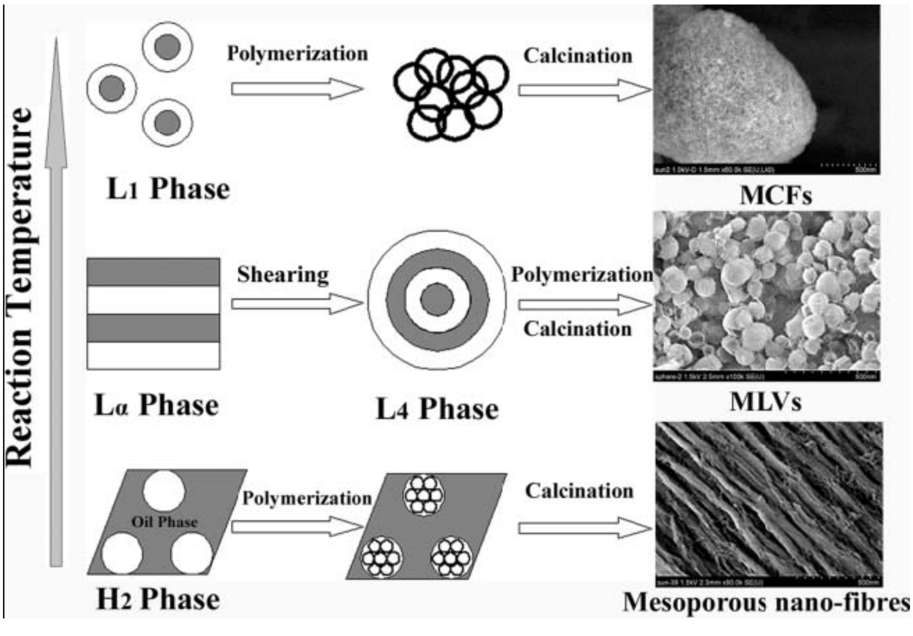


Fig. 1 SEM (a–c, e) and TEM (d, f) images of mesoporous silica nanofibres bundles (a–b) prepared at 303 K, MLVs (c–d) prepared at 313 K and MCFs (e–f) prepared at 333 K. Inset in Fig. 1d is higher magnified TEM image of one particle.

Fig. 1a shows that when the reaction temperature is lower than 308 K (*i.e.* 303 K), the products obtained are mainly bundles of nanosized fibres with a length of 8 to 30 µm. The diameter of those nanofibres range from 40 to 85 nm (Fig. 1b). The yield of the fibre-like silica is over 95% in the as-synthesized products. HRSEM image (Fig. 1b) suggests these nanofibres are actually well-ordered mesoporous silicas, which could be confirmed by the TEM image (Fig. S1 in the ESI). At the same time, the pore size of the mesoporous silica nanofibres judged from TEM is about 12 nm, which is consistent with the nitrogen sorption results (Fig. S2 in the ESI). The powder small-angle X-ray diffraction (SAXD) pattern (Fig. S3 in the ESI) show well-resolved reflections at d = 11.6 and 6.8 nm (2θ = 0.76 and 1.30°), as well as a shoulder peak at 5.9 nm ($2\theta = 1.48°$), which are consistent with the (100), (110) and (200) diffractions of the 2D hexagonal mesostructure with P6mm symmetry and with a unit cell parameter, a = 13.4 nm. Upon increasing the reaction temperature to 313 K, however, the structure of the products is completely different. They are mainly spherical particles with a diameter around 150 nm (Fig. 1c). The TEM image (Fig. 1d) indicates that these spheres are actually complex multilamellar vesicles (MLV) with a yield of over 80%, which was further confirmed by the nitrogen sorption results (Fig. S4 in the ESI). The MLVs normally have 3–5 layers and the inner layer vesicle is about 50 nm in diameter. The wall thickness of the vesicles is only *ca.* 5 nm. With a further increase of reaction temperature (333 K), the obtained materials changed significantly from MLVs to MCFs with spherical morphology (diameter around 1 µm). HRSEM and TEM images in Fig. 1e–f show that those MCFs have quite large pore size (35 nm), consistent with its N_2 adsorption–desorption isotherms (Fig. S5 in the ESI).

The phase behavior of oil–water–nonionic surfactant (especially pluronic series) emulsion systems has been widely studied and well understood.[8] Different structures, *e.g.*, micelles, lamellar, normal hexagon/inverse hexagon and cubic phases have been observed at different compositions of the systems.[8a–b] In the current decane–P123–water–TEOS quadru-component system, due to the effects of the oil phase[8b] and other factors (*e.g.*, the protonation of surfactant, the attachment of silica oligmers to the EO brushes,[13] alcohol derived from TEOS[14] as well as the introduction of inorganic salts), a slight change in temperature could induce a great shift of surfactant properties (*e.g.*, the relative affinity of surfactant for oil and water phases), which may lead to a significant change in morphology/structure of the emulsion system and thus those of the mineralized inorganic materials.

When the temperature is lower than 308 K (in this case, 303 K), a highly swollen inverse hexagonal phase (H_2),[8b] which is composed of hexagonally arranged 1D aqueous columns locally surrounded by decane,[8a,e,f] would be formed (Scheme 1). It provides 1-dimensional discrete aqueous spaces. At the same time, the hexagonal arrangement of silicate-doped P123 could be retained very well in the aqueous phase at a lower reaction temperature.[10b] Under the restriction of the surrounding oil phase, mesoporous nanofibres are thus produced.



Scheme 1 Proposed mechanism for the formation of different mesostructuredmaterials.

At an elevated temperature (313 K), a phase transition from a swollen inverse hexagonal phase (H_2) to a swollen multilamellar phase (L_α) took place. Under the proper shearing force, the L_α phase would be *in situ* organized into multilamellar vesicles (L_4),[8c] where the nanoscopic channels of the water phases were partitioned by decane (Scheme 1). The condensation/mineralization of inorganic silicate species is confined within the compartmentalized aqueous nanochannels, thus the MLV structures are successfully built. Further increasing the initial reaction temperature (333 K), an oil-in-water micellar phase (L_1) is preferred. At the relatively high temperature, the cross-linking reaction (inter-micelle condensation and fusion) occurs immediately with the formation of the micelles. After calcination, the oil cores and the surfactant were removed, and the MCF structures with pore size larger than 30 nm are obtained.

It should be mentioned that, similar to the synthesis of mesoporous materials (*e.g.*, MCM-41s, SBA-15), the concentration of surfactant in the current study is lower than that needed for the formation of lyotropic phase.[8*b*] The co-organization of organic and inorganic species was thought to be the key factor for the formation of the ordered mesoporous materials.[15] We believe that the synergetic effect of those two species is essential in controlling the formation/transformation of different emulsion morphologies, and therefore the corresponding inorganic mesoporous materials. In addition, the morphologies of the ordered mesoporous materials are different, depending on the alkanes used. For example, in the case of nonane, randomly aligned mesoporous nanofilaments are obtained at lower temperature (Fig. S6 in the ESI). The reason why variable morphologies result from the use of different alkanes is not yet fully understood. We speculate that it might be related to the stability of the H_2 phase in the current system.

In conclusion, the well-documented phase transformation in the water–oil (alkanes)–block copolymer surfactant system is applied to direct the mineralization of inorganic materials. Our results indicate that by carefully manipulating the reaction conditions, complex inorganic mesostructures can be built in one system by controlling the phase behavior of the synthetic mixture. As an example, present study shows that, with a lower TEOS : P123 ratio than that of conventional SBA-15, three totally different complex mesostrutures were obtained by simply altering the initial reaction temperature in the alkane–water–P123–TEOS system. At relatively low reaction temperature, the swollen inverse hexagonal phase (H_2) is formed. Confined by the oil phase (in this case, decane), the mesoporous nanofibres bundles are attained. On increasing the reaction temperature, however, a L_a phase is preferred. Driven by the shearing force, L_4 phase is formed, which leads to the formation of MLVs. Further increasing the reaction temperature, a phase transformation from L_α to L_1 takes place. Coupling with the interparticle collision and fusion, a MCF structure is obtained. This work, on one hand, would promote a further understanding of the phase behavior of the oil–water–surfactant. On the other hand, it also provides a general route to the controlled construction of different inorganic mesostructures which have potential applications in the fields of catalysis, adsorption–desorption and controlled drug release, *etc.* Further studies are in process. ± §

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Notes and references

±The synthetic procedure: 2.4 g of $EO_{20}PO_{70}EO_{20}$ (P123) was put into 84 ml HCl solution (1.30 M) and stirred at 303 K until the solution became clear. At this stage, 0.027 g of NH_4F was added. A mixture of TEOS and alkane (from heptane to dodecane, the final molar ratios, P123 : HCl : NH_4F : TEOS : H_2O : alkane = 1 : 261 : 1.8 : 48 : 11278 : 134) was then added into the solution at the given reaction temperature (303–333 K) under moderate mechanical stirring (*ca.* 360 rpm). The above mixture was stirred at the given constant temperature for 20 h, and then transferred into an autoclave for further reaction at 373 K for 48 h. The products were collected by filtration, dried in air, and calcined at 813 K for 5 h to remove the templates.

§ SEM was performed on a Hitachi S4800 field-emission scanning electron microscope; TEM was done on a Philips CM 200 transmission electron microscope; The N_2 adsorption–desorption isotherms were recorded on an ASAP 2000 instrument; powder X-ray diffraction (XRD) pattern was recorded on a Rigaku D/max-2500/PC diffractometer using Cu K_α radiation.

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12Our experiments indicate that these mesoporous structures could only be obtained when the molar ratio of TEOS to P123 decreased from 60 (the same as that of traditional SBA-15) to 48. In other words, a higher P123 : TEOS ratio is important for the formation of those materials.

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