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ARTICLE TYPE

# A simple ternary nonionic templating system for preparation of complex hierarchically meso-mesoporous silicas with 3D interconnected large mesopores†

Wei Wang,<sup>\*,a</sup> Huan Qi,<sup>b</sup> Haibo Long,<sup>b</sup> Xiaoyang Wang,<sup>b</sup> Hongqiang Ru<sup>b,\*</sup><sup>5</sup> Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

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This work for the first time demonstrated that hierarchically meso-mesoporous silicas can be facilely prepared in a simple ternary nonionic surfactant templating system (TEOS/HCl(aq.)/P123) based on previously reported partitioned cooperative self-assembly (PCSA) principle. As a result, unique clew-like hierarchically meso-mesoporous (HMM) silica particles with the first mode of worm-like mesostructures (3D-interconnected wormholes with pore size of 7-10 nm) and the second mode of 3D-interconnected intra-particulate mesochannels (16-32 nm in sizes) can be obtained in a controllable way without resorting to complicated synthetic procedures or special additives or multi-templates. Associated with the large mesopore sizes in both modes, very large mesoporosity (up to 2.37 cm<sup>3</sup>g<sup>-1</sup>) can be achieved. Based on systematic investigations on the synthetic conditions, synthetic domains for preparation of such HMM silicas were also presented. It is proposed that the formation of two modes mesoporosities follows different mechanisms: the first mode mesoporosity results from the self-assembly between P123 and silicate, though showing to be disordered due to the partitioning effect, while the formation of the second mode mesoporosity starts from loosely packed silicate/P123 hybrid aggregates/focs formed upon the 1<sup>st</sup> addition of TEOS, and then is initiated and finished by the 2<sup>nd</sup> TEOS addition. This synthesis protocol therefore constitutes a new, simple and reliable pathway to preparing HMM silicas.

## 1. Introduction

Following the discovery of ordered mesoporous silica in 1992,<sup>1</sup> extensive efforts have been directed towards the rational design and synthesis of mesoporous materials with well-defined structural, compositional and morphological properties.<sup>2</sup> Meanwhile, there exists special interest in the development of hierarchically mesoporous (sometimes also called bimodal or multimodal mesoporous) materials due to increasing demands for materials with mesostructures on multiple length scales, *e.g.*, micro-mesoporous materials,<sup>3</sup> macro-mesoporous<sup>4</sup> and meso-mesoporous materials.<sup>5-24</sup> In particular, thanks to hierarchical meso-mesoporous (HMM) structures and thus improved accessibility to interior pore areas or facilitated mass transport in the mesopore systems, HMM silicas have found appealing application as special hard templates<sup>6</sup> or in catalysis,<sup>8</sup> bioengineering<sup>9,10</sup> and adsorption,<sup>11</sup> etc.

With respect to the synthesis of HMM silicas, employments of multi-templates are often the choice, with one template designed for one mode of mesostructures. In such complex templating approaches, different combinations of templates, like surfactant plus hard-template<sup>12,13</sup> or surfactant plus surfactant,<sup>14-20</sup> are often employed, the latter of which is especially promising for its

simplicity and directness and thus can often be performed in a one-pot synthesis process. Nevertheless, in such syntheses using multiple surfactants, selected surfactants should possess either different enough micellization behaviors to avoid forming monomodal micelles or different molecular weights for differentiated mesopore sizes.<sup>14-20</sup> For example, it has been demonstrated that the combination of nonionic surfactants with different molecular weights or molecular structures often led to monomodal rather than multimodal mesoporous silicas.<sup>14</sup> In contrast, several research groups (Antonietti, et al.,<sup>15</sup> Blin, et al.,<sup>16</sup> Rankin, et al.,<sup>17</sup>) respectively demonstrated the success in preparing HMM silicas by using fluorinated and hydrogenated surfactants mixtures (*e.g.*, non-ionic surfactants), taking advantage of their difference in chemical and physical properties in forming micelles with divergent shapes or sizes and therefore multimodal mesoporosities. Similarly, Smarsly *et al.*, paired the KLE surfactant (poly(ethylene-co-butylene)-block-poly(ethylene oxide) with cationic surfactant (*e.g.*, CTAB) to prepare HMM silicas by taking advantage of their different hydrophilic-hydrophobic contrast and therefore different interactions between hydrophobic tails.<sup>13</sup> In the cases of using surfactants with close physicochemical properties, special measures need to be taken otherwise to secure the formation of hierarchical micellar

structure for templating HMM silicas, including step-sized templating method with each templating accomplished in each step, as report by Coppens et al.<sup>18</sup> Other than employing the combination of different surfactants, supplementary porosity can also be introduced under the assistance of post-treatments<sup>21</sup> or addition of additives.<sup>22</sup> Therefore, in order to harvest HMM structures, conventional templating approaches for monomodal mesoporous silicas necessitate some changes, in most cases into more complicated ones.

Additionally, there are some characteristics associated with HMM silicas derived from above mentioned templating approaches. Firstly, if the design of HMM structures relies on scheming selection of complex templates, the pore sizes will be limited to sizes of hydrophobic segments of commonly available surfactants:<sup>14-20</sup> the smaller pores are normally less than 7nm, and larger pore sizes are still rather small (<20 nm or less) due to the limits in molecular weights. Secondly, larger pores often result from the inter-particle pores,<sup>6,7,10,19,22c,23</sup> which are often less controllable. However, large pore size in HMM silicas can further broaden the application scope of such materials by accommodating large guest species, such as enzymes, cells, etc.<sup>8,9</sup> Additionally, the lack of interconnection between different modes of mesopores is often encountered, which might undermine the functioning of HMM silicas. Therefore, it is still highly desirable to develop a synthesis approach to preparing HMM silica with interconnected large mesopores (for each mode) and preferentially in a simple and facile one-pot synthesis approach.

After examination of current synthetic strategies for the synthesis of HMM silicas, it can be found that most efforts were devoted to the design of suitable combination of multi-templates, while far less attention was paid to the tune or adjustment to the inorganic building species, *i.e.*, silicate species, and their sol-gel hydrolysis/condensation reactions. Here comes the question, whether or not the control on sol-gel reactions of inorganic silica species, especially in the presence of surfactant template molecules, can be used to prepare and manipulate HMM silicas? Our recent works demonstrated that by partitioning the addition of inorganic precursor (sodium silicate) *via* a partitioned cooperative self-assembly (PCSA) principle, the mesostructures of SBA-15s can be facilely tailored, so can for the SBA-15s with plugs or constrictions in the mesochannels.<sup>24,25</sup> Moreover, by combining such PCSA principle with well-known organic pore swelling strategy, unique bimodal meso-mesoporous cellular foams can be handily obtained.<sup>26</sup> In the PCSA process, the addition of the sodium silicate was partitioned into two parts, with the 2<sup>nd</sup> part added some interval time after the 1<sup>st</sup> one, with the following synthesis procedures actually the same as those for conventional method for SBA-15. Such modification to the synthesis procedure, though 'simple', can allow flexible tune of silicate/surfactant hybrid interfaces by controlling the sol-gel reactions of silicates, and therefore bestow us an alternative to manipulating mesostructures of mesoporous silicas. These works motivated us to further explore the possibility of employing the PCSA principle to design and synthesize HMM silicas.

In this work, based on previously reported PCSA principle, it is for the first time demonstrated that tunable HMM silicas can be

prepared in a simple ternary nonionic surfactant templating system (TEOS/HCl(aq.)/P123) using tetraethoxysilane (TEOS) as precursor. In such system, neither additives nor multi-synthetic steps nor unconventional synthesis conditions were necessary except simply partitioning the addition of TEOS into the acidified P123 aqueous solutions. Such synthesis approach featured by simple synthesis compositions, facile synthesis procedure and high efficacy in mesostructural modulation sheds new light on the synthesis of HMM silicas and could further promote their applications. Specifically, three issues will be addressed in this work:

(1)What kind of HMM structure can be prepared *via* our approach?

(2)What are the synthesis domains or under what conditions HMM structures result?

(3)What is the possible formation mechanism of such HMM structures?

## 2. Experimental

**2.1 Chemicals.** The concentrated HCl (37 wt %, designated as c-HCl), tetraethoxysilane (TEOS, AR) were purchased from the Sinopharm Chemical Reagent Co., Ltd. Pluronic PEO<sub>20</sub>-PPO<sub>70</sub>-PEO<sub>20</sub> (P123 with Mw = 5800) was purchased from Aldrich. All the chemicals were used as received.

**2.2 Preparation of HMM silicas.** Typically: 2.0 g P123 was dissolved in 78.0 g de-ionized (DI) water and 11.9 g c-HCl under stirring (800 rpm) at 43 °C to form a clear solution, into which 1.7 g TEOS (1<sup>st</sup> addition) was dropped. Three hours later, the rest of 2.55 g TEOS (2<sup>nd</sup> addition) was then added in the same way. Upon the completion of addition of TEOS, the mixture was stirred at the same speed for 24 hrs at 43 °C and then transferred to an autoclave lined with PTFE for hydrothermal treatment (HTT) at 100 °C for another 24 hrs statically. The white product was collected by filtration, washing and then dried at 50°C overnight, followed by calcinations at 550 °C for 4 hrs with the heating ramp of 1.5 °C/min. The mass ratio of P123:TEOS:c-HCl:H<sub>2</sub>O is 1:2.1:5.95:39. The final calcined sample was thus designated as T4-3h-6@43H5.95, where, 'T' for TEOS, '4' and '6' stand for the mass percentage of TEOS added in the 1<sup>st</sup> (40%) and 2<sup>nd</sup> addition (60%), respectively, '3h' denotes for the interval time between two additions, '@43' denotes the low synthesis temperature and 'H5.95' denotes the mass ratio of the c-HCl to P123. Other naming can be deduced by analogy. HTT conditions were fixed to be at 100 °C for 24 hrs.

**2.3 Characterization.** Powder XRD patterns at 2θ angles from 0.6° to 3° were recorded at an interval of 0.01° on a Bruker D8 diffractometer using Cu Kr radiation (40kV, 120mA). Transmission electron microscopy was performed using a FEI Tecnai G2 F20 instrument operated at 200 kV. FE-SEM images were recorded using Hitachi Scanning Electron Microscope (S4800) on samples deposited with a very thin film of gold. Nitrogen adsorption isotherms were measured at -196 °C using Tristar 3020 volumetric adsorption analyzers manufactured by Micromeritics (Norcross, GA). The specific surface area of the samples was calculated using the BET method within the relative

pressure ( $p/p^0$ ) range of 0.04 to 0.2. The pore size distributions (PSDs) were determined based on adsorption branches using the KJS method.<sup>27</sup> The total pore volume was estimated from the amount adsorbed at a  $p/p^0$  of about 0.995. The micropore volumes were evaluated using the  $\alpha_s$ -plot method with the relationship of  $\alpha_s$  with  $p/p^0$  defined by the equation:  $\alpha_s = 0.1385(60.65 / (0.03071 - \ln(p/p^0)))^{0.3968}$  [ref 28]. The  $V_{mi}$  was calculated using the standard reduced adsorption,  $\alpha_s$ , interval from about 0.8 to 1.0. The first mode mesopore volume ( $V_I$ ) is the difference between the amounts of  $N_2$  adsorbed at the end of the 1<sup>st</sup> step capillary condensation and  $V_{mi}$ , while the pore volume of the 2<sup>nd</sup> mode ( $V_{II}$ ) is the difference between the  $V_{total}$  and ( $V_{mi} + V_I$ ). An example for these calculations was given in Fig. S1 (Electronic Supplementary Information, ESI†).

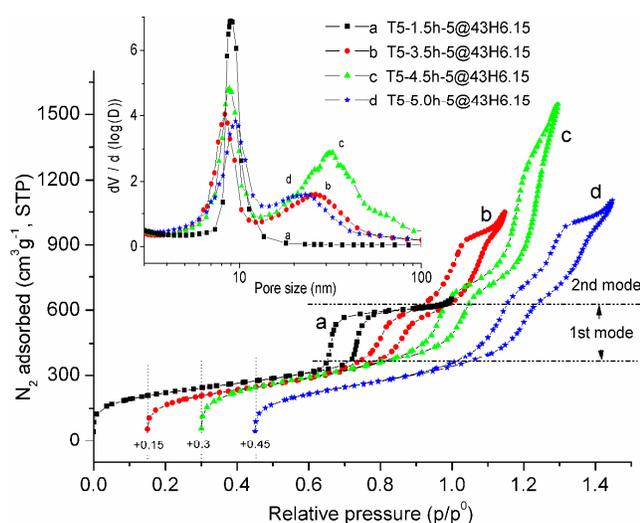


Fig. 1 Nitrogen adsorption-desorption isotherm curves and pore size distributions (Inset) of mesoporous silicas prepared with different interval times at 43°C with c-HCl to P123 mass ratio of 6.15. The capillary condensation/evaporation steps in the 2<sup>nd</sup> mode mesopores or in the 1<sup>st</sup> mode mesopores were marked above or between two dotted lines, respectively.

### 3. Results and discussion

#### 3.1 Hierarchically meso-mesoporous structures

The PCSA process itself has two variables that are adjustable in the synthesis: the addition combination and interval time. The former defines the amounts of TEOS added in two additions and the latter for time lasted between two additions. According to our previous reports on the PCSA process for preparation of SBA-15s, the first addition of silica precursor, *e.g.*, sodium silicate, should be able to induce substantial change to the silicate/P123 interface curvature but less than the amounts enough to induce prevailed condensation between the silicate species in the presence of P123 molecules.<sup>24</sup> Therefore, in order to study the influence of interval time on the mesostructures, the 1<sup>st</sup> TEOS addition was selected to be 50% of the total amounts of the TEOS (the 2<sup>nd</sup> addition is thus also 50%). We take this series of meso-silicas as an example to show what kind of HMM structures can be produced in the TEOS/HCl(aq.)/P123 ternary templating system based on PCSA principle.

Fig. 1 shows the  $N_2$  sorption results of mesoporous silicas prepared with varying interval times but fixed addition combinations of TEOS (T5-xh-5@43H6.15). Mesoporous silicas prepared with interval time of 1.5 hrs ( $x=1.5$  hrs, *i.e.*, T5-1.5h-5@43H6.15) shows to possess type-IV adsorption-desorption isotherm curve and H1 hysteresis loop, suggesting the formation of cylindrical mesopores. When the interval time was extended up to 3.5 hrs or longer, the adsorption-desorption isotherm curves show an interesting feature: other than the capillary condensation/evaporation step at low  $p/p^0$ , extra capillary condensation/evaporation steps (above the dotted line) at higher  $p/p^0$  become observable, corresponding to the presence of hierarchical/bimodal mesopore systems, which can also be seen from the PSDs shown in Fig. 1 (inset). The lower steps ( $p/p^0 \sim 0.75$ ) arise from  $N_2$  capillary condensation in mesopores typically templated by the P123 surfactant under similar conditions, which will be denoted as the 1<sup>st</sup> mode mesopores with typical KJS pore size of 8-10 nm.<sup>24,29</sup> The higher steps are attributed to the formation of the 2<sup>nd</sup> mode mesopores with pore size of 23-32 nm (Fig. 1, inset). The probable distributed 2<sup>nd</sup> mode mesopore size in a broadened PSD is as large as 32 nm for T5-4.5h-5@43H6.15, which shows the most prominent HMM structure prepared with the interval time of 4.5 hrs. Further increase in the interval time (T5-5h-5@43H6.15) does not lead to an improvement in the 2<sup>nd</sup> mode mesoporosity.

According to  $N_2$  sorption results summarized in Table S1 (ESI†, Note: this table is too large to be included in the manuscript), HMM silicas with high surface areas in excessive of 700  $m^2 g^{-1}$  and high pore volumes for the 1<sup>st</sup> mode ( $V_I=0.9-1.1$   $cm^3 g^{-1}$ ) plus the 2<sup>nd</sup> modes if present ( $V_{II}=0.7-1.34$   $cm^3 g^{-1}$ ) were obtained under such conditions. Here, a letter of 'Φ' was introduced and defined to be the ratio of  $V_{II}$  to  $V_I$  to index the hierarchical degree of HMM structures obtained. The high Φ value corresponds to high  $V_{II}$  with respect to the  $V_I$ , the latter of which is rather stable because  $V_I$  arises from P123 templating (Table S1, ESI†). The T5-4.5h-5@43H6.15 shows an extraordinary hierarchically meso-mesoporosity,  $V_{II}$  and Φ reaching 1.34  $cm^3 g^{-1}$  (total mesopore volume of 2.37  $cm^3 g^{-1}$ ) and 1.3, respectively. Such high mesopore volume reported in this work is due to the formation of large mesopores in both modes. In a few works that reported higher total pore volumes up to 3.5  $cm^3 g^{-1}$  by Sun *et al.*,<sup>18</sup> or Ikari *et al.*,<sup>7c</sup> or 2.54  $cm^3 g^{-1}$  by Haskouri *et al.*,<sup>7a</sup> either two-step synthesis procedure<sup>18</sup> or major contribution (over 50%) from the interparticle pores<sup>7a,7c</sup> is different from those reported in this work.

In order to examine the meso-orderings of resultant mesostructures, low-angle XRD patterns were collected and shown in Fig. 2. Except that T5-1.5h-5@43H6.15 shows a 2D hexagonally ordered mesostructures, other low-angle XRD patterns show only one broad low-angle XRD peak, which gets less resolved with the increase in the interval time from 3.5h to 5.0 h, indicative of the lack of long range-ordering. As far as the disordering in the 1<sup>st</sup> mode mesostructures is concerned, the mesostructures reported here resemble those of MSU-type meso-silicas with 3D interconnected wormhole-like mesopore arrangements.<sup>30</sup>

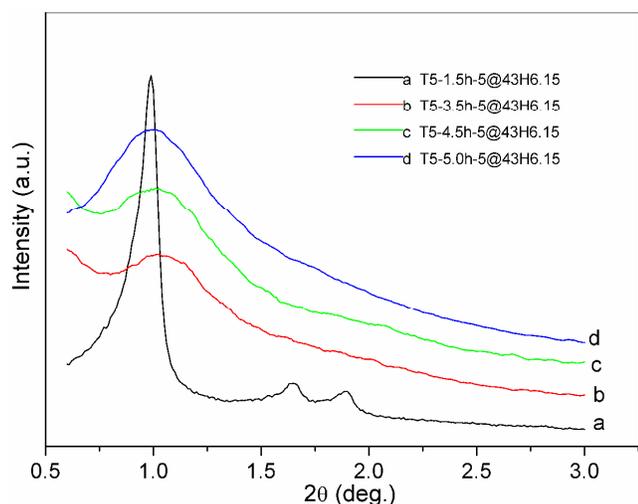


Fig. 2 Corresponding low-angle XRD patterns and calculated  $d_{100}$  spacings (inset table) of meso-silicas shown in Fig. 1.

It is known that the formation of ordered SBA-15 mesophases normally experiences different phases: the transformation of spherical micelles into cylindrical ones upon the addition of silica precursor, formation of largely worm-like mesophase with ongoing condensation and final the re-organization from worm-like mesophases into hexagonal ordered mesophases.<sup>29</sup> In the PCSA process based on TEOS, upon the 1<sup>st</sup> addition of TEOS, the silicate species thus produced will interact with the hydrophilic corona of P123 micelles to form silicate/P123 intermediate structures, which cannot proceed to produce ordered mesophases *via* prevailed condensation reactions due to the lack of enough inorganic silicate species until the 2<sup>nd</sup> addition of TEOS. The progressively rigidified silicate/P123 intermediate structures due to the on-going condensation reaction of silicate during the interval time to a much extent hinders the re-organization process and therefore impair the orderings of resultant meso-silicas. These explain the observation of broadened low-angle XRD reflection peaks shown in Fig. 2 and formation of disordered mesostructures in the 1<sup>st</sup> mode with long interval times.

Fig. 3 shows the TEM and FE-SEM images of T5-4.5h-5@43H6.15. TEM image directly shows the presence of disordered 1<sup>st</sup> mode mesopores and small lighter areas uniformly distributed in the particle as well, the latter of which can be assigned to presence of the 2<sup>nd</sup> mode mesopores. The discernible 2<sup>nd</sup> mode mesopore size on the TEM image (only in thin area or at particle edges) are in the range of 20–28 nm, close to those estimated from the nitrogen sorption results (Fig. 1, inset) if the overestimation of the pore sizes over 9 nm by KJS method<sup>31</sup> and slight underestimation by TEM were taken into consideration. FE-SEM image in Fig. 3 (inset) shows even clearer the presence of the HMM structures. The particle of T5-4.5h-5@43H6.15 is more like a ‘fluffy clew’ knitted by ‘yarns’. The sizes of voids surrounded by the ‘yarns’ in FE-SEM, which were confirmed to be mesochannels in TEM, are also consistent with those discerned by the TEM (Fig. 3). In contrast, monomodal meso-silica shows only smooth surfaces (Fig. S2, ESI<sup>†</sup>). In

combination with the TEM results, such ‘fluffy clew’ features can undoubtedly be attributed to the presence of 3-dimensionally large interconnected mesochannels (the 2<sup>nd</sup> mode mesopores), which are homogeneously distributed throughout the spheroidal particle. And, the ‘yarns’ contain the 1<sup>st</sup> mode mesopores. According to our knowledge, such unique HMM structures integrating large mesopores in both modes and high interconnectivity between them have not been reported so far.<sup>9–24</sup>

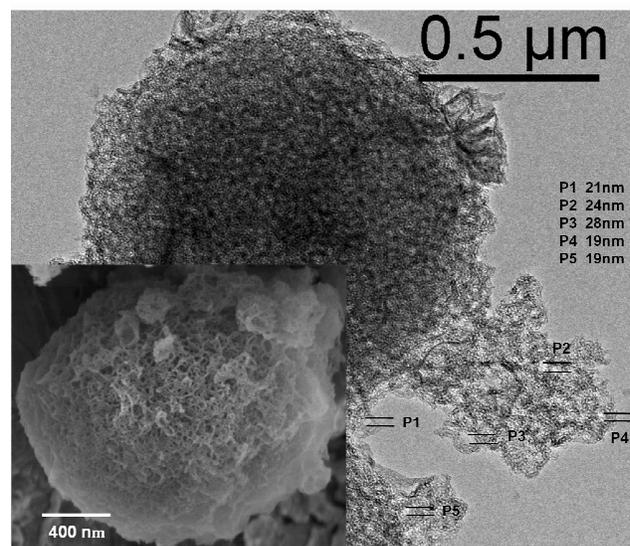


Fig. 3 Representative TEM image of T5-4.5h-5@43H6.15. The pore sizes of discernible large 2<sup>nd</sup> mode mesopores in thin area were also marked and listed. An inset (bottom left) shows the FE-SEM image of a particle.

The obtained hierarchically meso-mesoporous structures are thus confirmed to be the uniformly mixed mesostructures of 3-D interconnected 2<sup>nd</sup> mode large mesopores (23–32 nm by  $N_2$  sorption) and 3-D interconnected small wormholes (8–10 nm) for these series of HMM silicas. The connection between two modes of mesopores are also foreseeable, considering the short channels (~100 nm or less, Fig.S3, ESI<sup>†</sup>) of the 1<sup>st</sup> mode mesopores, interconnected nature and uniform distributions throughout the micron-sized particles for each mode mesopores. In particular, the preparations of these HMM silicas were realized in the simple ternary templating system, *i.e.*, TEOS/HCl(aq.)/P123, without using additives or multi-templates or post-treatments. Other than partitioned addition of TEOS to the acidified P123 solution, all other synthetic procedures are the same as those of SBA-15.<sup>24,32</sup> This opens a new route to the preparation of HMM silicas with distinct hierarchy in two modes of large interconnected mesopores.

### 3.2 Synthetic conditions and domains

In above series of mesoporous silicas (T5-xh-5@43H6.15), only the interval times were varied, during which the silicate hydrolysis/condensation reactions in the presence of P123 only took place. This strongly suggests that by tuning the conditions that influence the hydrolysis/condensation reaction of silicate and thus the intermediate silicate/P123 hybrid structures before the 2<sup>nd</sup> addition of TEOS, we can facilely manipulate HMM

structures in the final silica products. In such simple templating system based on PCSA principle, four variables that have influence the hydrolysis/condensation reaction of silicate upon the 1<sup>st</sup> addition of TEOS will be considered, including the addition combinations, interval time, acidity and synthesis temperature. These synthetic conditions will be systematically investigated to give a full profile of how the HMM structure are influenced and controlled; eventually synthetic domains can be pictured.

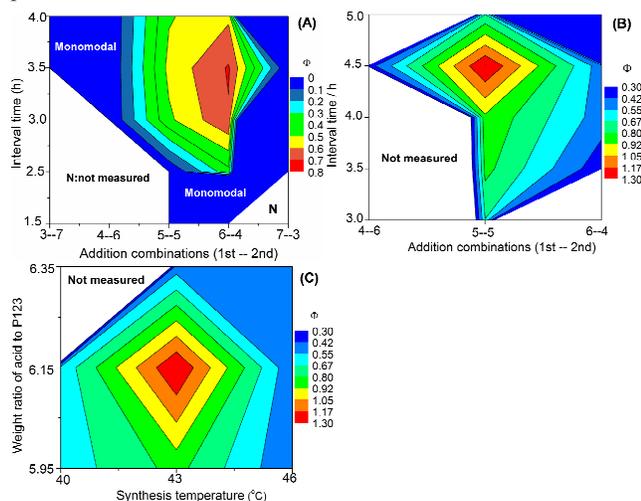


Fig. 4 Synthetic domains for HMM silicas prepared based on PCSA principle with different addition combinations and interval times at fixed synthesis temperature (43 °C) with mass ratios of c-HCl to P123 of (A) 5.95 and (B) 6.15 c-HCl, with respect to 1 P123: 2.1 TEOS: 39 H<sub>2</sub>O in synthesis compositions. (C) Synthetic domains for HMM silicas under different acidic conditions and low synthesis temperatures for a certain partitioning condition T5-4.5h-5. The plots of  $\Phi$  ( $V_{II} : V_I$ ) were plotted against synthetic conditions to index the degree of hierarchy in two modes mesoporosities.

**Interval time and addition combinations.** It has already been shown in Fig. 1 that the interval time plays a key role in producing HMM structures at a fixed addition combination of TEOS (T5-xh-5@43H6.15) at certain synthesis temperature and mass ratios of c-HCl to P123. In Fig. 4A & 4B, the synthetic domains were drawn by varying both the interval time and addition combinations at the same time at varying mass ratios of c-HCl to P123. It can be seen that both the addition combinations and interval time need to be taken into consideration in order to achieve as high as possible the 2<sup>nd</sup> mode mesoporosity relative to the 1<sup>st</sup> mode mesoporosity templated by the P123. With c-HCl of 5.95 with respect to 1 P123: 2.1 TEOS: 39 H<sub>2</sub>O, when the 1<sup>st</sup> addition of TEOS exceeds 70% or less than 40% of the total mass of TEOS, SBA-15s with monomodal mesostructures or very limited 2<sup>nd</sup> mode mesoporosity will result, irrespectively of interval time. Furthermore, in order to prepare the mesoporous silicas with prominent hierarchical mesostructures ( $\Phi > 0.5$ , yellow or red areas in Fig. 4A), the first addition of the TEOS should better fall in the range of 50-60% of the total mass of TEOS, and also the interval time should fall in the range of 3-4 hrs under the synthetic conditions specified. These again confirm

the key role of partitioning conditions on the evolution of HMM structures. Such results can also be seen from the corresponding N<sub>2</sub> sorption results and pore size distributions and low-angle XRD results shown in Fig. 5A and Fig. S4-S6 (ESI<sup>†</sup>). Under such selections in both addition combination and interval time, HMM structure with high  $\Phi$  values over 0.5 can be obtained (TS5-3.5h-5@43H5.95,  $\Phi=0.53$ ), where distinct two-step capillary condensation/desorption characteristics and two pore size distributions can be observed. Higher  $\Phi$  value is associated with more distinct two step capillary condensation/evaporation in isotherm curves and higher 2<sup>nd</sup> mode mesoporosity and roughly larger 2<sup>nd</sup> mode mesopore sizes (16-27 nm for this series).

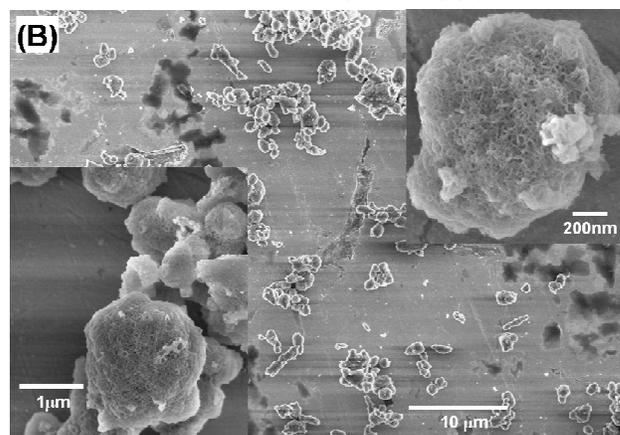
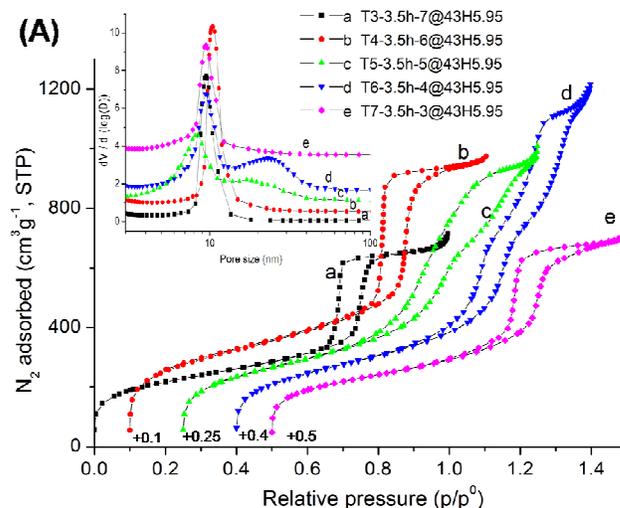


Fig. 5 (A) N<sub>2</sub> adsorption-desorption isotherm curves and pore size distributions (inset) of mesoporous silica prepared with different addition combinations but fixed interval time of 3.5 hrs. The isotherm curves of (b-d) in (A) were shifted horizontally for clarity. (B) FE-SEM image of T6-3.5h-5@43H5.95, the insets in (B) show the FE-SEM images taken at different magnifications.

In the cases with low acid (c-HCl:P123=5.95), the highest  $V_{II}$  of 0.77 and  $\Phi$  of 0.71 can be observed for TS6-3.5h-4@43H5.95. Similar 'fluffy clew' particle morphology and HMM structures can be seen in Fig. 5B and TEM images in Fig. S7 (ESI<sup>†</sup>). Under condition with higher amounts of acid (c-HCl:P123=6.15), we observed the similar trend (Fig. 4B): HMM silicas can be prepared with the roughly the same addition combinations and

interval times. However, the highest  $V_{II}$  ( $1.34 \text{ cm}^3\text{g}^{-1}$ ) and  $\Phi$  of 1.3 was observed for T5-4.5h-5@43H6.15. Therefore, though the addition combinations and interval times fall in a similar domain, in order to prepare HMM silica with high  $\Phi$  values, fine tuning of them is also needed to achieve the desired (e.g., the highest one) 2<sup>nd</sup> mode mesoporosity with respect to specific acidic and temperature conditions. This is because that though amounts of silicate species available for hydrolysis/condensation reactions can be controlled by the addition combination; they are not immune from the influence of other synthesis variables, such as interval time, acidity and temperature.

**Synthetic Acidity and Temperature.** Fig. 4C shows the dependence of HMM structures in terms of  $\Phi$  on different acidic conditions and synthesis temperatures for a certain partitioning condition T5-4.5-5. It can be seen that as long as the syntheses of HMM silicas are performed under the conditions with the temperature and acid falling in the range of 40-46 degree Celsius and 5.95-6.35, respectively, satisfactorily hierarchically mesostructures with the high  $\Phi$  over 0.5 can always be achieved based on PCSA principle using TEOS as precursor.

These observations on the influence of partitioning conditions and synthetic conditions on HMM structures indicate that there are some synthetic domains for the preparation of HMM silicas, which further validate two facts: (1) the formation of the HMM silicas depends on and thus can be reliably controlled by tuning the synthetic conditions investigated in this work. The mappings presented in Fig. 4 thus give a systematic view on the landscape of the 2<sup>nd</sup> mode mesoporosity in HMM structures thus derived with respect to synthetic conditions, which can be followed in preparation of desirable HMM silicas. (2) The sol-gel reaction of TEOS in the presence of P123 and resultant silicate/P123 intermediate structures play a key role in the formation of HMM structures, which will be discussed in below Section.

### 3.3 Formation mechanism of HMM structures

The presence of some synthetic domains for preparation of HMM silicas based on the PCSA principle suggests that the synthetic approach for HMM silicas is not a coincidence but a reproducible and controllable synthetic protocol, and that there must be an underlying mechanism to dictate. In the synthetic approach for HMM silicas, the partitioned addition of the TEOS not only disrupts the normal self-assembly of silicate species with P123, but also leads to the formation of 2<sup>nd</sup> mode of mesopore system. The formation mechanism of such HMM structures will show some new features compared to that observed for conventional SBA-15. Now, about the formation of HMM structure ('fluffy clews'), it is known for sure that the 1<sup>st</sup> mode of the mesopore system (the 'yarns') is formed through the self-assembly, though perturbed by the partitioned addition of silica precursor TEOS, between the P123 and silicate species. This can also easily be told from the pore sizes, which are in the range of 7-10 nm, typically value observed for the SBA-15s prepared using P123 as structural directing agent under similar conditions.<sup>24,32</sup>

The only question that was left open is the formation mechanism of the 2<sup>nd</sup> mode mesopore system (16□32 nm). We propose that the formation of the 2<sup>nd</sup> mode 3-D interconnected

intra-particulate mesopore starts from loosely packed silicate/P123 hybrid aggregates/flocs formed upon the 1<sup>st</sup> addition of TEOS, and then was initiated and finished by the 2<sup>nd</sup> TEOS addition. The evolution path and corresponding evidence were shown in left column and right column in Fig. 6, respectively.

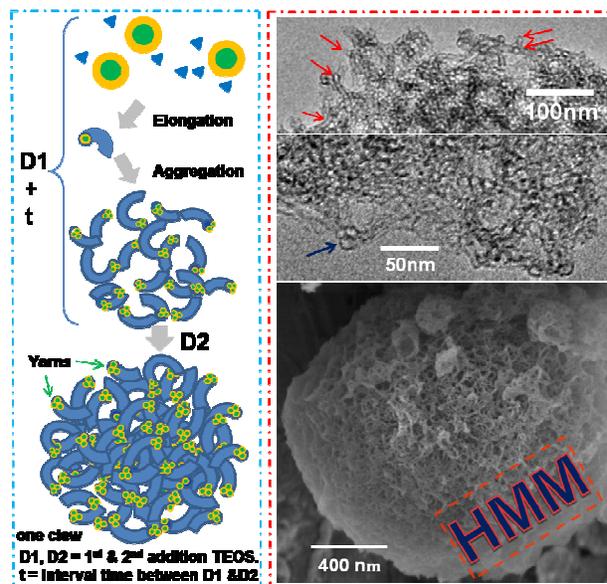


Fig. 6 Schematic of the evolution of HMM structures, from the coating of silicate on P123 micelles leading to the elongation of the micelles, and then the formation of aggregates/flocs, which experience the shrinkage and consolidation upon the 2<sup>nd</sup> addition of TEOS (left column). The direct TEM and FE-SEM evidences showing the 'knitting' of mesoporous 'yarns' made of one (arrows in the top TEM) or several (arrows in the middle TEM) elongated pore channels (elongated micelles before pore evacuation) in the right column.

The formation of ordered mesophase of conventional SBA-15 experiences several consecutive stages: the silica coating on P123 spherical micelles and appearance of elongated ones, which cluster to form aggregates (or called 'flocs') with to a great degree disordered meso-domains and eventually re-organize into ordered hexagonal mesophases. These flocs will transform into solid particles upon further condensation.<sup>29</sup> In the synthesis of HMM silicas based on PCSA principle, taking T5-4.5h-5@43H6.15 as example, the TEOS added in the 1<sup>st</sup> addition and its derivatives upon hydrolysis/condensation will also interact with and then form a coating on the hydrophilic coronas of P123 micelles, inducing the transformation of spherical micelles into elongated one. The elongated micelles, promoted by the progressive condensation reaction between coated silicate during the interval time, form silicate/P123 hybrid aggregates/flocs, as schematically shown in Fig. 6, left column. This process was confirmed by the experimental observation: the synthesis mixture became increasingly viscous and appeared to be translucent, not turbid with precipitates, in 4.5 hrs after the 1<sup>st</sup> addition of TEOS but prior to the 2<sup>nd</sup> addition of TEOS. However, such flocs are different from the ones observed in the conventional synthesis of SBA-15 in at least two aspects: (1) in these flocs, the poly-

condensation reaction did not prevail extensively compared with that observed in conventional SBA-15, because such translucent mixture can stand for quite long time (up to 24 hrs) without precipitating out, even after HTT for 24 hrs. This is mainly attributed to the restricted condensation reactions by limited (1/2 the normal dosage) amounts of silicate species. In contrast, it takes less than 30 mins to observe the precipitation by unaided eyes after the translucent 'floc' stage where TEOS is in abundance.<sup>29</sup> (2) In such flocs/aggregates full of 'properly' condensed silicate/P123 micelles, the packing is not as compact as in the case of conventional SBA-15. In the flocs at this stage (T5-4.5h) there probably exist significant amounts of the solvents (*i.e.*, H<sub>2</sub>O and ethanol). This was supported by often observed decreases in the 2<sup>nd</sup> mode mesopore volume with the increase in the synthesis temperature, acidity and interval time, which all promote the condensation of silicate species in silicate/P123 hybrid aggregates and thus progressive densification. For example, as can be seen from Table S1 (ESI<sup>†</sup>), the V<sub>II</sub> of 1.31 cm<sup>3</sup>g<sup>-1</sup> for T5-4.5h-5@43H6.15 decreased to 0.69 cm<sup>3</sup>g<sup>-1</sup> for T5-5.0h-5@43H6.15 with increased interval time or to 0.49 cm<sup>3</sup>g<sup>-1</sup> for T5-4.5h-5@43H6.35 with an increase in acidity. The V<sub>II</sub> decreases from 0.77 (T6-3.5h-4@43H5.95) to 0.58 cm<sup>3</sup>g<sup>-1</sup> (T6-4.0h-4@43H5.95) with increased interval time. At higher synthesis temperatures, lower V<sub>II</sub> around 0.4 cm<sup>3</sup>g<sup>-1</sup> are obtained. Additionally, as shown in the TEM images in Fig. 6, right column, the formation of very thin 'yarns' of only one (marked by arrow in top TEM image) or a few (marked by arrows in middle TEM image) elongated silica-coated P123 micelles directly corroborated above discussion: the condensation between silica-coated micelles and their packing are restricted to a great extent. With the addition of 2<sup>nd</sup> part TEOS, the condensation reaction between silicates will prevail, leading to consolidated silicate/P123 hybrid aggregates, which precipitate out from the synthesis mixture within 2 hrs after the 2<sup>nd</sup> addition of TEOS. Following hydrothermal treatment further promotes the hydrolysis and condensation of silicate species in the framework. The 1<sup>st</sup> mode mesostructures was confirmed not to change significantly according to the low-angle XRD patterns of as-prepared TS5-4.5-5@43H6.15 before and after HTT at 100 °C (Fig.S8, ESI<sup>†</sup>). After HTT and drying, the HMM structures eventually result after pore evacuation by calcination.

#### 4. Conclusion

In this work, it is for the first time demonstrated that the preparations of HMM silicas can be performed in a simple ternary surfactant templating system (TEOS/HCl(aq.)/P123) based on previously reported partitioned cooperative self-assembly principle. Unique clew-like HMM silica particles with the first mode worm-like mesostructures (3-D interconnected wormholes with pore size of 7□10 nm) and the second mode 3-D interconnected intra-particulate mesochannels (16□32 nm) can be obtained without resorting to either complicated synthetic procedures or multi-templates or special additives. The presence of some synthesis domains allow the HMM structures can be facilely and reliably manipulated. It is proposed that the

formation of the 1<sup>st</sup> mode mesopores arises from the classic self-assembly between P123 and silicate, though perturbed by the partitioning effects, while the formation of 2<sup>nd</sup> mode mesopores results from the consolidation by the 2<sup>nd</sup> TEOS addition of loosely packed silicate/P123 hybrid aggregates/flocs formed upon the 1<sup>st</sup> addition of TEOS. It is believed that the combination of large mesopore sizes and 3D interconnectivity in both modes and very high mesoporosities up to 2.37 cm<sup>3</sup>g<sup>-1</sup> will benefit such unique HMM silicas in application demanding fast mass transport or applications involving large guest species or high loadings.

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#### Notes and references

- <sup>a</sup> Key Laboratory for Anisotropy and Texture of Materials of Ministry of Education (ATM), Northeastern University, Shenyang110819, PR China; Tel: +86-24-83680248; E-mail: wangw@atm.neu.edu.cn
- <sup>b</sup> School of Materials and Metallurgy, Northeastern University, Shenyang 110819, PR China. Tel: +86-24-83680248; E-mail: ruhq@smm.neu.edu.cn
- <sup>†</sup> Electronic Supplementary Information (ESI) available: (Table S1) Physico-properties of meso-silicas prepared. (Fig. S1) Calculation of the micropore, 1<sup>st</sup> and 2<sup>nd</sup> mode mesopore volumes via the  $\alpha_s$ -plot method. (Fig. S2) FE-SEM results of monomodal mesoporous silica. (Fig. S3) TEM images showing the presence of short channels of the 1<sup>st</sup> mode mesopores in TS5-4.5h-5@43H6.15. (Fig.S4) N<sub>2</sub> sorption and corresponding pore size distributions, low-angle XRD results of HMM silicas with varying interval times of T5-xh-5@43H5.95 series. (Fig. S5) FE-SEM image of T5-3.5h-5@43H5.95. (Fig. S6) TEM image of T5-3.5h-5@43H5.95. (Fig. S7) TEM image of T6-3.5h-4@43H5.95. (Fig.S8) Low-angle XRD patterns of as-prepared TS5-4.5h-5@43H6.15 before and after hydrothermal treatments. See DOI: 10.1039/b000000x/
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