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PAPER

A novel liquid template corrosion approach for layered silica with various morphologies and different nanolayer thickness †

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A novel liquid template corrosion (LTC) method has been developed for the synthesis of layered silica materials with variety of morphologies, including hollow nanospheres, trilobite-like nanoparticles, spherical particles and a film resembling the van Gogh painting 'Starry Night'. Lamellar micelles and microemulsion droplets are first formed in an oil/water (O/W) mixture of ethyl acetate (EA), cetyltrimethylammonium bromide (CTAB) and water. After adding aqueous ammonia the EA becomes hydrolyzed, which results in corrosion of the microemulsion droplets. These droplets subsequently act as templates for the synthesis of silica formed by hydrolysis of tetraethyl orthosilicate. The morphological evolution of the silica can be tuned by varying the concentration of aqueous ammonia which controls the degree of corrosion of the microemulsion droplet templates. A possible mechanism is proposed to explain why the LTC approach affords layered silica nanostructured materials with various morphologies and nanolayer thickness (2.6–4.5 nm), rather than the usual ordered mesostructures formed in the absence of EA. Our method provides a simple way to fabricate a variety of building blocks for assembling nanomaterials with novel structures and functionality, which are not available using conventional template methods.

Introduction

New methods of materials fabrication are of fundamental importance in advancing science and technology.^{1–5} The sacrificial template method developed over the past decades has enabled the synthesis of various materials with different structures and morphologies,^{6,7} such as hollow structures and mesoporous materials.^{8,9} The sacrificial template approach has the advantage of simplicity, convenience and high selectivity.^{10–12} Hollow structures can be obtained by using either a hard or soft template in the synthesis process, followed by removal of the template by chemical reaction¹³ or calcination.¹⁴ For example, the sacrificial hard template method has been used for the synthesis of hollow spheres,^{15,16} ordered macroporous materials,¹⁷ nanotubes,^{18,19} nanopillars or nanowires,²⁰ mesoporous,²¹ and nanoporous materials.¹³ However, only one structure or morphology is typically obtained using this method, because the hard template is characterized by structural rigidity and resistance to changes of shape or volume. Soft templates offer a potential way to tailor the morphology of the final products. However although microemulsion droplets have been employed as a soft template in oil/water (O/W) systems for the synthesis of hollow spheres,^{22–25} it still remains a challenge to develop ways of altering the morphology of the microemulsion droplets in order to synthesise materials with different morphologies and structures.

In recent years, two-dimensional layered materials have attracted considerable attention and many different layered

materials have been fabricated including layered double hydroxides (LDH),^{26,27} graphene^{28,29} and layered montmorillonite materials.^{30,31} Layered silica materials have also been synthesized by sol–gel methods. Layered silica was first successfully prepared by Stucky and co-workers in 1994,³² who found that using C_{20–22}-alkyltrimethylammonium bromide as a template in acidic media at room temperature led to the formation of a lamellar material. Layered silica–dialkyldimethylammonium bromide nanocomposites were also obtained by Ogawa in 1997,³³ using dialkyldimethyl quarternary ammonium salt surfactants under acidic condition at room temperature. However, using smaller monoalkyltrimethyl quarternary ammonium salt surfactants, such as the readily available cetyltrimethylammonium bromide (CTAB), in alkaline media only afforded ordered mesoporous materials like MCM-41, and no layered materials could be synthesized.³⁴ This is because CTAB molecules only can form rod-like micelles instead of lamellar micelles under the conditions normally employed.

In this paper, we report a novel sacrificial template method where selective corrosion of a liquid template is employed in the synthesis of a variety of layered silica materials. The main steps in our liquid template corrosion (LTC) method are as follows: lamellar micelles in which ethyl acetate (EA) acts as a swelling agent^{35,36} and microemulsion droplets were formed as a liquid template by using a mixture of CTAB, ethyl acetate (EA) and water; the EA molecules were hydrolyzed by adding aqueous ammonia, which resulted in the liquid template being corroded and, following addition of tetraethyl orthosilicate (TEOS),

Table 1 Physicochemical properties and morphologies of silica particles prepared by tuning the concentration of aqueous ammonia

Sample	Aqueous ammonia concentration/mol L ⁻¹	BET surface area/m ² g ⁻¹	Pore diameter/nm	Total pore volume/cm ³ g ⁻¹	Morphology
L ₁	1.0	123	4.0	0.298	Hollow nanospheres
L ₃	3.0	133	3.9	0.306	Trilobite-like nanoparticles
L ₅	5.0	480	2.6	0.970	Spherical particles
L _{con}	13.4	429	2.8	1.107	'Starry Night'-like film

layered silica materials with different morphologies and structures were formed. As the concentration of aqueous ammonia was increased, the extent of corrosion of the template varied, leading to changes in the morphologies of the final layered silica product, with hollow nanospheres, trilobite-like nanoparticles, spherical particles and a film resembling the van Gogh painting 'Starry Night' being formed under different conditions. To the best of our knowledge, this is the first time that such a flexible method for preparing layered nanomaterials with different morphology has been reported.

Experimental section

Materials

Cetyltrimethylammonium bromide (CTAB) (Analytical Reagent (A.R.), Tianjin Jinke Fine Chemicals Institute, China), tetraethyl orthosilicate (TEOS) (A.R., Beijing Chemical Factory, China), ammonia solution (25%) (A.R., Beijing Beihua Fine Chemical Product Limited Company, China) and ethyl acetate (EA) (A.R., Beijing Chemical Factory, China) were used as received without any further purification.

Preparation of layered silica materials

The layered silica materials with different morphologies were synthesized by the following procedure: 1.38 g of CTAB was added to 66 mL of deionized water in a 250 mL three-neck flask, and then 20 mL of EA was added into the flask with stirring at room temperature resulting in an emulsion. After 30 min, 14 mL of an aqueous ammonia solution of the desired concentration (x mol L⁻¹, see Table 1) was added. Then the mixture was vigorously stirred for 15 min, and 7.2 mL of TEOS was quickly added dropwise to the mixture. The molar ratio of the final mixture was 3.23 TEOS:0.38 CTAB:20.47 EA: 1.4x NH₃.H₂O:444 H₂O. The resulting mixture was vigorously stirred at room temperature for 30 min, and was then transferred into a Teflon-lined autoclave and heated at 373 K under autogenous pressure for 24 h. The product was separated by filtration, washed with deionized water, and dried at 333 K in air for 6 h. The as-synthesized solid product was collected and calcined at 823 K for 6 h in air to remove CTAB. The samples are denoted as L_x (see Table 1).

Characterization

The layered silica products were characterized by scanning electron microscopy (SEM), using a Hitachi S-4700 microscope

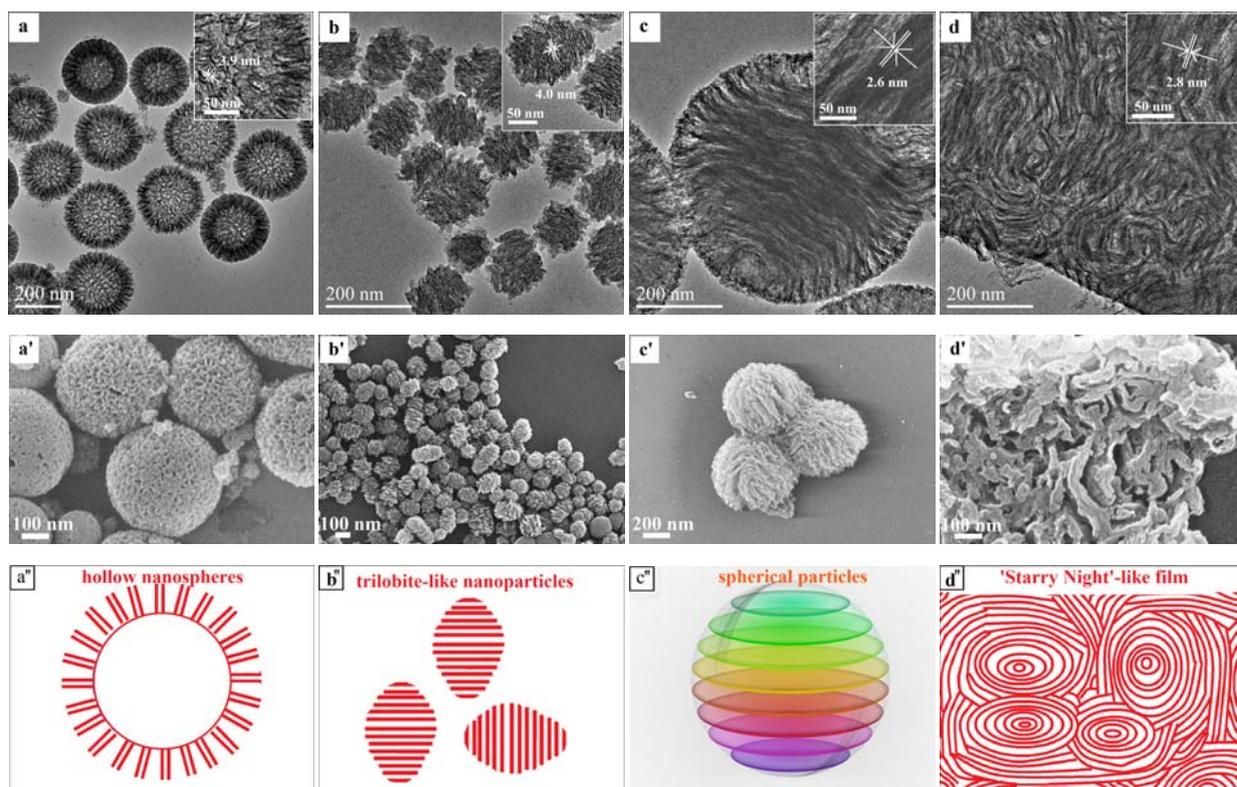
operated at an accelerating voltage of 30 kV. The samples were coated with platinum prior to the analysis. High-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL JEM-3010 microscope with an accelerating voltage of 200 kV. Powdered samples for HRTEM measurements were suspended in ethanol and then dropped onto a Cu grid with a lacey carbon film (Beijing Xinxing Vraim Technology Co., Ltd). Nitrogen adsorption isotherms were obtained on a Micromeritics ASAP 2020 apparatus. Before the nitrogen adsorption measurements, the samples were pretreated by degassing in vacuum at 573 K for 8 h. The Brunauer–Emmett–Teller (BET) specific surface area was calculated using adsorption data in the relative pressure range of $P/P_0 = 0.05–0.25$. The pore size distribution was determined from the desorption branch using the Barrett–Joyner–Halenda (BJH) method. The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure (P/P_0) of 0.99.

Results and discussion

Structural characterization

The morphologies and structures of the layered silica materials prepared using the LTC approach by tuning the concentration of aqueous ammonia are shown in Fig. 1. The sample L₁ (Table 1), prepared with the lowest concentration of ammonia, consists of spherical nanoparticles of ca. 200–500 nm in size (Fig. 1a, 1a'). Almost all of the spherical particles have a hollow cavity, as shown by the contrast between the dark edge and pale center in the HRTEM image in Fig. 1a. The shells of these hollow nanospheres have a thickness of ca. 50 nm, and are composed of folded layers (Fig. 1a). Layered folds on the surface of the hollow nanospheres were also observed (Fig. 1a'). The HRTEM image in the inset in Fig. 1a shows that the shells are in fact layered, and the interlayer distance was estimated to be 3.9 nm. The layered folds observed on the shell of the hollow nanospheres can be attributed to the self-assembly of EA and CTAB to form lamellar micelles on which silica condensed during the sol–gel reaction of TEOS. EA plays an important role in the synthesis process and affects the state of aggregation of surfactant micelles, which changes from cylindrical micelles to spherical micelles to lamellar micelles. It may also form microemulsion droplets which act as a soft template for formation of the hollow structures.

Sample L₃, prepared with a higher ammonia concentration (Table 1), consists of nanoparticles of 100–150 nm in size with a trilobite-like morphology (Figs. 1b and 1b"). The contrast and



5 **Fig. 1** HRTEM images and SEM images of the samples prepared by tuning the concentration of aqueous ammonia and their morphology illustrations: a, a' and a'' (1.0 mol L⁻¹); b, b' and b'' (3.0 mol L⁻¹); c, c' and c'' (5.0 mol L⁻¹); d, d' and d'' (13.4 mol L⁻¹).

distribution of dark and pale stripes of nanoparticles (Fig. 1b) indicates that the nanoparticles self-assembled layer by layer, and the SEM image (Fig. 1b') confirms that the nanoparticle is trilobite-like and composed of nanolayers. The HRTEM image (the inset in Fig. 1b) also shows that the nanoparticles have a layered structure, and the interlayer distance is estimated to be 4.0 nm. We suggest that the increase in the concentration of aqueous ammonia resulted in corrosion of the microemulsion droplets making them smaller, and the lamellar micelles around the droplet became compressed. Beyond a certain limit, the droplet collapsed, and the lamellar micelles redispersed into the mixture and reassembled to form the trilobite-like silica nanoparticles.

On further increasing the concentration of aqueous ammonia to 5 mol L⁻¹, material L₅ with a spherical particle morphology (Fig. 1c and 1c'') was formed, with the size of these particles (about 450 nm) being larger than that of the sample L₃. The contrast and distribution of dark and pale stripes (Fig. 1c) in the spherical particles also indicate that the particle was self-assembled layer by layer, and the SEM image (Fig. 1c') shows that the spherical particle is composed of layered silica. The HRTEM image (the inset in Fig. 1c) indicates that the particle was self-assembled layer by layer and the interlayer distance is estimated to be 2.6 nm. This suggests that as the concentration of aqueous ammonia was further increased, the lamellar micelles were reassembled after the droplet collapsed and the self-assembled layered nanoparticles grew into spherical layered particles with a different interlayer distance from that in L₃.

By using concentrated aqueous ammonia (13.4 mol L⁻¹), the resulting material (sample L_{con}) had a morphology resembling

like Van Gogh's painting 'Starry Night' (Fig. 1d and 1d''). The HRTEM image (Fig. 1d) shows that the film was self-assembled layer by layer, and the HRTEM image (the inset in Fig. 1d) indicates that the distance between the layers is 2.8 nm. The SEM image (Fig. 1d') shows that the film is composed of layered silica, and some bent layers were observed in the film. The formation of this morphology can be attributed to the high concentration of aqueous ammonia consuming most of EA, which results in aggregation of the layered silica particles to form a film. The above results indicate that silica particles with different morphologies and different layer thickness can be successfully fabricated by changing the concentration of aqueous ammonia.

The nitrogen adsorption-desorption isotherms of the layered samples (Fig. 2) exhibited Type IV patterns with H3-type (type B) hysteresis loops. In H3-type hysteresis loops, the ascending and descending boundary curves are sloping and usually the desorption branch also includes a steep region at which the remaining condensate suddenly comes out of the pores as a consequence of the so-called tensile strength effect. Parallel plate structures with slit-shaped pores typically give rise to this type of hysteresis loop, with the ascending boundary curve of the isotherm following a trajectory similar to that obtained with nonporous adsorbents but without converging to any limiting adsorption value.³⁷ Therefore the nitrogen adsorption-desorption isotherms in Fig. 2 suggest that the silica samples are layered materials with slit-shaped pores, which is consistent with the HRTEM and SEM observations. The physicochemical properties are listed in Table 1. For sample L₁, a steep increase in nitrogen uptake occurs at P/P₀ of 0.8–1.0, suggesting the presence of

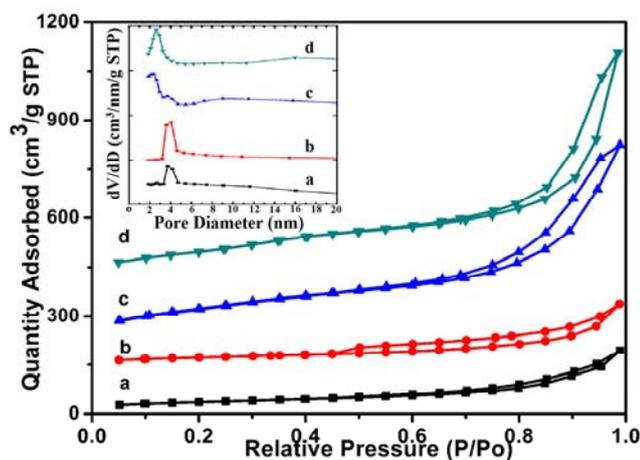


Fig. 2 Nitrogen adsorption-desorption isotherms and pore size distributions (inset) of the samples: (a) L_1 , (b) L_3 , (c) L_5 , and (d) L_{con} .

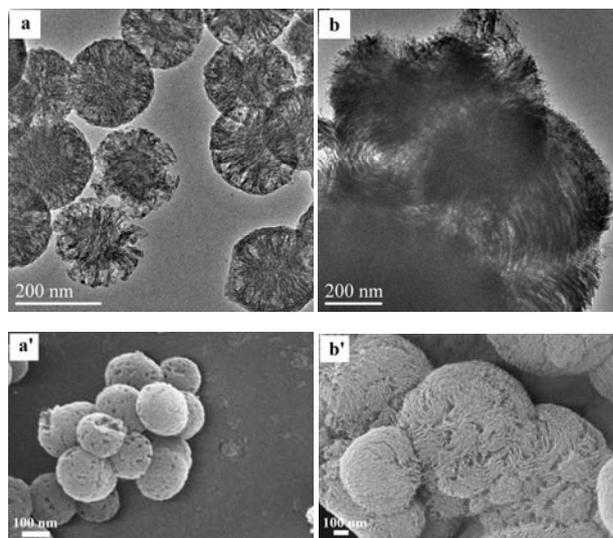


Fig. 3 HRTEM images and SEM images of the transition-state samples: (a, a') L_4 ; (b, b') L_7 .

textural (disordered) porosity, or the presence of slit-shaped pores, and the desorption branch of the sample has an extended slow decline. This suggests that sample L_1 has narrow slit-shaped pores, but that these pores are not uniform. The slit-shaped pores are about 4.0 nm in width as calculated by the Barrett-Joyner-Halenda (BJH) method (inset of Fig. 2a). For the sample L_3 , a large H3-type hysteresis loop occurs in the P/P_0 range of 0.5–1.0 and a steep decline in nitrogen desorption occurs at P/P_0 of 0.5–0.45 (Fig. 2b), which is characteristic of uniform slit-shaped pores. The pore width of sample L_3 is about 3.9 nm (inset of Fig. 2b). Samples L_5 and L_{con} have similar nitrogen sorption isotherms, indicating that they have similar pore structures. Figs. 2c and 2d show that a steep increase in nitrogen uptake occurs at P/P_0 of 0.9–1.0 and the desorption curves have an extended slow decline at P/P_0 of 1.0–0.7, suggesting the presence of irregular slit-shaped pores. The widths of the narrow slit-like pores of L_5 and L_{con} (insets of Fig. 2c and 2d) are about 2.6 nm and 2.8 nm, respectively. These slit-like pores are not uniform and smaller than those of L_3 . The Brunauer–Emmett–Teller (BET) specific surface areas and the total pore volumes of these layered samples are also shown in Table 1. The conclusions from the nitrogen adsorption–desorption measurements are in broad agreement with the SEM and HRTEM observations. In the LTC method, the liquid template became increasingly corroded as the concentration of ammonia was raised and the droplet eventually collapsed, resulting in the formation of layered silica materials with different morphologies. The diameter of the narrow slit-like pores depends on the interlayer spacing in the lamellar micelles CTAB, which in turn is affected by the presence of EA as a swelling agent.

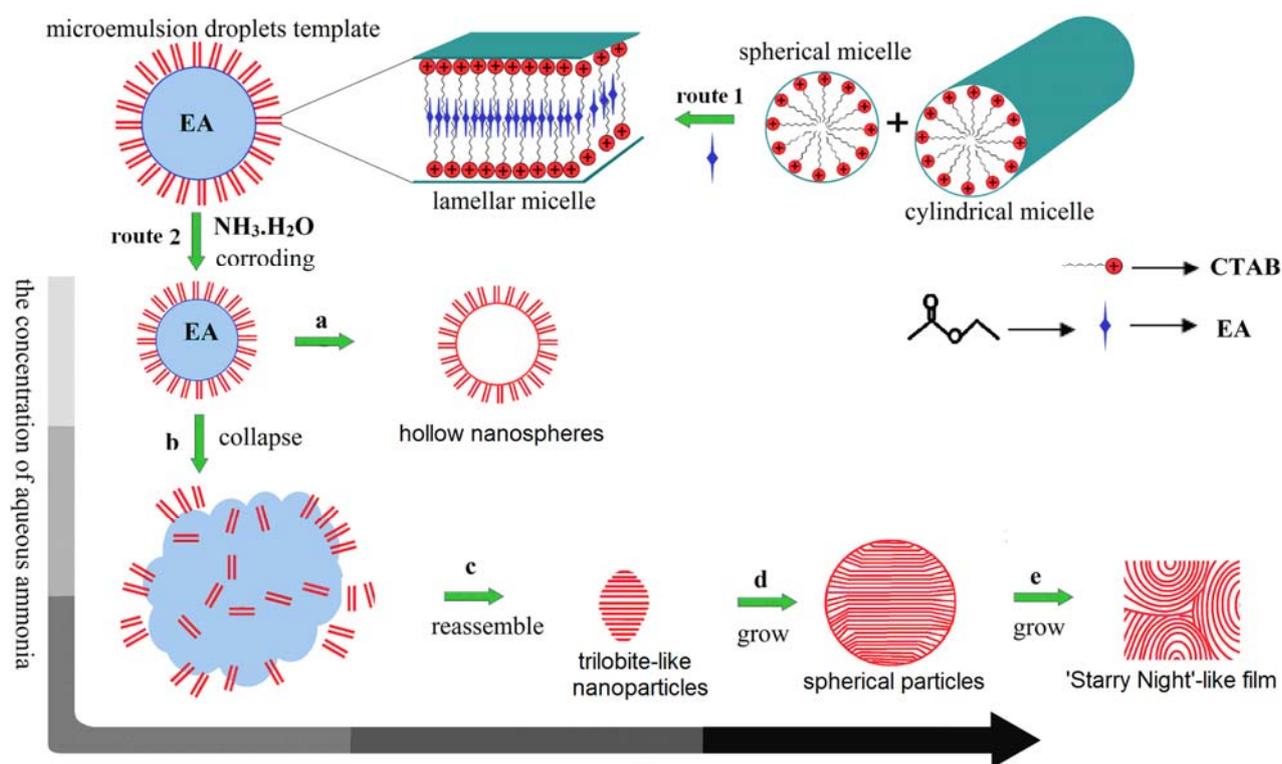
Intermediate morphologies of layered silica

To further investigate the role of the concentration of aqueous ammonia in the evolution of the morphology from trilobite-like nanoparticles to the 'Starry Night'-like film, syntheses with two intermediate concentrations of aqueous ammonia (4.0 mol L^{-1} and 7.0 mol L^{-1}) were carried out. The corresponding silica samples are denoted L_4 and L_7 , respectively. As shown in Fig. 3, L_4 consists of nanospheres of ca. 150–200 nm in size. The HRTEM (Fig. 3a) and SEM (Fig. 3a') images show that the particles had an intermediate morphology between those of

samples L_3 and L_5 , consisting of a trilobite-like particle inside a hollow sphere. This confirms that the concentration of the aqueous ammonia controls the evolution of the sample morphology. Comparison of Fig. 3b and Fig. 1c shows that L_7 possesses a layered structure and the particle size is larger than that of sample L_5 . The corresponding SEM image (Fig. 3b') shows that the particles are different from sample L_5 and possess a layered structure. Furthermore, this morphology was intermediate between the spherical particles and 'the Starry Night'-like film, again confirming the way in which the increasing concentration of aqueous ammonia controls the evolution of the particle morphology.

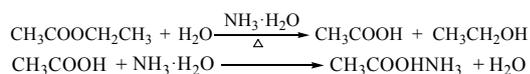
Mechanism of the LTC method

The above results clearly show that layered silica materials with different morphologies can be successfully fabricated using the LTC method. The morphology and nanolayer thickness can be controlled by tuning the concentration of aqueous ammonia. We propose a mechanism shown in Scheme 1 to explain the formation of lamellar micelles and the basis of the LTC approach for preparing layered silicas with various morphologies. When EA was added to the solution of CTAB and water, cylindrical micelles and microemulsion droplets formed. It has been shown that cylindrical micelles and spherical micelles are converted into lamellar micelles in the presence of EA as a swelling agent.^{35,36} EA molecules are hydrophobic, like octane which is often used in O/W mixtures, and can enter into the cylindrical micelle and spherical micelles, and change the state of aggregation of CTAB micelles. Although EA and octane are both hydrophobic molecules, their polarity and molecular structure are different, so that whereas the CTAB molecules form spherical single micelles in the presence of octane³⁶, they form lamellar micelles after addition of EA (Scheme 1, route 1). The remainder of the EA molecules formed microemulsion droplets, and the lamellar micelles gathered at the surface of the droplets to form the microemulsion droplet templates. When aqueous ammonia was added, the EA molecules were hydrolyzed in the resulting alkaline environment, which selectively corroded the microemulsion template in the O/W system. The hydrolysis



Scheme 1 Schematic illustration of the formation of lamellar micelles (route 1) and the LTC approach for preparing layered silica with different morphologies (route 2).

5 reaction can be formulated as follows:



As the hydrolysis products CH₃COONH₄ and ethanol are readily soluble in water, the microemulsion droplet templates become
 10 corroded (Scheme 1). The microemulsion droplets were not severely corroded at low concentration of aqueous ammonia (1.0 mol L⁻¹), and the droplets did not collapse. When the silica precursor (TEOS) was added it underwent hydrolysis by ammonia, followed by assembly of the resulting negatively
 15 charged silicate anions on the cationic surface of the lamellar micelles. Finally, condensation of self-assembled silicate anions led to the formation of hollow silica nanospheres (Scheme 1a, corresponding to Fig. 1a). On increasing the concentration of aqueous ammonia to 3.0 mol L⁻¹, more EA molecules in the
 20 microemulsion droplets become hydrolyzed, which results in the droplet becoming smaller and smaller. Therefore the space available to the lamellar micelles gathered on the microemulsion droplets becomes compressed, and when the extent of corrosion reaches a limiting value, collapse of the microemulsion droplet template occurred (Scheme 1b). The lamellar micelles
 25 redispersed into the reaction mixtures, and the liquid template disappeared. The remaining unhydrolyzed EA played the role of separating the lamellar micelles, which therefore only reassembled in small areas. After adding TEOS, condensation of the self-assembled silicate anions led to the formation of layered
 30 trilobite-like nanoparticles (Scheme 1c, corresponding to Fig. 1b). When the concentration of aqueous ammonia was increased to 5

mol L⁻¹, the microemulsion droplet template became severely corroded and readily collapsed. The lamellar micelles redispersed
 35 into the mixture, and as the concentration of unhydrolyzed EA was relatively low, the lamellar micelles tended to gather into bigger aggregates. After adding TEOS, condensation of the self-assembled silicate anions on the lamellar micelles resulted in aggregation leading to larger layered spherical particles (Scheme
 40 1d, corresponding to Fig. 1c). Finally, when concentrated aqueous ammonia was added, a layered film was obtained (Scheme 1e, corresponding to Fig. 1d). Concentrated aqueous ammonia consumed the most of EA molecules and the lamellar micelles readily aggregate to form large films, which eventually
 45 results in the formation of the 'Starry Night'-like film. When EA acts as a swelling agent and enters into the lamellar micelles, it is protected from hydrolysis by the surfactant molecules and the lamellar micelles are not destroyed by addition of excess ammonia. Our results clearly show that the presence of
 50 hydrophobic molecules like EA leads to the formation of particles with a layered structure instead of the conventional ordered mesostructures. Interestingly, we found that using other esters like butyl acetate in place of EA in the LTC method also afforded similar morphologies of layered silica (see Fig. S1†).

55 Conclusions

A novel LTC method has been successfully developed to synthesize layered silica materials with a variety of morphologies. Lamellar micelles and microemulsion droplets are formed in reaction mixtures containing EA, CTAB and water. EA
 60 hydrolyzed on addition of aqueous ammonia and the liquid

template became corroded, which resulted in collapse of the template droplets. By tuning the concentration of aqueous ammonia, morphological evolution of the layered silica materials was observed from hollow nanospheres at low concentrations of ammonia to trilobite-like nanoparticles, to spherical particles and finally to a 'Starry Night'-like film with concentrated ammonia solution, with a concomitant change in layer thickness (in the range 2.6–4.5 nm). The presence of the organic solvent EA has been shown to be the key to obtaining layered structures rather than the conventional ordered mesostructures generally observed in O/W template syntheses. Our methodology provides a simple and novel way to fabricate a variety of building blocks for assembling nanomaterials with novel structure and functionality. The resulting layered silica materials with different morphologies may have a variety of potential applications. For example, the hollow spherical layered silica particles can be used as a drug delivery carrier,^{36,38} the high surface area and abundance of surface hydroxyl groups in the layered silica materials suggests they may find application as catalysts and catalyst supports,^{39,40} and the presence of three-dimensional channels and lamellar spaces such as those found in the layered silica materials has been suggested to give rise to applications in the areas of ionic conductivity and exchange.⁴¹

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Notes and references

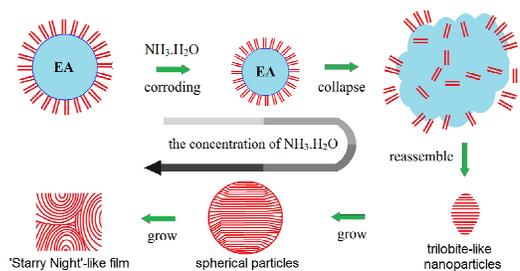
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