NJC

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc

NJC

RSCPublishing

LETTER

Cite this: DOI: 10.1039/c3nj00000x

Fabrication of highly ordered mesoporous silica with the assistance of phosphate

Yan-Qing Wang[a], Chun-Ming Zheng [b*], Zhao-Jia Liu[a], Ming-Lin Guo[a,b*]

Received 00th XXXXX 2013,
Accepted 00th XXXXX 2013

DOI: 10.1039/c3nj00000x

www.rsc.org/njc

A simple route to prepare ordered mesoporous silica with uniform pore size distribution was reported, which was synthesized at quasi-neutral pH with the assistance of phosphate using sodium silicate as silicon source. The products prepared at varying pH were investigated and ordered mesoporous silica with uniform pore structure was synthesized at the pH of 6.15.

Mesoporous silica with ordered uniform nanopores have been given much attention due to their many possible applications such as adsorption [1], catalysis [2-4], drug delivery [5, 6], energy conversion and storage [7, 8]. Highly ordered mesoporous silica SBA-15 synthesized by commercial amphiphilic block copolymer surfactants (Pluronic P123) has been attracted much attention [9, 10]. But most of synthesis procedures made use of relatively expensive silicon alkoxides, such as tetraethoxysilane (TEOS), as Si source [11-14]. This results in the cost too high to meet the need of extensive application. Sodium silicate is much less expensive as compared with TEOS. It has also be an attractive silica source for low-cost synthesis of ordered mesoporous silica [15-19]. In the course of ordered mesoporous silica SBA-15 synthesis, it has been reported that the concentration of P123 and interaction between it and poly-silicate species directly effect on the formation of highly ordered mesoporous materials [20]. And the addition of some salts to the solution of P123 can enhance the self-assembly of the Pluronic micelles and complexes of Pluronic micelles and poly-silicate species, which favor to assemble and eventually form mesoporous silica with different morphologies according to the thermodynamics of the solution and the dissolved substances [21-23]. The effects of ion strength in non-ionic surfactant templating systems were started with the pioneering work of Yu et al [24], followed by reports on the growth of single-crystal-like mesoporous silica [25], control of mesostructural regularity [26, 27], and many other results [28-30]. However, the synthesis condition was always under strongly acidic conditions and needed a long mesostructural formation time. As for synthesis of ordered mesoporous silica at quasi-neutral pH, synthesis of MSU-H [16,17] involves addition of the mixture of the surfactant and an amount of acetic acid equivalent to the hydroxide content of the sodium silicate solution to the sodium silicate solution, while synthesis of COK-12 [18,19] involves addition of sodium silicate solution to citrate/citric acid buffered triblock copolymer solution at room temperature, but how to develop a new method for the synthesis of highly ordered mesoporous silica from sodium silicate is still a challenge.

Here, we reported a rapid formation route for ordered mesoporous silica with the assistance of phosphate. The SBA-15-like ordered mesoporous silica was obtained in a short time using sodium silicate as silicon source at room temperature. In the course of mesostructural silica formation with sodium silicate, direct quenching of silicate structure in dilute surfactant P123-acidic solution and followed by adding of phosphate in time will advantage to control of polymerization and gelation problems about sodium silicate from acidic to quasi-neutral pH. These favor to enhance interaction between Pluronic micelles and poly-silicate species and rate of mesostructural silica formation. The adding of phosphate not only had the function of salting-out, but also flocculation and pH adjuster in the synthesis procedure. The influences of pH on preparing ordered mesopurous silica were also investigated and determined the optimal condition. In the optimal pH synthesis condition, with the long static time the morphology of ordered mesoporous silica was changed and became uniform. The rapid and commercial preparation route of ordered mesoporous silica may enable new applications such as the encapsulation of fragile biomolecules and loading metal compounds.

The experiments indicate that ordered mesoporous silica can be obtained with the assistance of phosphate, which demonstrate the potential of a Pluronic P123/phosphate system to guide the production of silica structures composed of hexagons under directly quenching of silicate structure of sodium silicate. Synthesis details see Table 1.

Table 1 Synthesis details of TPU samples

Entry	Na_2SiO_3 $\cdot 9H_2O$(g)	Na_2HPO_4 $\cdot 12H_2O$(g)	P123 (g)	3.73M HCl(ml)	H_2O (ml)
TPU-1	3.80	6.44	1.50	13.6	90
TPU-2	3.80	6.44	1.50	12.6	90
TPU-3	3.80	6.44	1.50	11.8	90
TPU-4	3.80	6.44	1.50	10.7	90
TPU-5	3.80	6.44	1.50	9.7	90

In the course of mesoporous silica synthesis with sodium silicate, the pH of the system is controlled by the dosage of excess of HCl after neutralizing the hydroxide content of the sodium silicate solution. When the same quantity of phosphate is used, because HCl can reacts with Na_2HPO_4 to form NaH_2PO_4, thus, for entries using different amounts of HCl will form the phosphate buffer solution with different composition, which favors the pH control. By tracking analysis of pH acidity meter, the pH of five entries of Table 1 is 5.51, 6.15, 6.42, 6.91 and 7.40, respectively.

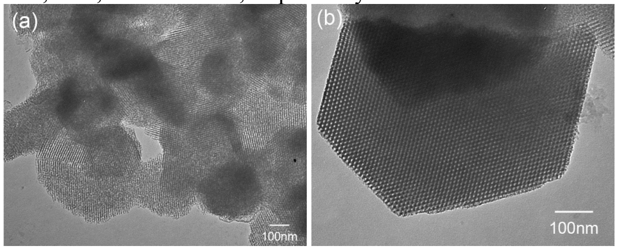


Fig. 1 Transmission electron microscopy (TEM) images of TPU-2, (a) low and (b) high magnification.

The transmission electron microscopy (TEM) images of TPU-2 show in Fig.1 reveal that the morphology of TPU-2 is plate particles of 200-600 nm with thickness of ca. 100-200 nm (Fig.1a and Fig. S1 of SEM images in †ESI) and highly ordered parallel cylindrical pore channels with 2D-hexagonal mesostructure (Fig.1b).

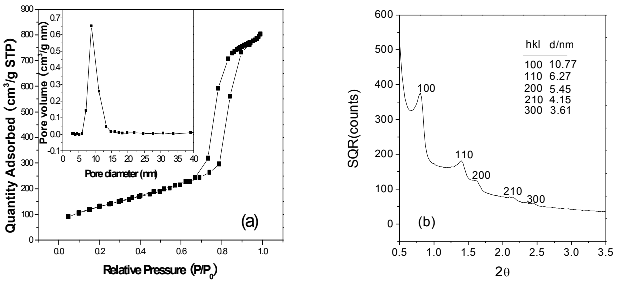


Fig.2 (a) Nitrogen adsorption and desorption isotherms of TPU-2. Inset: Pore size distribution derived from the desorption branch of isotherm using BJH calculations. (b) Small-angle X-ray scattering pattern (SAXS) of TPU-2.

Fig 2(a) displays a typical type IV nitrogen sorption isotherm with an H1 hysteresis loop, which is the characteristic of highly ordered pore channels from TPU-2. The BET surface area is 466.6 $m^2\cdot g^{-1}$ and the total pore volume at $P/P_0 = 0.99$ is 1.243 $cm^3\cdot g^{-1}$. The small-angle X-ray scattering (SAXS) of TPU-2 (Fig. 2b) shows five resolved peaks that are indexed as (100), (110), (200), (210) and (300) reflections associated with p6mm hexagonal symmetry [14], which indicate the obtained TPU-2 has a high degree of hexagonal mesoscopic organization. The intense peak of $d_{(100)} = 10.8$ nm is corresponded to a large unit-cell parameter $a_{(100)} = 12.4$ nm. Wall thickness is estimated to be ca. 3.6 nm corresponding to SBA-15 with the wall thickness of 3.1-6.4 nm. Comparing with other P6mm-type mesoporous silica materials in detail, the TPU-2 is classified as a structural analogue of SBA-15 and MSU-H. The TPU-2 had a mean pore diameter of ca. 8.8 nm according to BJH model (see inset in Fig. 2(a)) applied to the desorption branch of the isotherm, which is larger than the pore size reported for an SBA-15 material synthesized at 35 °C, viz. 5.7 nm [31] and equivalent to MSU-H synthesized at 35 − 45 °C with pore sizes of 7.6 − 8.9 nm [32]. A comparison with our prepared COK-12 sample[18] reveals that TPU-2 has larger mean pore diameter, higher BET surface area and larger total pore volume than these of COK-12. Interestingly, their nitrogen adsorption and desorption isotherms (Fig. S2 in †ESI) have obvious differences; their desorption branches are almost in the same relative pressure (0.76) position, while adsorption branch of TPU-2 are evident in smaller relative pressure position than that of COK-12, suggest that both have different adsorption properties. In other word, the structure of surface of TUP-2 may be different from that of COK-12.

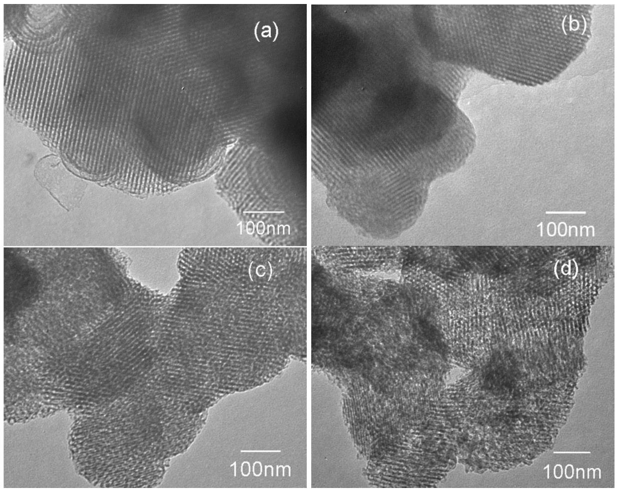


Fig. 3 TEM images of TPU-1(a), TPU-3(b), TPU-4(c) and TPU-5(d).

Fig. 3 shows the TEM images of TPU-1, TPU-3, TPU-4 and TPU-5. The TEM image of TPU-1 in Fig. 3(a) indicates the mesoporous silica prepared at pH of 5.51 would appear onion circles-like structure, which may influence the regularity of mesopores. The rest TEM images of Fig. 3 demonstrate some extent of ordered mesopores decrease with changing the pH of synthesis condition from 6.42, 6.91 to 7.40. The results suggest the pH adjusted by phosphat plays an important role in the formation of ordered mesoporous silica with uniform pores.

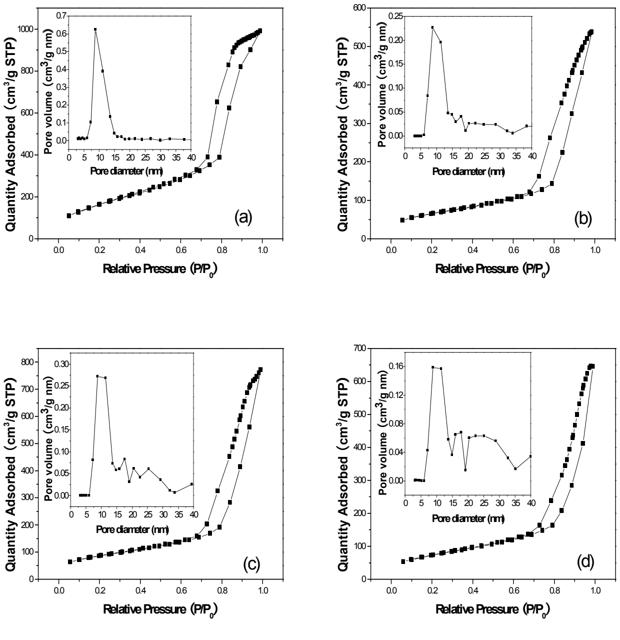


Fig. 4 Nitrogen adsorption and desorption isotherms of TPU-1(a), TPU-3(b), TPU-4(c) and TPU-5(d). Inset: Pore size distributions

derived from the desorption branch of isotherm using BJH calculations.

As shown in Fig. 4, the samples of TPU-3, TPU-4 and TPU-5 display type Ⅳ isotherms with an H3 hysteresis loops in the physisorption measurement, which due to the existence of large mesopores that aggregated by sheet particles. The BJH pore size distributions (insets of Fig. 4) of them also confirm the ununiformity of their pore size distributions and existence of large mesopores. The TPU-1 sample display type Ⅳ isotherms with an H1 hysteresis loops, which is similar to that of TPU-2. But its mesopore diameter, unit cell diameter and wall thickness (show in Table 2) are smaller than that of TPU-2, respectively. It may due to condensation of silica cluster aggregate for TPU-1is incomplete compare to TPU-2. The results above demonstrate the ordered mesoporous silica with uniform pore structure is synthesized under the pH condition of 6.15.

Table 2 Characteristics of TPU samples synthesized in various conditions.

Samples	D_{BJ}[a] (nm)	a_{100}[b] (nm)	W[c] (nm)	S_{BET}[d] ($m^2 \cdot g^{-1}$)	V_{total}[e] ($cm^3 \cdot g^{-1}$)
TPU-1	8.7	11.3	2.6	604.6	1.534
TPU-2	8.8	12.4	3.6	466.3	1.243
TPU-3	8.8	11.9	3.1	227.8	0.832
TPU-4	8.8	12.8	4.0	301.0	1.194
TPU-5	8.9	12.4	3.6	261.4	0.998
TPU-6	8.6	12.4	3.8	348.3	1.033

[a] Mesopore diameter. [b] Unit cell parameter. [c] Wall thickness. [d] BET specific surface area. [e] Total pore volume.

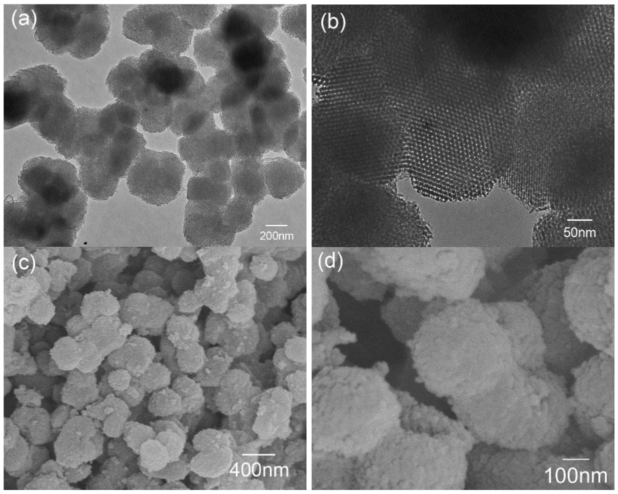


Fig. 5 TEM images of TPU-6, (a) low and (b) high magnification. Scanning electron microscopy (SEM) images of TPU-6, (c) low and (d) high magnification.

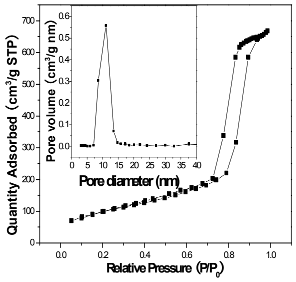


Fig. 6 Nitrogen adsorption and desorption isotherms of TPU-6, Inset: Pore size distribution derived from the desorption branch of isotherm using BJH calculations.

Based on the formation of ordered mesoporous silica at the pH of 6.15, the uniform spherical mesoporous silica (TPU-6) was prepared by adding static time for 24 h. As shown in Fig 5(a, c), the morphology of TPU-6 is spherical particle with size of 300-500 nm, which is different to the plate morphology of TPU-2. The images in Fig 5(b) and Fig 5(d) indicate that TPU-6 had highly ordered parallel cylindrical pore channels and the spherical material is aggregation of tiny particles. The regular aggregation of tiny particles favors the formation of highly ordered mesostructural silica. Fig 6 displays a typical type IV nitrogen sorption isotherm with an H1 hysteresis loop of TPU-6, which indicated its highly ordered pore channel. Parameters characterizing the porosity of the investigated samples are presented in Table 2 and the SAXS (Fig. S3 in †ESI) is similar to that of TPU-2. As listed in Table 2, compared to the TPU-2, TPU-6 has the same unit cell parameter and larger wall thickness. It may due to the continuous condensation within the pore wall during the static condition for 24 h.

On the basis of the results described above, the formation mechanism and influences of pH conditions on TPU samples are discussed as follows: as adjuster of pH, when Na_2HPO_4 was added into surfactant P123-acidic-silicic acid solution, the solution went rapidly to near-neutral pH conditions. This favored formation of tiny uncharged silicate oligomers [19], which were low negatively charged or uncharged. At this time, the polymerization rate of the silicate oligomers was slow. Phosphates act as the flocculating agent and bridging agent between hydroxyl groups on surface of the silicate oligomers and PEO moiety of P123 by hydrogen bonds, an assembly process might be departed from spherical uncharged core-shell P123-silica micelles. The high salt concentration in the solution promoted hydrophobic interactions with surfactant micelles and silica accumulation in the PEO shell, and aggregation of the spherical micelles led to cylindrical micelles when the degree of aggregation could reach to a suitable level. The formation of silicate-surfactant assembly to ordered mesostructures could occur successfully. The rate of condensation reaction of the silicate oligomers to form gel silica was faster when pH increases [33]. The faster aggregation caused the silica particles grow before the mesostructural silica was formed, which led to the formation of TPU-3, TPU-4 and TPU-5 at the pH of 6.42, 6.91 and 7.40, respectively. Hence, with the synergistic effect of increased pH and salt-out agent, there was the optimal synthesis condition to form ordered mesoporous silica with uniform pore size distribution. The adding static time for TPU-6 can drive the silica condensation and assembly to become more complete, which may have an impact on the morphology of the particle.

As pH adjuster and salt-out agent, phosphate plays an important role in the synthesis of ordered mesoporous silica. The dropwise adding of phosphate is essential, which may favor the regular assemble process of silicate oligomers and surfactant for the formation of highly ordered mesostructure. The final pH conditions affect the synthesis of highly ordered mesoporous silica and the static time affects its formation morphology. The process favors to prepare metal salt phosphate/mesoporous silica composite via one-pot synthesis condition, such as silver phosphate/mesoporous silica and zirconium phosphate/mesoporous silica composites [34]. It is rapid, reproducible, and suitable to commercially viable synthesis conditions. No operational problems are foreseen for a large-scale version of highly ordered mesoporous silica.

Experimental

All the chemicals were purchased from Tianjin Kermel Chemical Reagent Co. Ltd., China, except Pluronic P123, which was obtained from Sigma. In a typical synthesis, 1.50 g of P123 was dissolved in 12.6 mL HCl (3.73 M) and 30 mL of water, followed by the mixture of 3.80 g of sodium silicate and 30 mL of water was slowly added while stirring at ambient temperature; then, the solution of 6.44 g of $Na_2HPO_4{\cdot}12H_2O$ and 20 mL of water was added dropwise. The precipitation was appeared by flocculation with the dropwise addition of Na_2HPO_4 solution. Using pH400 acidity meter measured and recorded the pH value of the mixture system. Consequently, the mixture was transferred to a teflon-flask for hydrothermal treatment at 110 °C for 24 h. The solid products were filtered, washed with water, dried in air and calcined under air at 550 °C for 4 h. The samples were designated as TPU-2. Follow the similar process, the synthesis details of TPU-1, TPU-3, TPU-4 and TPU-5 are listed at Table 1. The synthesis of TPU-6 was the same with TPU-2 except for adding of under static condition for 24 h.

We are grateful for the support of the National Natural Science Foundation of China (no. 51208357).

Notes and references

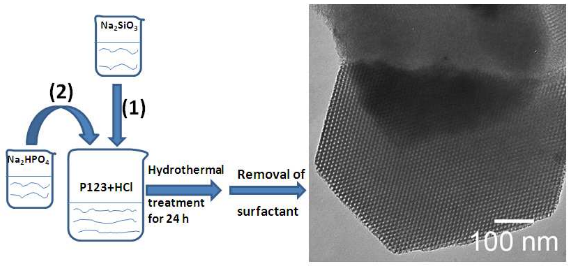
[a] School of Environment and Chemical Engineering, [b] Key Laboratory of Hollow Fiber Membrane Materials and Membrane Process, Tianjin Polytechnic University, Tianjin 300387, China.

*Corresponding author: Tel: +8622 8395 5451. E-mail: guomlin@yahoo.com (M-L Guo).

Electronic Supplementary Information (ESI) available. See DOI: 10.1039/c000000x/

1 M. Hartmann, Chem. Mater. 2005, 17, 4577-4593.
2 A. Taguchi, F. Schüth, Micr. Meso Mater. 2005, 77, 1-45.
3 Y. Wan, Y.F. Shi, D.Y. Zhao, Chem. Commun. 2007, 9, 897-926.
4 Y. Wan, D.Y. Zhao, Chem. Rev. 2007, 107, 2821-2860.
5 V.R. Maria, B. Francisco, A. Daniel, Angew. Chem. Int. Ed. 2007, 46, 7548-7558.
6 J.M. Rosenholm; C. Sahlgren; M. Lindén, Nanoscale. 2010, 2, 1870-1883.
7 M.C. Orilall, U. Wiesner, Chem. Soc. Rev. 2011, 40, 520-535.
8 Y.P. Zhai, Y.Q. Dou, D.Y. Zhao, P.F. Fulvio, R.T. Mayes, S. Dai, Adv. Mater. 2011, 23, 4828-4850.
9 M.H. Huang, A. Choudrey, P.D. Yang, Chem. Commun. 2000, 12, 1063-1064.
10 S. Jun, S.H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, J. Am. Chem. Soc. 2000, 122, 10712-10713.
11 C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature. 1992, 359, 710-712.
12 J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 1992, 114, 10834-10843.
13 D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, J. Am. Chem. Soc. 1998, 120, 6024-6036.
14 D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Science. 1998, 279, 548-552.
15 C. Jo, K. Kim, R. Ryoo, Micropor. Mesopor. Mater. 2009, 124, 45-51.
16 S.S. Kim, T.R. Pauly, T.J. Pinnavaia, Chem. Commun. 2000, 17, 1661-1662.
17 S.S. Kim, A. Karkamkar, T.J. Pinnavaia, M. Kruk, M. Jaroniec, J. Phys. Chem. B. 2001, 105,7663-7670.
18 J. Jammaer, A. Aerts, J. D'Haen, J.W. Seo, J.A. Martens, J. Mater. Chem. 2009, 19, 8290-8293.
19 J. Jammaer, T.S. vanErp, A. Aerts, C.E.A. Kirschhock, J.A. Martens, J. Am. Chem. Soc. 2011, 133, 13737-13745.
20 B.A. Placidus, L. Sangyun, C. Dragos, Micropor. Mesopor Mater. 2005, 81, 191-200.
21 Y.L. Su, X. F. Wei, H.Z. Liu, J. Colloid Interface Sci. 2003, 264, 526-531.
22 J.P. Mata, P.R. Majhi, C. Guo, H.Z. Liu, P. Bahadur, J. Colloid Interface Sci. 2005, 292, 548-556.
23 B.L. Newalkar, S. Komarneni, Chem. Mater. 2001, 13, 4573-4579.
24 C. Yu, B. Tian, J. Fan, G.D. Stucky, D. Zhao, Chem. Commun. 2001, 24, 2726-2727.
25 C. Yu, B. Tian, J. Fan, G.D. Stucky, D. Zhao, J. Am. Chem. Soc. 2002, 124, 4556-4557.
26 K. Flodstrōm, V. Alfredsson, N. Kāllrot, J. Am. Chem. Soc. 2003, 125,4402-4403.
27 J. Tang, C. Yu, X. Zhou, X. Yan, D. Zhao, Chem. Commun. 2004, 19, 2240-2241.
28 Y. Wang, B. Zibrowius, C. Yang, B. Spliethoff, F. Schüth, Chem.Commun. 2004, 1, 46-47.
29 W.P. Schmidt, P. Yang, D.I. Margolese, B.F. Chmelka, G.D. Stucky, Adv. Mater. 1999, 11,303-307.
30 C. Li, Y. Wang, Y. Guo, X. Liu, Y. Guo, Z. Zhang, Y. Wang, G. Lu, Chem. Mater. 2007, 19, 173-178.
31 M. Kruk, M. Jaroniec, C.H. Ko, R. Ryoo, Chem. Mater. 2000, 12, 1961-1968.
32 S.S. Kim, A. Karkamkar, T.J. Pinnavaia, M. Kruk, M. Jaroniec, J. Phys. Chem. B. 2001, 105, 7663-7670.
33 A.R. Nanik, W. Ika, R.J. Sri, S. Heru, Colloid. Surface. A 2015, 476, 1–7.
34 J.Y. Yang, C.M. Zheng, Y.Q. Wang, M.L. Guo, RSC Adv., 2014, 4, 42971-42976.

Graphic abstract



Highly ordered mesoporous silica was prepared with the assistance of phosphate at the pH of 6.15 using sodium silicate as silicon resource.