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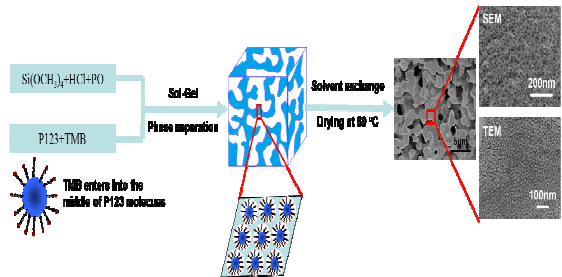
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Graphical Abstract



The uniform spherical mesopores was successfully prepared by combining the polymerization-induced phase separation with epoxide-mediated sol-gel route

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ARTICLE TYPE

Spontaneous preparation of hierarchically porous silica monoliths with uniform spherical mesopores confined in well-defined macroporous framework

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Abstract: Hierarchically porous silica monoliths with well-defined interconnected macropores and uniform spherical mesopores were spontaneously prepared by combining the polymerization-induced phase separation with epoxide-mediated sol-gel route without any complicated aging and drying and high-temperature heat treatment. The precise controlling for pore structures can be realized by using propylene oxide (PO) as the gelation mediation agent, poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) (P123) as the phase-separation inducer as well as the structure-directing agent and 1,3,5-trimethylbenzene (TMB) as the micelle-swelling agent. The as-prepared silica monolith possesses an interesting hierarchically porous structure constructed by 10 nm uniform spherical mesopores confined in macroporous framework of well-defined 1 μm macropores, and exhibits a BET surface area as high as 848 $\text{m}^2\cdot\text{g}^{-1}$. Heat treatment at 400-800 $^{\circ}\text{C}$ gradually decreases the BET surface area to 195 $\text{m}^2\cdot\text{g}^{-1}$, while most of the uniform mesoporous structure remains intact.

Keywords: Hierarchical porous structures, silica monolith; macropores, uniform mesopores, epoxide-mediated, sol-gel, phase separation

1. Introduction

Hierarchically structured porous materials, displaying multiple-level porosity integrated in a single architecture, have recently triggered extensive research because of their fascinating features such as high surface area, facilitated interface transport and advanced mass transport kinetics.¹⁻³ Compared with single-sized porous materials, hierarchically porous materials in the form of monolith have more superior properties and applications.⁴⁻¹² The incorporation of mesopores into macroporous architectures offers an alternative strategy to greatly minimise diffusion barriers and potentially enhance the distribution of active sites. Simulations suggest that in the Knudsen diffusion regime, where the reactants/products are able to enter/exit mesopores but experience attendant diffusion, such bi-modal pore structures can significantly improve active site accessibility.¹³ Porous silica with a hierarchical organized pore structure is desired for a broad variety of applications, including chromatography, sensing, controlled release, scaffolds for biomedical applications and catalysis, due to the multiple benefits that arise from each of the pore size regimes, e.g. (uniform) mesopores (2-50 nm) provide size- or shape selectivity and high specific surface area, and (interconnected) macropores (>50 nm) facilitate mass transport through the material to the active sites.

In the last few years, significant research efforts were devoted in the synthesis of hierarchically organized materials with structures that exhibit pores on different length scales, especially in preparation of hierarchical structure with uniform mesopores integrated in well defined macropores.^{14,15} As we have known, the utilization of surfactant self-assemblies to direct the silica mineralization process is the most commonly studied route towards the synthesis of highly ordered mesoporous silica.¹⁶ The general idea of using amphiphilic molecules as templates is based on the fact that such systems can simultaneously form a hybrid surfactant/silica interface and self-assemble into robust and regular superstructures. Surfactants which are commonly used in the synthesis of ordered mesoporous silica are frequently classified according to the nature of the interactions between their polar group and the hydrolyzed silica precursors. On the other hand, evaporation-induced self-assembly (EISA), micellar templating routes,¹⁷⁻²⁰ emulsion-based templating²¹⁻³⁶ and advances in the understanding of polymerization-induced phase separation as well as sol-gel processing strategies,²⁷⁻³⁵ have enabled access to a large variety of different hierarchically organized porous materials. The basis for a rational design of pore structures on multiple length scales by chemical phase separation has been developed. However, a deeper understanding is still necessary for hierarchically organized porous materials.

Despite dramatic progress in the synthesis of mesoporous or macroporous materials, the preparation of materials with well-defined macroporous monoliths and uniform or ordered mesopores still remains a challenging task. Nakanishi et.³⁶ reported an organic-inorganic hybrid gel with hierarchical macroporous structure in the system containing 1,2-bis(trimethoxysilyl)-ethane (BTME) as a Si source and P123 as a structure-directing agent. Later, they³⁷ reported that in the TMOS-based system, the integration of ordered mesopores into homogeneously accessible macroporous arrays can be achieved via the completely spontaneous chemical process in the presence of P123 and TMB. Zhong et.³⁸ synthesized hybrid monolith with hierarchically macro-mesoporous structure by a sol-gel process from the mixture of 1,4-bis(triethoxysilyl)benzene (BTEB) and tetraethoxysilane (TEOS) using poly(ethylene oxide)-block-poly(propylene oxide)-blockpoly(ethylene oxide) (P123) as structure-directing agent under acid medium. The ordered mesoporous structure is embedded in the skeleton of the well-defined interconnected macropores of the hybrid monolith. Hwang et.³⁹ reported a simple one-pot strategy for the synthesis of inorganic oxide materials with multiscale porosity, the inorganic precursor and block copolymer are co-assembled into an ordered mesostructure (microphase separation), while the in situ polymerized organic precursor forms organic-rich macrodomains (macrophase separation) around which the mesostructure grows. Calcination generates hierarchical meso/macroporous SiO₂ and TiO₂ with three-dimensionally interconnected pore networks. In all the work mentioned above, complicated aging and drying and further treatment, such as supercritical fluid extraction and high-temperature and exquisite heat treatment, were required to remove the template to acquire ideal structure, which lead to much extent negatively effects its practical application. And up to date, hierarchically organized porous materials with uniform or ordered mesopores confined in well-defined macropores have not yet to achieve the level of sophistication and well control and the purpose of fine tailoring the architecture.

In this work, we present the spontaneous preparation and characterization of pure silica monoliths having a hierarchically organized pore structures from the silica system of TMOS-HCl-PO-P123-TMB. The epoxide PO was added to mediate sol-gel transition with a milder way because of its strong nucleophilic properties and irreversible ring-opening reaction, while P123 was used as the phase separation inducer as well as structure-directing agent. Combining the polymerization-induced phase separation with epoxide-mediated sol-gel route, hierarchically porous silica monolith with well-defined interconnected macropores and uniform spherical mesopores was obtained without any complicated aging and drying and high-temperature heat treatment to remove the template agent. The pore structures with both well-defined interconnected macropores and uniform spherical mesopores show high BET surface area and superior thermal stability, and the macro- and mesoporous structure can intactly remain after heat treatment up to 800 °C. The resultant hierarchically porous silica monolith could be a promising material for a broad variety of applications.

2. Experimental part

2.1 Materials

Tetramethoxysilane (TMOS, Aldrich, 98%) and propylene oxide (PO, Aldrich, 99.5%) were used as the silica source and gelation mediation agent, respectively. Hydrochloric acid (HCl, Aladdin Ind Co. (China), 0.01 mol·L⁻¹) and ethanol (Sinopharm Chemical Reagent Co., Ltd. (China)) were the catalyst and solvent respectively. Poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide)(P123) obtained from Aldrich, with an average molecular mass of 5800, was used as the phase-separation inducer as well as the structure-directing agent, and 1,3,5-trimethylbenzene (TMB) purchased from Aladdin Ind Co. (China) was used as the micelle-swelling agent.

2.2 Preparation of hierarchically porous silica monolith.

The starting compositions for the preparation of hierarchically porous silica monolith were listed in Table 1, and the synthesis of the sample was as follows in detail. Firstly, a given amount of P123 was homogeneously dissolved in 0.01 mol·L⁻¹ hydrochloric acid solution. A given amount of TMB was added to the initial mixture and homogenized by vigorous stirring. Then, TMOS was added at room temperature under vigorous stirring for hydrolysis. After vigorous stirring for 1 h, appropriate amount of PO was added into the solution. When the solution became homogeneous, the resultant solution was poured into a glass tube. The glass tube was sealed and kept at 40 °C for gelation, and subsequently the gel was aged at 40 °C for 3 d. The solvent exchange process was conducted by exchanging the solution in the glass tube with ethanol every 24 h for three times, and most of the liquid phases (such as the solvent, ring-opening reaction product) would be replaced by ethanol. After dried at 60 °C for 3 d, hierarchically porous silica monolith was obtained. Some of the dried gels were heat-treated at various temperatures between 400 and 1400 °C for 1 h in air. For comparison, the samples without TMB were also prepared to investigate the individual effect of P123 on phase separation of this system.

Table 1 Starting compositions of samples in the study.

	TMOS /mL	HCl /mL	P123 /g	<i>m</i> _{TMB} / <i>m</i> _{P123}	PO /mL
MP1	3	7.2	1.50	0	1.4
MP2	3	7.2	1.75	0	1.4
MP3	3	7.2	2.00	0	1.4
MP4	3	7.2	2.13	0	1.4
MP5	3	7.2	1.75	0	0
MP6	3	7.2	1.75	0	0.5
MP7	3	7.2	1.75	0	1.0
MP8	3	7.2	1.75	0	1.2
MP9	3	7.2	1.75	0	1.5
MP10	3	7.2	1.75	0	1.7
MPT1	3	7.2	1.75	0.12	1.4

MPT2	3	7.2	1.75	0.24	1.4
MPT3	3	7.2	1.75	0.36	1.4
MPT4	3	7.2	1.75	0.48	1.4
MPT5	3	7.2	1.75	0.48	0
MPT6	3	7.2	1.75	0.48	0.5
MPT7	3	7.2	1.75	0.48	1.0
MPT8	3	7.2	1.75	0.48	1.2
MPT9	3	7.2	1.75	0.48	1.5
MPT10	3	7.2	1.75	0.48	1.7

2.3 Characterization

Morphology and microstructure of the fractured surfaces of the samples were characterized by a scanning electron microscope (SEM, SU-70, Hitachi, Ltd., Japan) and a transmission electron microscope (TEM, Tecnai G2 F20 S TWIN, FEI, USA). Chemical bonding information on the dried gels was confirmed by Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700, Thermo Fisher Scientific., USA). Macropore size distribution of the dried gel monolith was evaluated by mercury intrusion porosimetry (Belsorp mini II, Bel Japan Inc., Toyonaka, Japan, and AutoPore IV 9510, Micromeritics Ins Ltd., USA). Meso- and micropores were characterized by an N₂ adsorption-desorption apparatus (Autosorb-1-C, Quantachrome Ins., USA), and the samples were degassed at 150 °C under vacuum before each N₂ adsorption-desorption measurement. The BJH method was applied to adsorption branch to derive mesopores size distributions.

3. Results and discussion

3.1 Formation of hierarchically porous silica monolith in TMOS-HCl-PO-P123-TMB system.

3.1.1 Control for macroporous morphology of silica monolith in the absence of TMB.

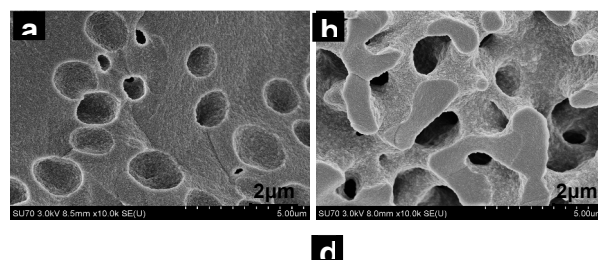
In the TMOS-HCl-PO-P123 system, P123 was homogeneously dissolved in 0.01 mol·L⁻¹ hydrochloric acid solution, and the H⁺ will rapidly catalyze the hydrolysis of added TMOS. When PO was added to the solution and time elapsed, the phase separation and the sol-gel transition proceeded spontaneously in a closed and static condition at a constant temperature (40 °C). Due to the strong nucleophilic properties and irreversible ring-opening reaction of PO to immobilize the conjugate base (Cl⁻ in the present case), the pH of the solution homogeneously increases from <1 to 3-4 immediately, which accelerates the polycondensation reaction and eventually induces the sol-gel transition. In contrast, the addition of P123 did not have an important effect on the gelation time but induced the phase separation to form macroporous structure after drying. Due to P123 molecule consisting of hydrophilic PEO chains on the both ends and hydrophobic PPO chains in the middle, attractive interaction between the silica oligomers and P123 molecules are expected, which results in silica oligomers absorbed by the incorporated molecules-PEO chains and the polymerizing silica distributed to P123-rich phase. Thus the whole system separates

into two phases; one is rich in silica-P123 and the other in solvent. The final gel morphology with controlled macropores and mesopores is determined by the competitive kinetics between the domain coarsening by phase separation and the structure freezing by sol-gel transition.

For the purpose of obtaining macroporous structure, the effects of PO and P123 contents on the phase separation and sol-gel transition were respectively investigated in detail. In a constant PO content (1.4 mL), when the P123 content was small, colorless and transparent or translucent gels were obtained. As the P123 content was increased to 1.50 g and above, the gels became opaque white, indicating the occurrence of phase separation. In a constant P123 content (1.75 g), the gelation time of the system without PO reached more than 10 h, and rapidly decreased with the addition of PO. When the PO content increased from 0 to 1.7 mL, the gelation time shortened from >10 h to about 1 h, and the appearance of gel changed from transparent, translucent to opaque white. The above phenomenon indicate that the transient structure derived from phase separation and the timing of the sol-gel transition parallel to phase separation can be adjusted by appropriate amounts of P123 and PO. The gels with 1.50-2.13 g of P123 and 0-1.7 mL PO were subjected to SEM observation in order to characterize the macropore structures respectively.

Fig. 1 shows SEM images of dried gels prepared with varied P123 contents. Only isolated multicavities are observed in the sample with the P123 content of 1.50 g (MP1), and the multicavities irregularly distribute in dense matrix, indicating a low phase separation (Fig. 1a). When the P123 content increases to 1.75 g (MP2), a homogeneous macrostructure with interconnected macropores and cocontinuous skeletons is obtained (Fig. 1b). Further decrease in P123 content leads to a coarsened cocontinuous structure (Figs. 1c and 1d).

Fig. 2 shows SEM images of dried gels containing 1.75 g P123 prepared with varied PO contents. It can be seen that PO content has an effect on the macroporous structure of silica monolith. In the absence of PO, the gel with no macropores is obtained (Fig. 2a). After the addition of PO, the morphologies vary remarkably as the macroporous structure becomes coarsened. In MP6 (0.5 mL), only isolated pores of about 5 μm are observed (Fig. 2b), homogeneous cocontinuous gel skeleton with smooth skeleton surfaces are obtained when the PO content is 1.0 mL and above (Figs. 2c-2e). A further increase in PO content leads to a coarsened cocontinuous structure and the enlarged macropore size (Figs. 2f-2g).



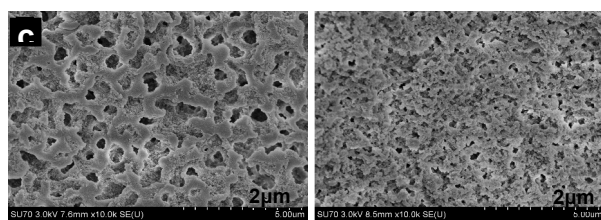


Fig. 1 SEM images of the dried gels prepared with varied m_{P123} : (a) 1.5 g (MP1), (b) 1.75 g (MP2), (c) 2.0 g (MP3) and (d) 2.13 g (MP4).

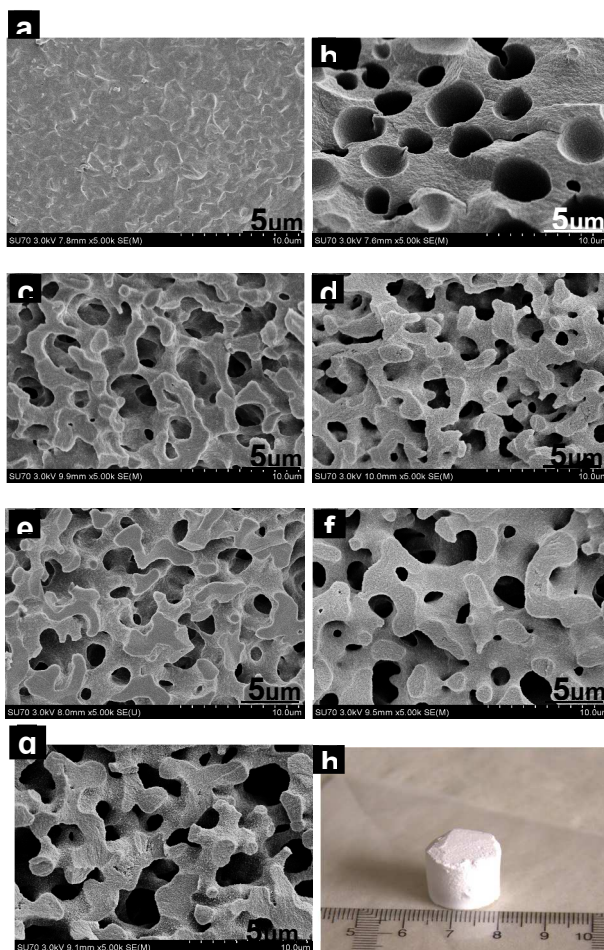


Fig. 2 SEM images of the dried gels containing 1.75 g P123 prepared with varied PO contents: (a) 0 mL (MP5), (b) 0.5 mL (MP6), (c) 1.0 mL (MP7), (d) 1.2 mL (MP8), (e) 1.4 mL (MP2), (f) 1.5 mL (MP9), (g) 1.7 mL (MP10) and (h) the appearance of MP2 monolith.

In the case of the sol-gel accompanied by phase separation, the morphologies in submicrometer- to-micrometer scale of the gels are formed by fixing the transient morphologies formed during the phase separation. The increase in pore size is a result of the higher phase-separation tendency between the gel and liquid phases. It can be concluded that an increase in P123 content enhances the phase separation and cocontinuous structure is obtained with a moderate amount of P123 additions. Further additions of P123, however, lead to the formation of gels without macropores, which indicates that phase separation in the system is suppressed also at higher P123 content. It can also be concluded that PO influences both macropores and the gel

skeletons. Because PO accelerates the increase of the pH value, the timing of the sol-gel transition parallel to phase separation is controlled by the addition of PO. When there is no PO or little PO, the timing of the sol-gel transition lags behind the phase separation, and the transient structure in the later phase-separating stage is obtained. The timing of the sol-gel transition is just matching with the suitable phase separation when the PO content increases to a certain value, and a transient structure with interconnected macropores and cocontinuous skeletons is fixed. The further increase in PO content brings out the advanced sol-gel transition, which results in obtaining the transient structure with a small domain size in the early phase-separating stage. The choice of appropriate amount of PO allows the formation of gels with controlled smooth cocontinuous structure. In contrast, in this work, the MP2 sample with the P123 content of 1.75 g and the PO content of 1.4 mL has a relatively well-controlled macrostructure, which will be used for the foundation of introducing the uniform mesostructures into the cocontinuous skeletons to construct the hierarchically porous structure.

3.1.2 Introduction of uniform spherical mesopores in the presence of TMB.

As mentioned above, it has been testified that P123 affects the sol-gel and phase separation process playing as a phase separation inducer. Afterwards, a certain amount of TMB as micelle-swelling agent was added to introduce uniform spherical mesopores into cocontinuous skeletons. Fig. 3 shows selected SEM photographs of the gels prepared with the addition of TMB. With an addition of TMB, the morphology turns from isolated to interconnected macropores with a fibrous appearance accompanied by the gradual increase in the domain size. Thus, the morphological evolution with an addition of TMB accompanies a slight anisotropy in the interconnected macroporous structure in the limited concentration region. As shown in Fig. 3d, at optimum amounts of TMB (TMB/P123 mass ratio of 0.48), the phase-separated structure still shows a cocontinuous structure with well-defined macropores. We can assume that the amount of TMB is also an important parameter of affecting the phase separation process, and thus the macroporous structures of the silica monolith changes with varied amount of TMB as well as P123.

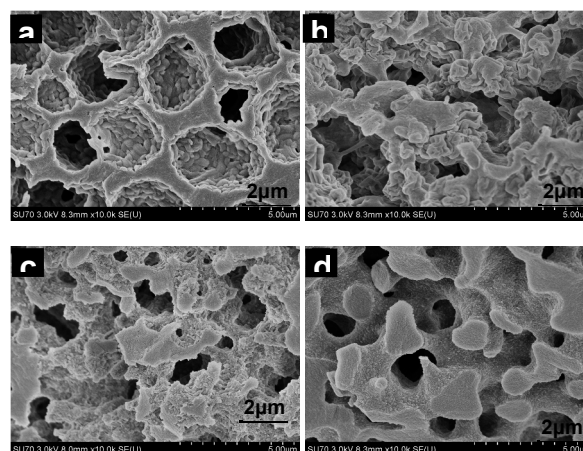


Fig. 3 SEM images of the dried gels prepared with varied m_{TMB}/m_{P123} : (a) 0.12 (MPT1), (b) 0.24 (MPT2), (c) 0.36 (MPT3) and (d) 0.48 (MPT4).

Fig. 4 shows SEM images of dried gels with $m_{\text{TMB}}/m_{\text{P123}}$ of 0.48 prepared with varied PO contents. It can be seen that PO content has an effect on the macroporous structure of silica monolith. In the absence of PO, there exist irregular isolate macropores in the gel (Fig. 4a). After the addition of PO, the morphologies change remarkably with the increase of PO. Compared with the samples containing without TMB (Fig. 2), the macroporous structure with homogeneous interconnected macropores and cocontinuous skeleton is only obtained in MPT4 sample (Fig. 4e), while the macroporous structures are changed or removed in the other samples (Figs. 4c, 4d, 4f and 4g). It indicates that only the appropriate amount of PO allows the formation of gels with controlled cocontinuous macrostructure for the monoliths with both P123 and TMB.

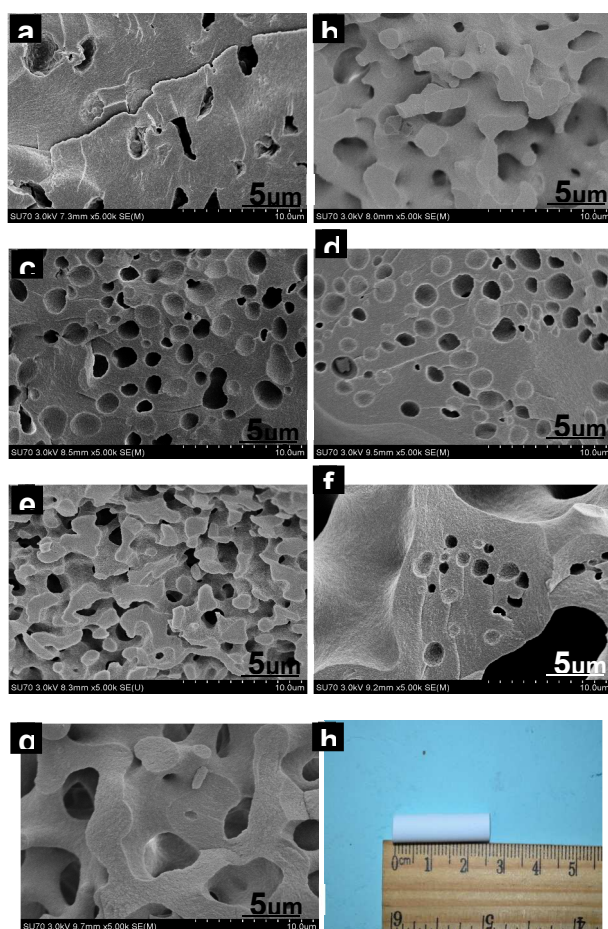


Fig. 4 SEM images of the dried gels at $m_{\text{TMB}}/m_{\text{P123}} = 0.48$ prepared with varied PO contents: (a) 0 mL (MPT5), (b) 0.5 mL (MPT6), (c) 1.0 mL (MPT7), (d) 1.2 mL (MPT8), (e) 1.4 mL (MPT4) (f) 1.5 mL (MPT9), (g) 1.7 mL (MPT10) and (h) the appearance of MPT4 monolith.

that there are many disordered mesopores because of the stacking particle aggregates without TMB (MP2), while uniform mesopores were successfully introduced into the skeleton with an appropriate addition of TMB (MPT4). As we have known, PEO-based nonionic surfactants such as Pluronic P123 enabled the synthesis of uniform silica phases in relatively dilute aqueous solution. In the system of TMOS-HCl-P123-PO, Pluronic P123 acts as a template or the structure-directing agent as well. The problem is that the micro/mesopores formed merely depending on the self-organization of the micelle produced by P123 are smaller and disorder, thus these micro-mesopores can not be made full use of in the practical applications. Here we adopt TMB as the micelle-swelling agent.

On the basis of epoxide-mediated sol-gel route, combining with the structure-directing of P123, uniform mesopores were incorporated into the cocontinuous skeletons by adding TMB to stabilize the cylindrical micelles of P123. TEM images of the obtained silica monolith (Figs. 5c and 5d) show relatively different microstructures. The monolith derived without TMB contains some disordered mesopores, which is formed by the aggregation of particles or aggregates in accordance with the SEM images. TEM micrographs of hierarchically monolithic silica prepared with TMB indicate that relatively uniform mesopores confined in the skeletons, and the mesopore size is approximately 10 nm.

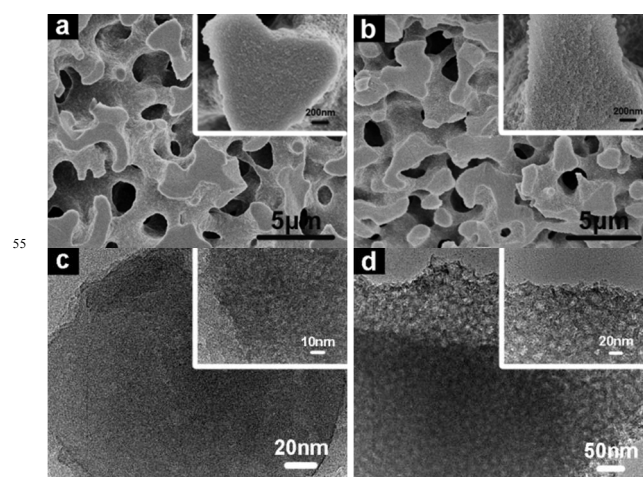


Fig. 5 SEM and TEM images of silica monoliths MP2 (without TMB) (a, c) and MPT4 (with TMB) (b, d), and the inset are magnified SEM and TEM images.

3.2 Pore structures of hierarchically porous silica monolith.

We investigate the pore structures of the resultant hierarchically porous silica monoliths with (MPT4) and without TMB (MP2). Fig. 6 shows adsorption isotherms and corresponding mesopore size distributions of the gels without and with addition of TMB. Drastic changes both in isotherm and in mesopore size distribution can be recognized. The adsorption branch for the samples prepared with TMB exhibits a distinct inflection corresponding to sharper mesopore size distribution, which can be confirmed in the corresponding differential mesopore size

distribution curves. The overall shape of the adsorption-desorption hysteresis loop turns from H2 (without TMB) to H1 (with TMB) of IUPAC classification. In contrast, the hysteresis loop of the sample with TMB is quite big with a rectangular-like shape. The type H2 hysteresis is observed in many inorganic oxide gels with interconnected networks of pores with variations in their size and shape, while the type H1 is commonly observed in adsorbents with a sharp distribution of uniform-shaped pores including MCM-41 type highly ordered mesoporous materials. It indicates that the mesopores in the sample with TMB are uniform or relatively ordered.

The BET surface areas of the gels without and with TMB are 920 and 848 $\text{m}^2\cdot\text{g}^{-1}$, respectively. The relatively high surface area of silica monolith without TMB predominantly because of the small mesopores less than 5 nm derived by aggregation of particles. For the sample prepared with TMB, the surface area remains as high as 848 $\text{m}^2\cdot\text{g}^{-1}$, and uniform mesopores were well integrated in well-defined macroporous framework. As shown by the BJH pore-size distribution curves obtained using the adsorption branch (Fig. 6b), the most dominant mesopore diameters of 2 and 10 nm are observed from the gels without and with TMB, respectively, which indicates that the addition of TMB enlarges the size of mesopores. From these data, the addition of a small amount of TMB is assumed to enhance the self organization of P123 to transform the pore system from random to cylindrical in shape without significantly affecting the median pore size.

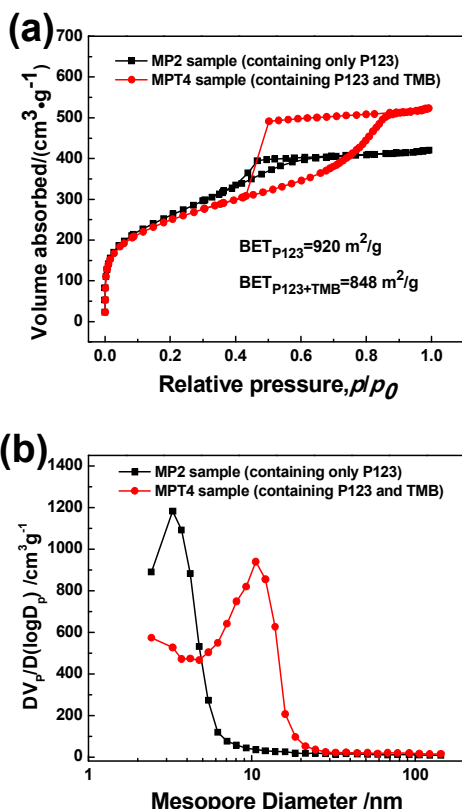


Fig. 6 Nitrogen adsorption-desorption isotherms (a) and BJH mesopore size distribution of silica monoliths without (MP2) and with TMB (MPT4).

A detailed characterization of macropores present in the as-prepared monolithic silica was carried out by mercury porosimetry (Fig. 7). The macropore size distribution curve of silica without TMB shows a sharp distribution in the micrometer region and the median size of the macropores is 1.5 μm . By comparison, the macropore distribution curve of silica with TMB still possesses a relatively sharp pore size distribution, and the median macropore size is approximately 1 μm , which is lower than the sample without TMB, indicating that the addition of TMB slightly affects the macrostructure to some extent.

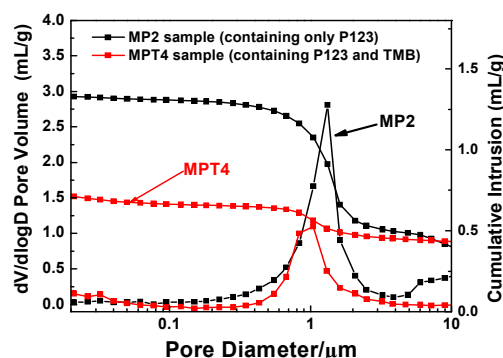


Fig. 7 Macropore size distributions of silica monoliths without (MP2) and with TMB (MPT4).

Differential thermal analysis curves of the obtained silica monoliths prepared without and with TMB are given in Fig. 8a. It is observed that the DTA curves display relative consistency in samples with and without TMB. The evaporation of remaining water and organic solvent takes place below 200 $^{\circ}\text{C}$. The exothermic peak at around 200 $^{\circ}\text{C}$ is attributed to the decomposition of P123 and the residue organic species. It is investigated that P123 is preferentially distributed into the precipitate phase when the morphology of macroscopic double phase is obtained. The endothermic peak at around 800 $^{\circ}\text{C}$ is due to the crystallization of silica monolith. TGA of the MP2 and MPT4 samples shows that most of the weight loss occurred at around 200 $^{\circ}\text{C}$. The weight loss is ascribed to the removal of the rest organic compound from dried monoliths, which can be confirmed in DTA curves as well. The weight loss of the MPT4 sample is as same as that of the MP2 one from 200 $^{\circ}\text{C}$, which indicate that TMB has been removed. FT-IR spectra of the obtained silica monoliths prepared without and with TMB are

given in Fig. 8b. For both conditions, the broad band around 3360 cm^{-1} can be attributed to surface silanols and adsorbed water molecules, whose deformational vibrations cause the absorption band near 1630 cm^{-1} ; the absorption bands at 1051 and 797 cm^{-1} are assigned to Si-O-Si groups. The stretching vibration of the CH₂ groups around 2940 cm^{-1} indicates the presence of surfactant PEO chains on the end of P123 molecules. The spectrum of SiO₂ without and with TMB is almost identical. There are no further bands about TMB for both conditions, possibly because that the addition of TMB may enter into the middle of P123 molecules and is finally removed by solvent exchange or drying process, not changing the final composition of silica monolith.

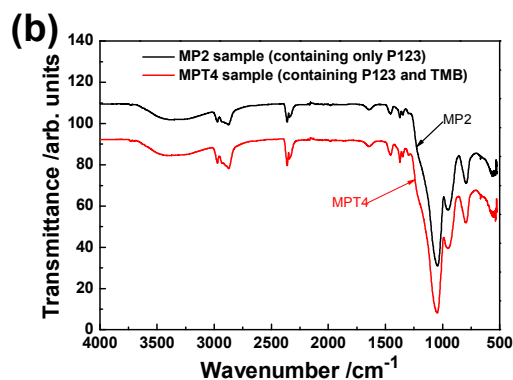
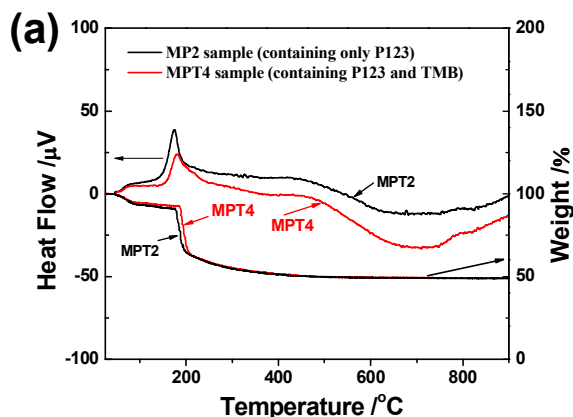
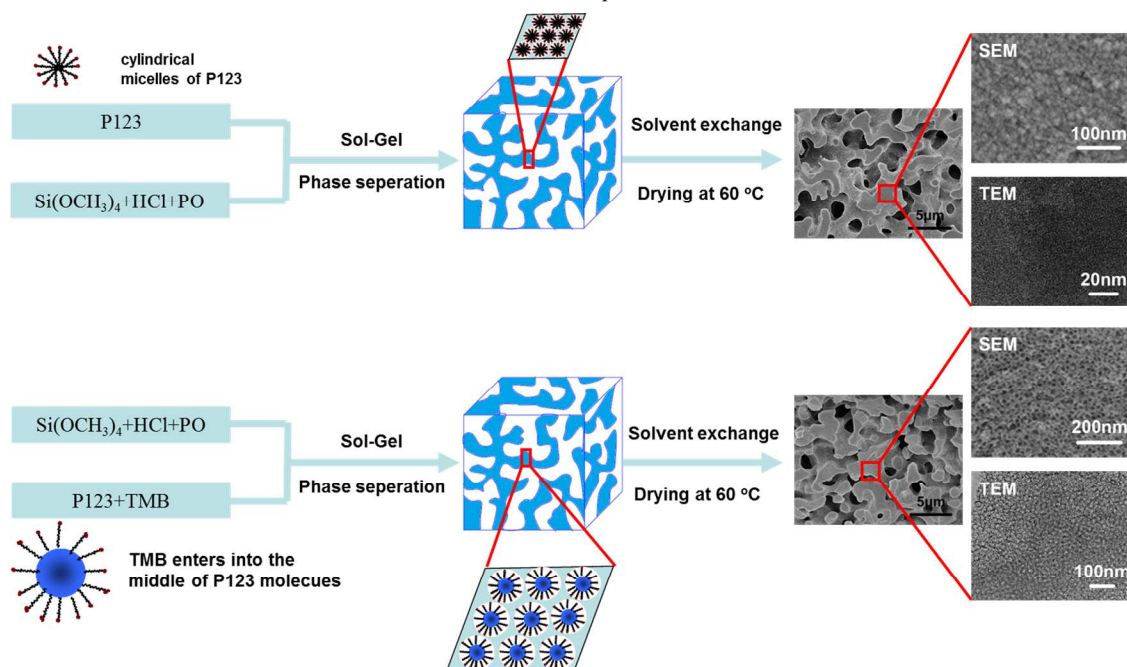


Fig. 8 DTA/TGA curves (a) and FT-IR spectra (b) of silica monoliths without (MP2) and with TMB (MPT4).



Combining results of adsorption isotherms, mercury porosimetry and FT-IR spectra analysis, it could be concluded the mechanism of spontaneous preparation of pure silica monoliths having both well-defined interconnected macropores and uniform spherical mesopores, as shown in Scheme 1. In the TMOS-HCl-PO-P123 system, the micelle-swelling agent TMB enters into the middle of P123 molecules and stabilizes the assemblage of P123-silica adducts in the whole process of sol-gel accompanied by phase separation, resulting in the expansion of mesopores and slight influence on macropores. After solvent exchange and drying process, TMB is removed.



Scheme 1 Spontaneous preparation of pure silica monoliths having both well-defined interconnected macropores and uniform spherical mesopores.

3.3 Thermal stability of hierarchically porous silica monoliths.

Heat treatment at $400\text{--}1400\text{ }^{\circ}\text{C}$ of the resultant hierarchically

porous silica monolith (MPT4) was conducted to investigate the thermal stability of the macro-mesoporous structure as well as the

influence of high temperature on the surface area of the monoliths. TEM photographs show that there is no obvious change in the microstructure morphology and the uniform mesoporous structure remains intact after heat treatment at 400-800 °C (Figs. 9a-9d), while at 1000 °C and above, the mesoporous structure is entirely collapsed, and at the same time, the amorphous silica monolith begins to undergo crystalline transition (Figs. 9e and 9f).

Observed from the TEM images of the samples before and after heat treatment (Fig. 5b and Fig. 9), the sample with both P123 and TMB has mesocellular foam (MCF) structure, in which spherical mesopores are connected by windows with smaller size. This is the reason why the hysteresis loop of the sample with both P123 and TMB is quite big with a rectangular-like shape (Fig. 6a).

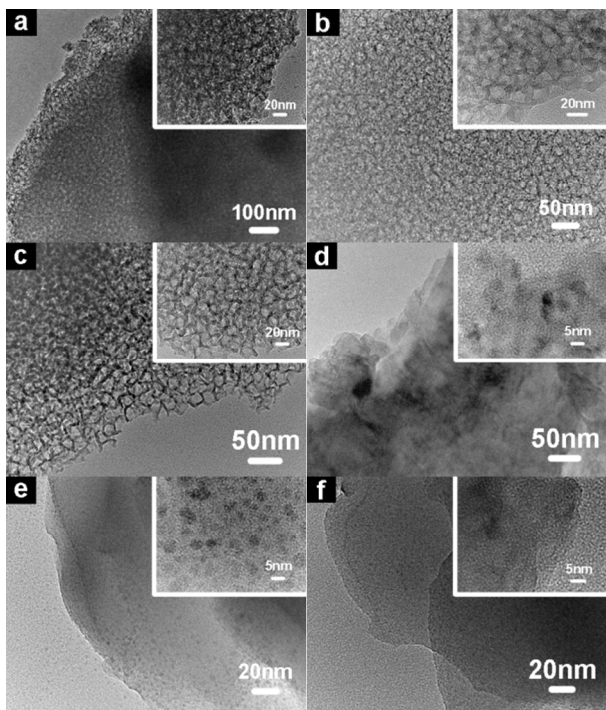


Fig. 9 TEM photographs of hierarchical porous silica monoliths (MPT4) at varied heat treatment temperatures: (a) 400 °C, (b) 600 °C, (c) 800 °C, (d) 1000 °C, (e) 1200 °C, (f) 1400 °C, and the inset pictures are HRTEM images.

Fig. 10 shows nitrogen adsorption-desorption isotherms and BJH mesopore size distribution of silica monolith (MPT4) after heat treatment at 400-1400 °C, and the corresponding BET surface area and BJH pore volume are listed in Table 2. Drastic changes both in isotherm and in pore size distribution can be recognized. The overall shape of the adsorption-desorption hysteresis loop was observed to be H1 of IUPAC classification when temperature lower than 800 °C, implying that the uniform spherical mesopores still exist. The BET surface area reduces to 727, 587 and 195 m²·g⁻¹ by heat treatment at 400, 600 and 800 °C, respectively, and the pore volume decreases gradually either. Compared with the dried gel (Fig. 6), the median mesopore size of the heat-treated

gels decreases from 10 to 3 nm, and the mesopore size distribution becomes narrower after heat treatment. It is also seen that further change in the mesopore size does not obviously occur with the temperature rising from 400 to 800 °C, indicating the reservation of most uniform mesoporous structure. In contrast, the BET surface area changes much more after heat treatment. When the dried sample was heat-treated at 400 °C, the BET surface area decreased from 848 to 727 m²·g⁻¹ slightly. As known, the value of BET surface area is contributed by the micropores or small mesopores. It indicates that heat-treatment at 400 °C eliminates some of the micropores or small mesopores, resulting in the decrease of BET surface area. When the heat-treatment temperature increases from 400 to 800 °C, the BET surface area decreased to 195 m²·g⁻¹ slightly, indicating that a large amount of micropores or small mesopores disappears. Further increase in temperature (from 1000 to 1400 °C) leads to the disappearance of the mesopores absolutely, even the macropores. It can be concluded that most of the uniform mesoporous structure remains intact while the surface area decreases gradually corresponding with the heat treatment temperature rising from 400 to 800 °C, indicating a superior thermal stability. It is in accordance with the TEM photographs.

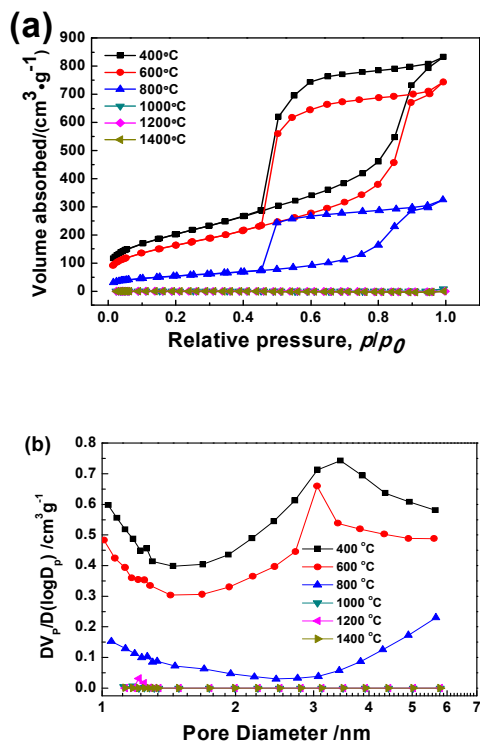


Fig. 10 Nitrogen adsorption-desorption isotherms (a) and BJH mesopore size distributions (b) of hierarchical porous silica monoliths (MPT4) at varied heat treatment temperatures.

Table 2 Pore characterization analysis of hierarchical porous silica monoliths (MPT4) at varied heat treatment temperatures.

T /°C	S _p /m ² ·g ⁻¹	V _{pore} /cm ³ ·g ⁻¹
Dried monolith	848	0.808

400	727	1.289
600	587	1.150
800	195	0.503
1000	1.5	0.036
1200	0	0
1400	0	0

Conclusions

In summary, unique hierarchically porous silica monolith was successfully prepared by combining the polymerization-induced phase separation with epoxide-mediated sol-gel route without any complicated aging and drying and high-temperature heat treatment. The as-prepared silica monolith displays a characteristic of hierarchically porous structure which has both well-defined interconnected macropores and uniform spherical mesopores. The resultant hierarchically porous silica monolith exhibits a BET surface area as high as $848 \text{ m}^2\text{g}^{-1}$, a mesopore size of 10 nm and a macropore size of 1 μm . Heat treatment at 400-800 °C does not spoil the macroporous structure, the uniform spherical mesoporous structure remains intact, although the surface area decreases gradually corresponding with rising the heat treatment temperature.

Notes and references

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