



Structural control of mesoporous silicas with large nanopores in a mild buffer solution

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ABSTRACT

In this study, a simple synthesis strategy has been developed for the systematic control of the structure and pore size of the mesoporous silicas through adjusting the ratio of tetraethoxysilane (TEOS) to tetramethoxysilane (TMOS) in a mild acidic buffer solution (acetic acid–sodium acetate pH 4.4) or the pH value using poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO₂₀PO₇₀EO₂₀) as a structure-directing agent. By varying the molar ratio of TEOS to TMOS, mesoporous silicas with 2-D hexagonal (*p6mm*) pore arrangement, onion-like lamellar structure, mixed phase (vesicular hierarchical structure and cellular foam), and nanofoams with large uniform spherical cells can be obtained. Simultaneously, the pore diameter can be varied in the range of 9–50 nm. The differences in the hydrolysis and polymerization rates between TEOS and TMOS were found to play a key role in the phase transformation of the final products. When TEOS was employed as the only silica precursor, the mesostructure and pore diameter of the resultant materials could be controlled through either varying the solution pH or the addition of fluoride ion to the synthesis system. Increasing the solution pH values from 3.2 to 5.1 induces the structure transformation from uniform wormhole mesostructure to nanofoams with large uniform spherical cells, then to aggregated and collapsed vesicle-like nanofoam structure accompanied by the increase of pore diameter from 7 to 50 nm. By addition of the fluoride ion, uniform macroporous nanofoam structure (ca. 100 nm in diameter) similar to the cell wall of diatoms was obtained.

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1. Introduction

Recently, the mesoporous materials with large pore size in the range of 10–50 nm [1–4] and hierarchical nanoarchitecture at multiple length scales (e.g., mesocellular foams [5–11], vesicles [12,13], or macroporous ordered siliceous foams [4,14,15]) have attracted growing research interests because of their potential applications as catalyst support, electrode for supercapacitor, and adsorbent for protein and pollutant, etc. Surfactant-induced self assembly method has been widely employed for the synthesis of inorganic materials or organic polymer with well-defined nanostructures [16–23]. However, it still remains a challenge for the synthesis of mesoporous silicas with pore size at the boundary of meso scale and macro scale by using surfactant-templating method. In the presence of organic additives, such as trimethylbenzene (TMB), mesostructured cellular foams (MCFs) composed of uniformly sized, large spherical cells (24–42 nm) interconnected by uniform windows (9–19 nm) were synthesized using nonionic

block copolymer as template [5–7]. Nevertheless, organic auxiliaries are often toxic, and environment-unfriendly. It is desirable to develop a synthesis method for mesoporous silicas with tunable mesostructure and large pore size in the range of 10–100 nm using surfactant-templating methods in the absence of organic additives.

Mesoporous silicas synthesized under mild conditions, allows a wide range control of pore size, shape, and structure, and provides inspiration for potential alternative routes to synthesize mesoporous silica with large pore size [8,9,11,13–15,24–27]. Under pH value of 6.3–6.4, Kim and Hyeon et al. reported the synthesis of hierarchically ordered mesocellular materials (HMMS) using triblock copolymer P123 as the structure-directing agent [9]. Pinnaia et al. reported that biomimetic vesicular structures (300–800 nm) with shell thickness of 100–250 nm, and interlamellar pore size of 2.0–2.7 nm can be formed in aqueous solution by utilizing neutral diamine Bola-type surfactants H₂N(CH₂)_nNH₂ (*n* = 12–22) as structure director [12]. Later, the same group reported the synthesis of thiol-functionalized mesostructured silica vesicles (100–200 nm) by co-condensation of sodium silicate and 3-(mercaptopropyl)trimethoxysilane (MPTMS) using triblock copolymer under neutral condition [13]. Recently, Yu and co-workers reported that macroporous siliceous foams with diameters larger than 100 nm can be prepared in buffer solutions (pH 5.0)

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Table 1

Physicochemical properties of the mesoporous silicas synthesized with different TEOS and TMOS molar ratio

Sample	TEOS (mol.%)	TMOS (mol.%)	NH ₄ F/TEOS (mol.%)	BET surface area (m ² g ⁻¹)	Pore diameter (nm) ^a	Total pore volume (cm ³ g ⁻¹)	Micropore volume V _{mic} ^b (cm ³ g ⁻¹)
S1	0	100	0	760 ^c	9.3 ^c	1.17 ^c	0.08
S2	5	95	0	715	9.1	1.44	–
S3	10	90	0	728	11 and 18.5	1.34	–
S4	30	70	0	626	31	1.82	0.06
S5	50	50	0	666	28	1.76	0.05
S6	70	30	0	567	49	1.94	0.04
S7	100	0	0	576 ^d	16 ^d	1.62 ^d	0.04
S8	100	0	2	382	11 and 43	1.89	–
S9	100	0	5	326	13 and 112	1.74	–
S10	100	0	10	334	46	1.75	–

^a Calculated from adsorption branch.^b V_{mic} is the micropore volume calculated from the *t* plots.^c From Ref. [11].^d From Ref. [4].**Table 2**

Physicochemical properties of mesoporous silicas synthesized using TEOS as silica precursor with different solution pH value in the range of 3.2–5.1

Sample	pH	d spacing (nm)	BET surface area (m ² g ⁻¹)	Pore diameter (nm) ^a	Total pore volume (cm ³ g ⁻¹)
S11	3.2	10.3	1004	7.1	1.7
S12	3.6	11	924	8.1	1.5
S13	4.1	12.3	767	11.3	1.62
S7	4.4	–	576 ^b	16 ^b	1.62 ^b
S14	5.1	–	336	46	1.86

^a Calculated from adsorption branch.^b From Ref. [4].

[14,15]. More recently, Chen and Cheng reported that under acid-free conditions using tetraethoxysilane (TEOS) as the silica precursor and P123 as the template, mesoporous silica materials with MCFs structure were synthesized with the aid of salt and alcohol [8].

Although the synthesis of silicas with different mesostructure and large pore size has been reported, very few studies concern

the systematic control of the structure, and pore size of the mesoporous silicas. We have recently reported that the thioether-bridged mesoporous organosilicas with different mesostructures can be controllably synthesized by simply tuning the molar ratio of tetramethoxysilane (TMOS) and bis[3-(triethoxysilyl)propyl]tetrasulfide (TESPTS) in *Si-P123-NaAc-HAc-ethanol-H₂O* system [11]. We also found that ordered mesoporous silicas with tunable pore size (10–15 nm) can be synthesized from mixtures of sodium silicate and TEOS in a similar system [4]. These allow us to control the mesostructures, and pore size by controlling the hydrolysis and polymerization rates of silica precursors. To further expand the scope of this method, herein, we describe a systematic study on the synthesis of mesoporous silicas with large nanopores through controlling the hydrolysis and polymerization rates of silica precursors. The mesostructure and pore size of the resultant materials can be controlled by varying the molar ratio of TEOS/(TEOS + TMOS). Moreover, when only TEOS was employed as the silica precursor, the mesostructure, and pore diameter of the resultant materials could be controlled through either varying the solution pH from 3.2 to 5.1 or the addition of fluoride ion to the synthesis system.

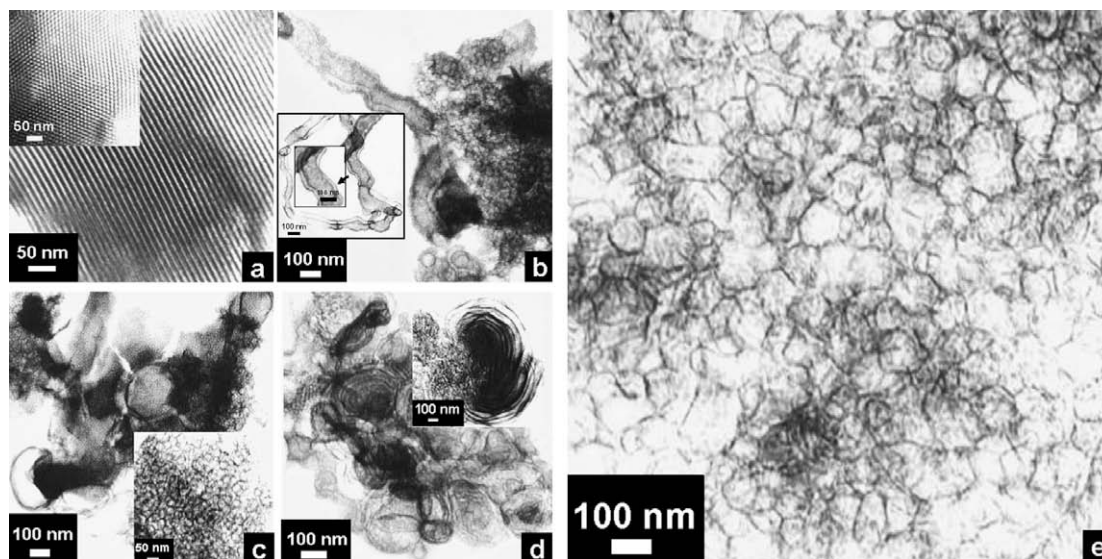


Fig. 1. Transmission electron microscopy (TEM) images for mesoporous silica synthesized with different TEOS/(TEOS + TMOS) ratio: (a) TEOS/(TEOS + TMOS) molar ratio of 0 (S1), (b) TEOS/(TEOS + TMOS) molar ratio of 0.3 (S4), (c) TEOS/(TEOS + TMOS) molar ratio of 0.5 (S5), (d) TEOS/(TEOS + TMOS) molar ratio of 0.7 (S6), (e) TEOS/(TEOS + TMOS) molar ratio of 1.0 (S7). (the TEM images of S1 and S7 are from Refs. [11] and [4], respectively).

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