Structural Transcription of Organogels to Mesoporous Silicas: A Chain-length Dependent Morphology and Pore Texture

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Here, we report a chain-length dependent morphology and pore structure tailing of mesoporous silica templated from organogels, which is formed by primary alkylamine and ethylene glycol at room temperature. As the chain length of alkylamine changes from 12 to 18, the resulted materials exhibit a morphology change from layers to spheres and platelets, respectively. SEM and TEM observation revealed that these shapes appear to be inherited from their parent organogels. Further pore structure characterization by nitrogen sorption analysis demonstrates that all the resulted silicas exhibit typical IV isotherms indicative of uniform mesopores, and their pore sizes are dependent on the chain length of alkylamine used.

Key Words : Mesoporous silicas, Organogel, Primary alkylamine, Morphology change, Chain length

Introduction

Since the first report in 1992,[1] the supramolecular assembly approach to pore-size and morphology-controllable mesoporous silica-based materials have generated considerable interests because of their structure-sensitive properties for a wide spectrum of applications.[2-4] A variety of mesostructures, from MCM,[1,5] AMS[4] to HMS[6] and SBA[7] series, can be readily fabricated using cationic, anionic, nonionic, and polymeric surfactants as the templates. It is well known that chain lengths of surfactants and their self-assembly structures in solvents can somehow tune the pore sizes and shapes of the silicas. However, in most case, it still remains a challenge to accurately template the final replicas from soft aggregates. This is based on the fact that the templating process is rather fluxional and dynamic with various uncontrollable interactions between silica precursor and soft assemblies, handicapping to rational design.

Recently, the discovery of low molecular organgels (LMOGs) and their successful structure transcription to silicon-based materials provide us a possible solution.[8-13] Due to limited movement of precursors around the network of LMOGs by their solid-like properties, the resulted materials can retain the original morphology of LMOGs even after the removal of templates. That is to say, the shape and structure of final products may be transcriptable from the original organogels. Since the first report by Shinkai's group in 1998,[14] silicon-based materials of diverse shapes have been prepared through tailoring the structure of gelators and solvents or catalysts, such as helics, single and multi-walled tube, fibers, spheres, and sheet-like structures, *etc.*[15-20] However, these methodologies do not generally produce mesoporous silica except that of Sanchez and Yang *et al.*,[21-25] who have recently reported the formation of uniform meso-

porous structures. Despite of these examples, the preparation of mesoporous silica from physical gels still remains a challenge. The key reason relies on the fact that in most case, the known surfactant systems used for the preparation of mesoporous silica cannot interact with organic solvents easily to form organogels. Also, the gelators employed in the past are structurally complicated and hard to be synthesized, which greatly limits their further applications. Therefore, to develop various gel systems from the simple surfactants for mesoporous materials not only gives us a new insight to understanding the templating process, but also a possibility for scalable industrial applications.

Primary alkylamines were firstly applied by Pinnavaia on the preparation of HMS, which exhibited a chain-length dependent pore sizes. Recently, they are shown to form efficient gelators to various solvents.[26] For example, in our previous report,[27,28] we found that the formation of organogel is mainly driven by the interaction between alkylamines and ethylene glycol (solvent). The introduction of sodium oleate can alter the solubility of hexadecylamines in ethylene glycol leading to the morphology change from spheres to fibres, which is based on the nucleation-crystallization mechanism.[29,30]

In the present work, we demonstrate a chain-length dependent morphology and pore structure of mesoporous silicas, using organogels pre-formed by primary alkylamines (R-NH$_2$, R=12, 14, 16, 18) in ethylene glycol as templates. As the chain length of alkylamines varies from 12 to 18, morphologies of resulted silica can change from layers to spheres and platelets, just as the cases observed in the parent organogels. Compared to the approach of mesoporous silica templated from using alkylamine in water, our report provides a new direction to tailor the morphology and pore structure based on their solubility change of alkylamine in ethylene glycol.

Experimental

Materials. Hexadecylamine (purity ≥ 98%, Aldrich), octyl-decylamine, tetradecylamine, and dodecylamine were provided by Jiangsu Feixiang Chemical Co. Ltd. Ethylene glycol was purchased from Sinopharm Chemical Reagent Co. Ltd (SCRC). All the reagents were of analytical grade and used without further purification.

Synthetic Routes. In a typical experiment, 0.2 g alkyl-amine was added to ethylene glycol with stirring under heating conditions to form a homogeneous system. Then, it was cooled at a fixed temperature statically to form organo-gels.

Mesoporous silica was prepared based on the organogel preformed by hexadecylamine in ethylene glycol with addition of methanol as the co-solvent and tetraethoxylsilane (TEOS) as a silica source. In a typical experiment, 0.2 g hexadecylamine, a fixed amount of TEOS and 0.8 g methanol were added to 4.8 g ethylene glycol with continuous stirring at 50 °C to form an organic solution. After a known quantity of distilled water was blended into the above solution for the hydrolysis of TEOS, the mixture was kept at room temperature for 10 days in order to produce the as-synthesized product. The molar ratios of hexadecylamine: TEOS:H_2O used were set at 1:3:12. Mesoporous silica can be obtained after the calcination of the as-synthesized product at 560 °C for 8 h.

Characterization. Optical microscopic images were taken using an Olympus BX51 optical microscope equipped with crossed polarization lenses and TP 94 heat stage. A drop of heated solution was placed on a glass plate to form a gel. The photographs of the gel fibers were acquired digitally.

Scanning electron microscopic images were taken from KYKY-EM3200 (KYKY Technology Development Ltd.) operated at 30 KV. A piece of the gel was first placed on a glass and pretreated at low pressure (> 10^{-5} Torr) for 3 days to remove the solvent and volatiles. Then the sample was coated by gold sputtering prior to examination.

N_2 adsorption isotherm was measured at 77 K on a Micromeritics ASAP 2020 volumetric adsorption analyzer.
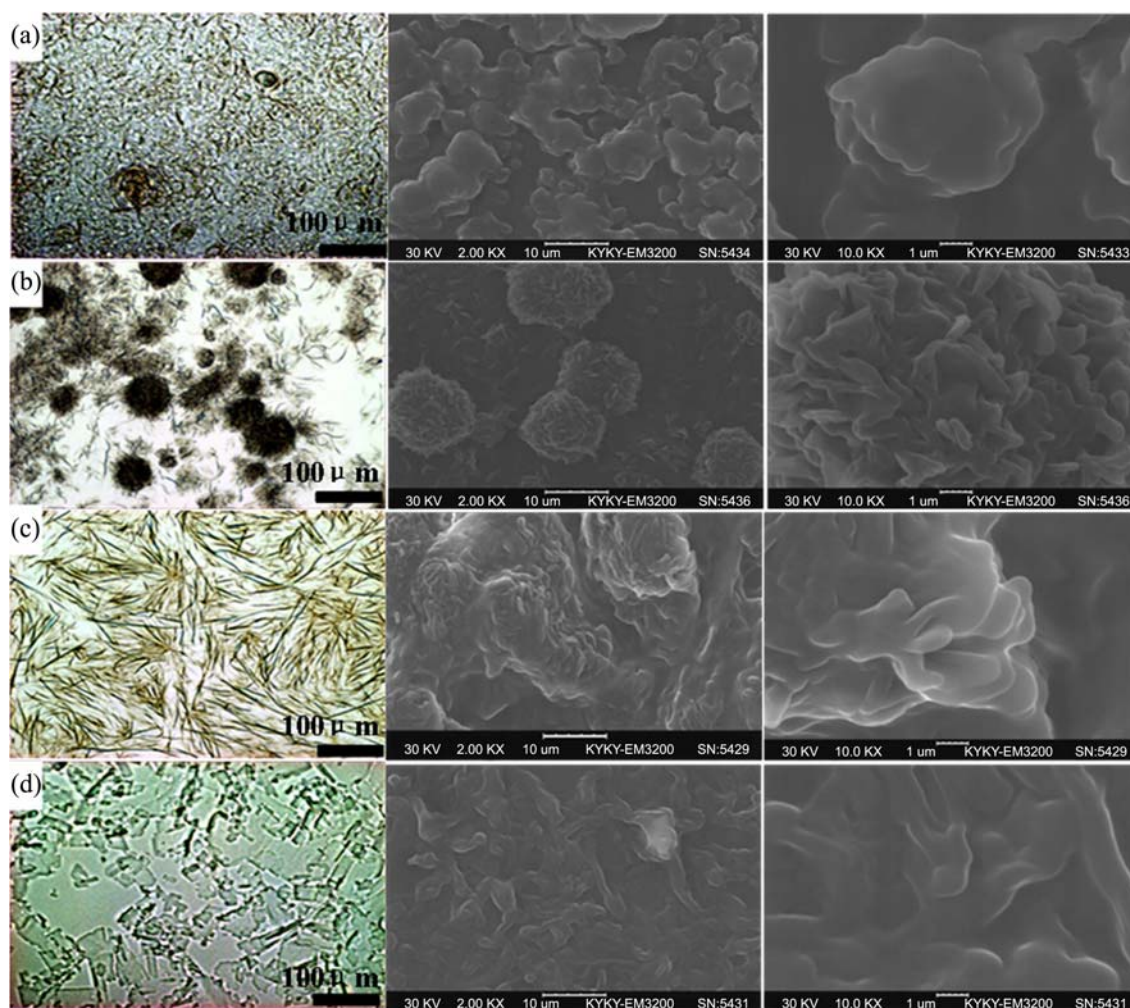
Figure 1. Optical and scanning electron microscopic images of organogels formed by pre-dissolving alkylamine of various carbon chain lengths in ethylene glycol; (a) octyldecylamine (C18); (b) hexadecylamine (C16); (c) tetradecylamine (C14); (d) dodecylamine (C12). In each series, the first image was acquired by optical microscopy with the scale bar as 100 μm, and the latter two images were captured by SEM in different magnifications.

All powder samples were outgassed under vacuum for 6 h at 423 K prior to the measurement. Specific surface area of mesoporous materials was calculated using data acquired in relative pressure range from 0.05 to 0.25 by the Brunauer-Emmett-Teller (BET) method. Total pore volume was determined from the nitrogen adsorbed quantities at a relative pressure of about 0.995. The pore size distribution was obtained from desorption branches of nitrogen isotherms using the Barrett-Joyner-Halenda (BJH) model.

Results and Discussion

Morphology Variation as a Function of Chain Length of Alkylamines. In a typical experiment, 0.2 g alkylamine was added to 4.8 g ethylene glycol with stirring under 60 °C to form a homogeneous system. Then, it was cooled at room temperature statically for several minutes to generate organogels. The morphologies of the soft assemblies were recorded by both optical and scanning electron microscopy. As shown in the optical microscopic images of Figure 1, the fibrous gels exhibit different appearances ranging from layers, spheres to platelets as the carbon chain length of alkylamine varies from C12 to C18. From further magnified imaging acquired by SEM it is evident that these structures are indeed all comprised of interconnected fibers. Thus, the carbon chain length in alkylamine clearly appears to play an important role in the final morphology of their organogels.

In the previous report,[28] we demonstrated that the interaction between alkylamines and ethylene glycol played important roles in the organogel formation, and the gelation process was driven by crystal salting out phenomea. Accordingly, the introduction of sodium oleate can increase the solubility of hexadecylamine and changed their gelation rate, resulting in different kinetically trapped gel morphologies ranging from spheres to dispersed fibers. It is noted that the solubility of alkylamine should generally increase with the decrease of chain length, and thus giving different supersaturation values when they are cooled from high temperature. Correspondingly, the final gels revealed distinct morphologies controlled by their gelation rates, ranging from layers, spheres to platelets for C12 to C18.

Structure Transcription from Organogels to Mesoporous Silica. It is well known that structure transcription from physical gels to mesoporous silica remains still a hard work. In order to control silica structure by chain length change, we firstly investigate the effect of various experimental factors on the morphology of templated silica. In the present work, various preparation conditions, such as molar ratios of hexadecylamine (HDA) with TEOS, and the addition of co-solvents have been studied using HDA as a model system.

The effect of TEOS on material morphologies. At a fixed concentration of HDA, the effect of TEOS on the structural transcription has been examined, with different molar ratios of HDA and TEOS at 1:3, 1:5 to 1:8. As shown in Figure 2(a), all the silica replicas revealed typical type-IV isotherms with distinctive capillary condensation profile, indicative of uniform mesopores. It is found that the hysteresis loops are
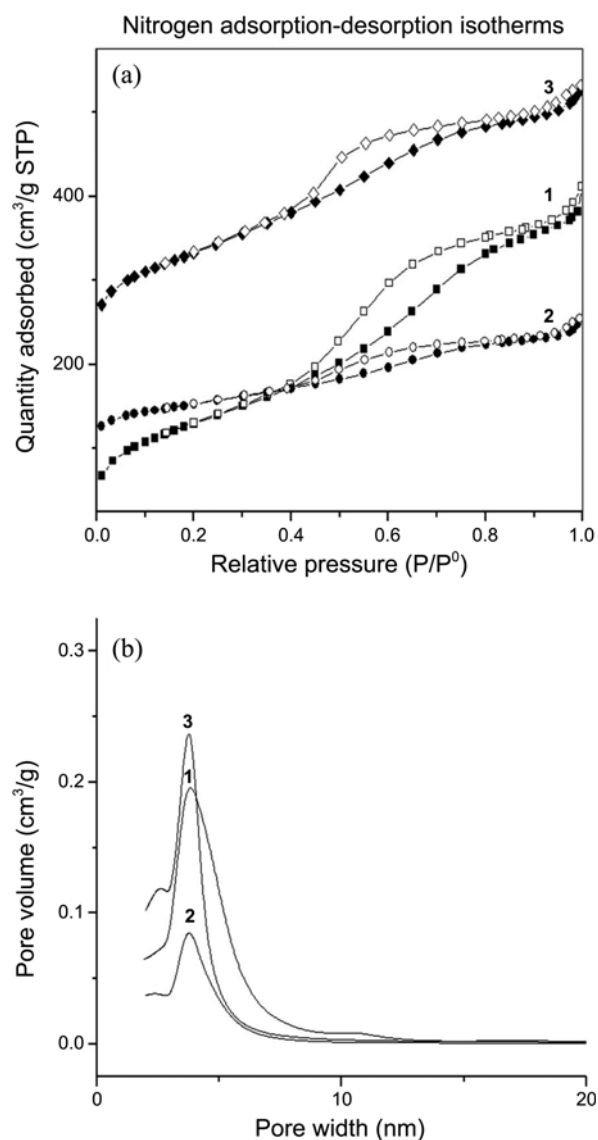
Figure 2. Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) of mesoporous materials with various molar ratio between HDA and silica precursors. **1**. 1:3; **2**.1:5; **3**. 1:8.

H2-type just as the case in HMS molecular sieves, possibly implying the presence of mesoporous worm-like channels. These characters can be also verified by small-angle XRD and TEM (shown later). In Figure 2(b), narrow pore size distribution centered at about 3.7 nm can been matched with the inter-layer distances of hexadecylamine, demonstrating that primary alkylamines are involved into the structure formation process. The detailed structural parameters of resulted materials can be found in Table S1 (supporting information). From the table, it is clear that the produced materials exhibit high specfic area of about 480 m^2/g at molar ratio as 1:3 and 1:8, and the largest pore volume of 0.64 cm^3/g at 1:3. From these results, it is not difficult to propose that low addition of TEOS is appreciated for the structural transcription.

The morphologies of resulted mesoporous silica were also examined by SEM and TEM observation. As shown in
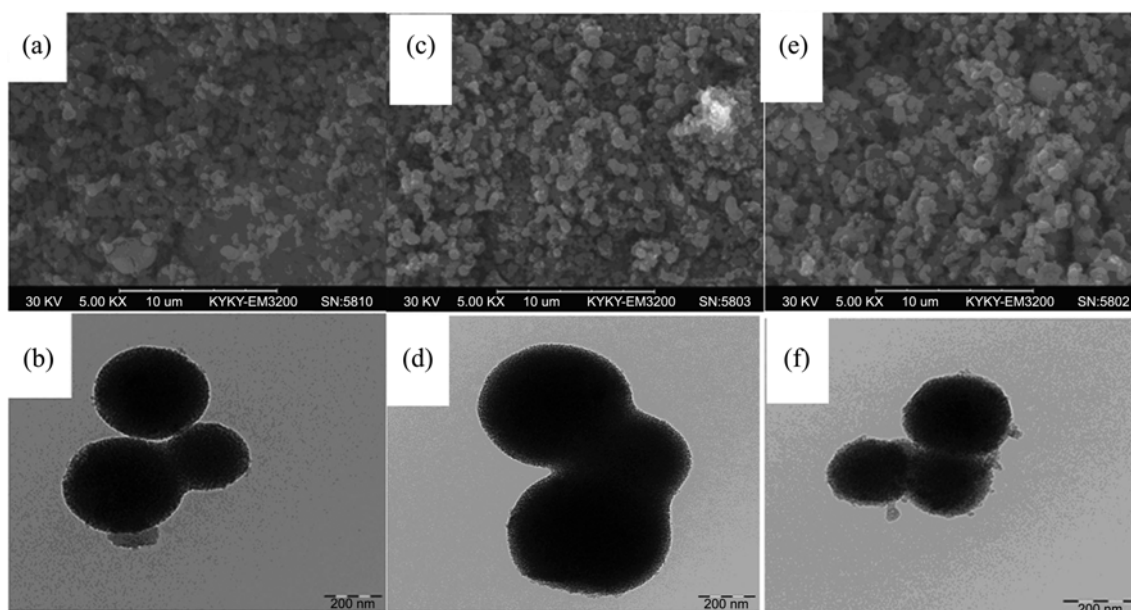
Figure 3. SEM and TEM images acquired for mesoporous materials synthesized from various molar ratios between hexadecylamine and silica precursors: (a-b) 1:3; (c-d) 1:5; (e-f) 1:8, respectively.

Figure 3, all the produced silicas revealed sphere-like structures with similar size, despite of different molar ratio between HDA and TEOS. As the increase of TEOS from 3:1 to 8:1, the sphere-like structures tend to fuse into larger spheres, possibly due to the uncontrolled gelation. Compared with their organogel templates (Figure 1(b)), their particle size seems to be much smaller.

In the common sense, the size change was mostly ascribed to the calcination step in the silica preparation, which can lead to the structural shrinkage from as-synthesized templates to final silica pore dimension. In our present work, the introduction of methanol is also believed to play an important role for the size reduction, which increased the solubility of alkylamines and smaller length-scale organogels just like the case ocurred for sodium soaps. This deduction was further justified by TEM observation as shown in Figure S1. From the TEM images, it is apparent that the gel formed in the presence of methanol reveals sphere-like structure with a size of about 150 nm, similar with its final mesoprous replicas in Figure 3(b).

The Effect of Co-Solvents. Under the optimized molar ratio of HDA and TEOS as 1:3, we also examined the effect of co-solvents on the structure transcription. Using methanol, ethanol, propanol, or butanol as the co-solvent, four various silica materials have been generated, respectively. In the former three co-solvents, the resulted silicas show type-IV curves with a clear nitrogen condensation profile (Figure 4(a)). As shown in Table S2, the mesoporous silica obtained in methanol possesses a maximum surface area and pore volume to be 477 m^2/g and 0.64 m^2/g, respectively. And their specific surface area and pore volume tend to decrease from methanol to 1-propanol, accordingly the pore size distribution becomes irregular. It is interesting to find that in the case of butanol, the product reveals type-V isotherm,

indicative of the absence of intra-pore (Figure 4(b)). These differences are probably arisen from the diffusion of silica precursor into organogel structures, since chain-length increase from methanol to 1-butanol could result in less compatible system in the presence of TEOS and ethylene glycol, and hence giving an inefficient infilitration.

To further ensure the appropriate co-solvent, SEM and TEM characterization were also performed for the generated mesoporous silicas in various alcohols. As shown in Figure 5, the mesoporous silicas acquired from methanol to propanol revealed dispersive spheres to fused sphere-like structures with the chain-length increase of co-solvent. Oppositely, the materials generated from butanol exhibited some irregular structures except fused spheres. These changes are probably produced by the compatibility of co-solvent with organogels system. As the carbon chain increases, the co-solvents tend to be nonpolar from methanol to butanol, and noncompatible with the organogels. Accordingly, the morphology different the original gels were produced.

Chain-length dependent morphology control of mesoporous silica. From the above results, it is clear that the organogel structures can be efficiently templated into mesoporous silica with the molar ratio of hexadecylamine and TEOS as 1:3, and in the presence of co-solvent methanol. Under this reaction condition, we prepared the mesoporous silica with different morphologies templated from the organogels of alkylamine from C12 to C18 in ethylene glycol. The resulted materials were characterized with nitrogen adsorption experiments, as shown in Figure 6. It is apparent that the four silica materials acquired from organogels indeed exhibited the isotherms of IV type with distinct capillary condensation profile, indicative of uniform mesopores (Figure 6(a)). The surface areas and pore parameters of these resulted materials are given in Table S3, in which four mesoporous silicas
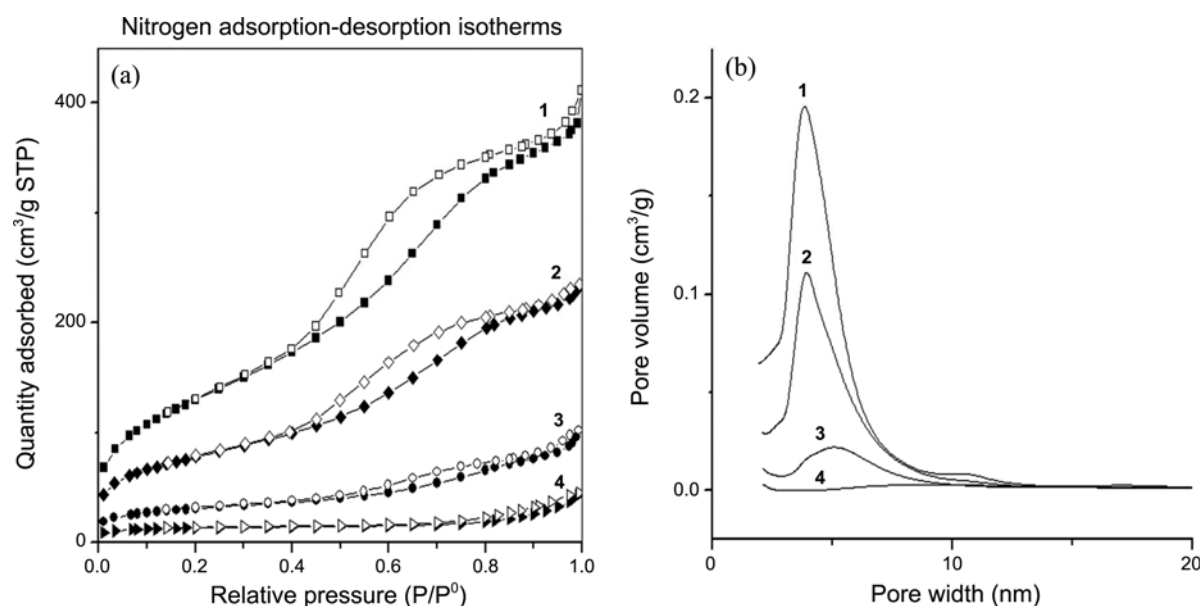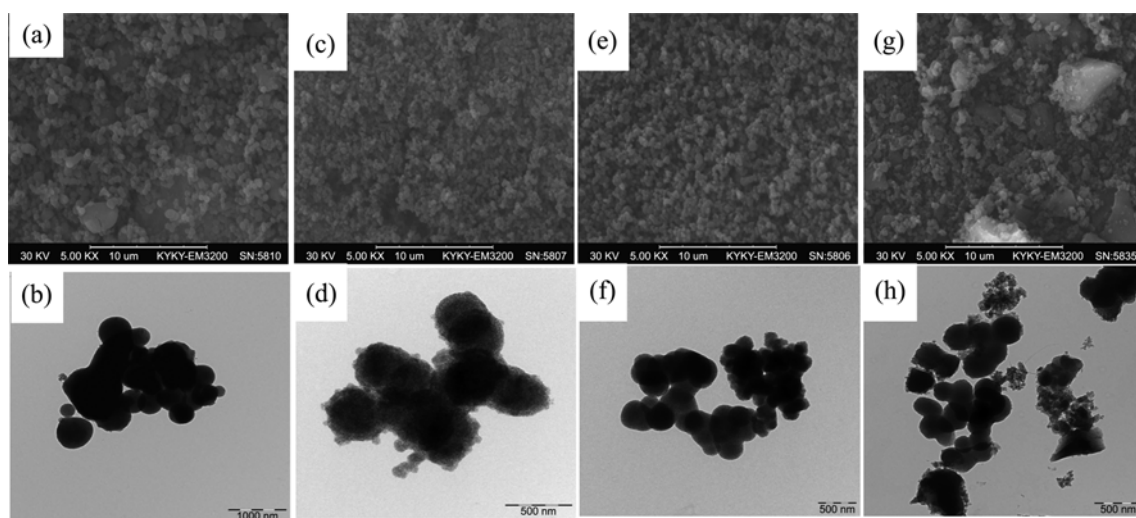
Figure 4. Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) of mesoporous materials templated from hexadecylamine in EG with various cosolvents. **1**. methanol; **2**. ethanol; **3**. propanol; **4**. butanol.

reveal high specific surface area of about 500 m^2/g and chain-length dependent pore size from 3.0 nm to 4.0 nm. These results clearly reveal that our soft lamella layered organogels can act as templates for the synthesis of mesoporous silica materials as similar to the MCM41 structures using surfactant self-assemblies reported in the literature.[1]

To confirm the success in templating the morphology of these soft organogels to solid mesoporous materials, SEM and TEM characterizations were shown in Figure 7. From the SEM and TEM images in the Figures 7(a) and 7(b), it is clear that the resulted materials exhibit various morphologies from piece-like structure to irregular platelets corresponding very well to those images of their parent gel morphologies, as previously shown in Figure 1. From C12 to C18,

the porous structures of sheet-like, coexistence of sheet-like and sphere, sphere, and platelet are clearly observed with only small differences in the relative sizes from their original gels.

As a powerful tool for the direct morphology observation, nowadays, high-resolution TEM characterization has been widely applied in the analysis of the size and structure of mesoporous materials. In the present work, the produced four materials have been also investigated by high-resolution TEM observation. As shown in Figure 8, all the silicas show typical worm-like porous structure just as the case reported for HMS. As the chain length of alkylamines increases from C12 to C16, the pore channels seem to be more regular, contrarily, the mesopores for C18 are most irregular than

Figure 5. SEM and TEM pictures acquired for materials synthesized in different co-solvents: (a-b) methanol; (c-d) ethanol; (e-f) propanol; (e-f) butanol; respectively.
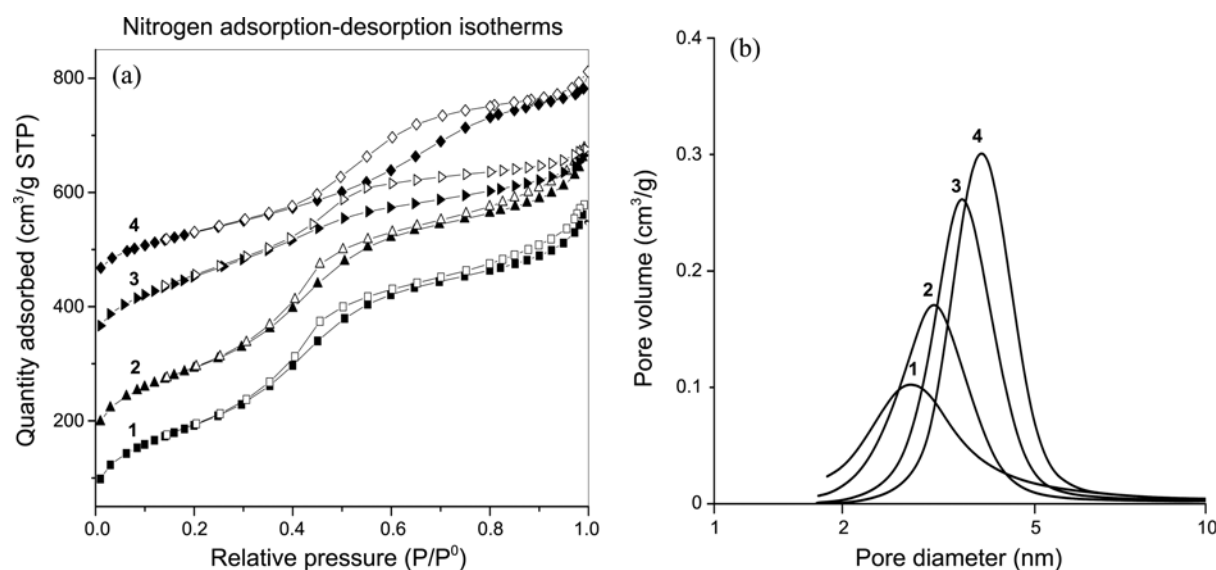
Figure 6. Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) of mesoporous materials by alkylamine with various carbon chain length in ethylene glycol. **1**. dodecylamine; **2**. tetradecylamine; **3**. hexadecylamine; **4**. octyldecylamine. The inset image in B is the magnification of the pore size distribution of mesoporous materials templated from tetradecylamine organogel.
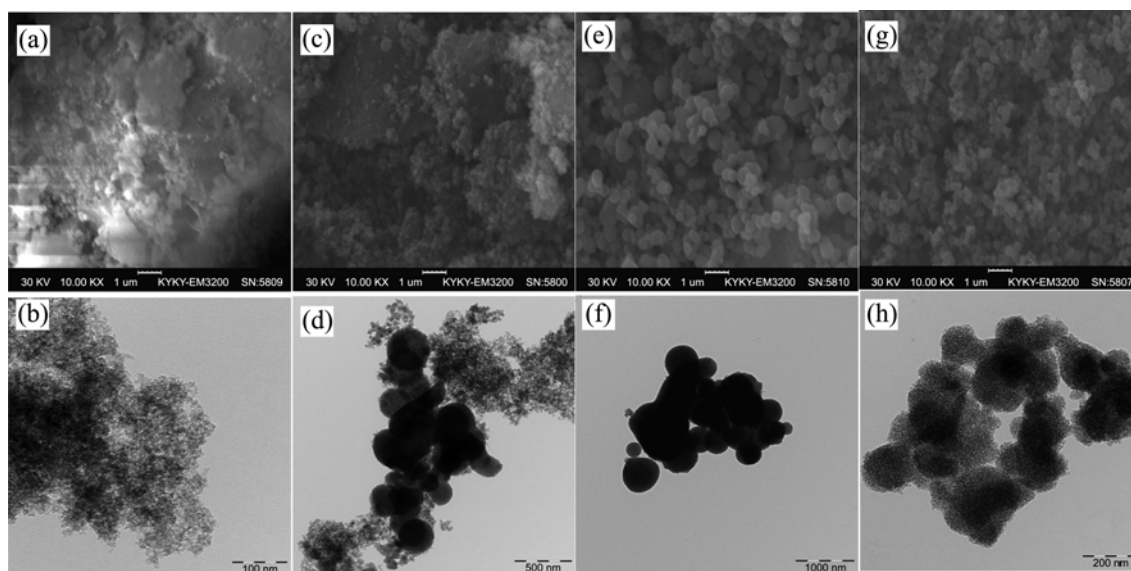

Figure 7. SEM and TEM pictures acquired for materials synthesized from organogels obtained using various chain-length primary alkylamine in EG: (a-b) dodecylamine; (c-d) tetradecylamine; (e-f) hexadecylamine; (g-h) octyldecylamine; respectively.

other ones. These changes are probably generated by the chain-length difference, since too long carbon chain such as 18 is not favorable for the regular soft-asemblies. In Figure 8, it is also found that the size of mesopores increase from 2.8 nm to 4.0 nm for C12 to C18, corresponding to their molecular sizes. It seems that ethylene glycol has no effect on the pore size, maybe ascribed to structure shrinkage during calcination due to their small sizes. It is noted that low concentration of hexadecylamine at 1.0 wt % (no gel formation) produced only bulk silica without any evidence of mesopore (not shown here). The results clearly suggest the mesoporous silicas can be only acquired from organogel systems, and the morphology and pore structure are strongly

dependent on the chain-length of alkylamine but no clear dependence on the nature of solvent molecule (ethylene glycol) in contrast with those reported in the case of poly-ethyleneglycol.[31]

The pore structures were also examined by small-angle XRD. In the XRD patterns (Figure 9), the four materials all exhibited one similar peak at about 2^0, just as the case observed for HMS, typical of worm-like mesopores, in accordance with TEM results. It is also found that the diffraction peak for all the materials tends to be moved to the low-angle direction from C12 to C18. According to Bragg equation, their corresponding dimension sizes should increase with the ascend of chain length, and the values change from
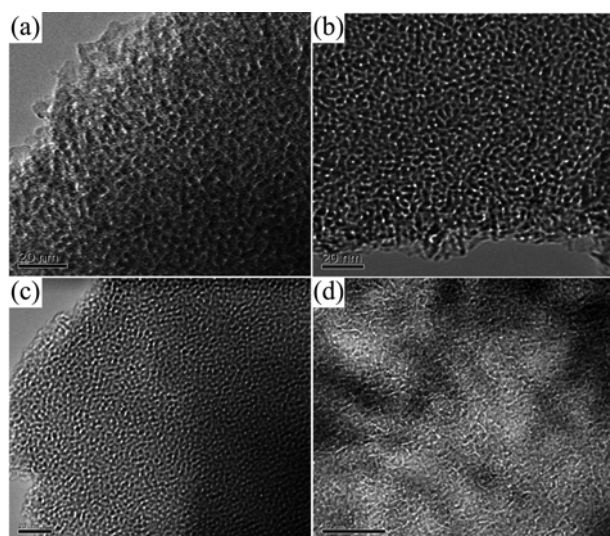
Figure 8. HRTEM images of the resulted silica templated from organogels formed by alkylamines of various chain lengths in ethylene glycol. (a) dodecylamine, (b) tetradecylamine, (c) hexadecylamine, and (d) octyldecylamine, respectively.
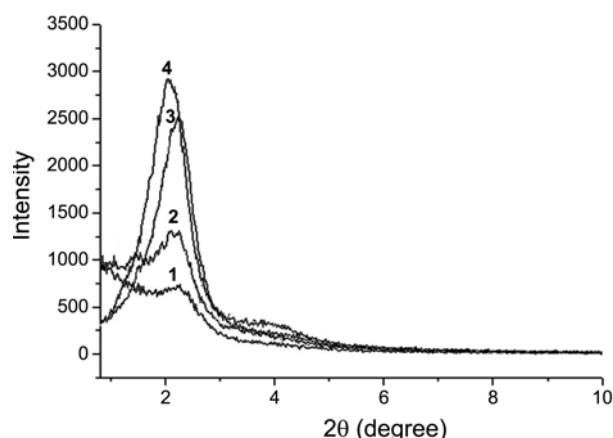
Figure 9. Small-angle XRD patterns of the resulted silica templated from organogels formed by alkylamines of various chain lengths in ethylene glycol. **1**. dodecylamine, **2**. tetradecylamine, **3**. hexadecylamine, and **4**. octyldecylamine, respectively.

3.2 nm to 4.1 nm. Associated the TEM results, it is clear that the pore-wall thickness should increase in combination with their pore size difference. The detailed reason for this change remains still unknown, and a further study should be performed.

Conclusion

We report chain-length dependent shape changes of organogels formed from alkylamine in ethylene glycol. A series of morphologies ranging from sheet-like, spheres to platelets is believed to be produced from the solubility difference of alkylamines from C12 to C18 in ethylene glycol. Using these organogels as templates we demonstrate a chain-length dependent morphology and pore structure of synthesised mesoporous silicas at room temperature. As the chain length

of alkylamine increases from 12 to 18 in ethylene glycol, morphology of the resulted silica changes from layer-like to spheres and platelets, corresponding to their orginial organogel shapes, and their worm-like pore size is also increased.

Supporting Information. The structural parameters of mesoporous silicas and TEM images for the organogel formed in the presence of methanol can be found here.

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