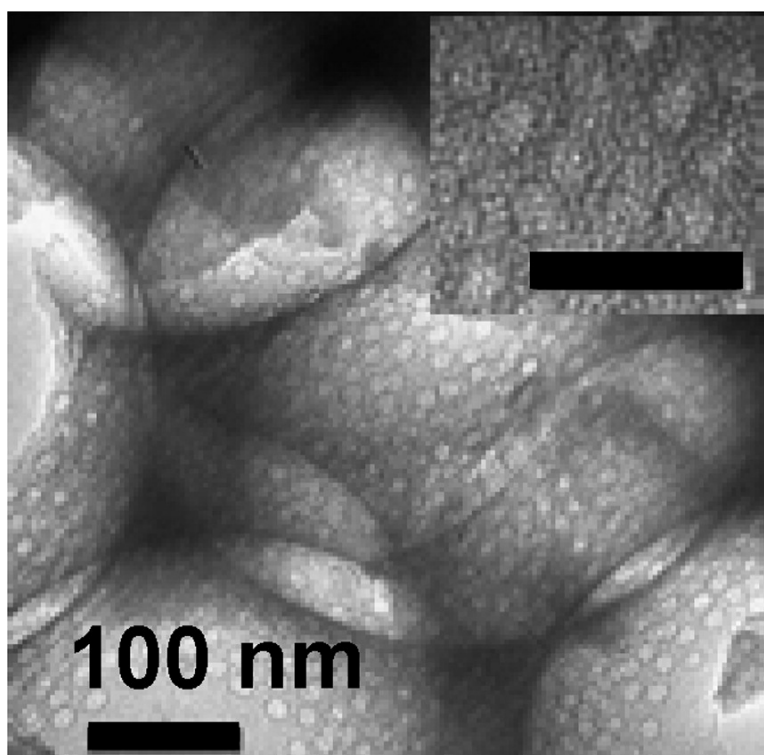


Hierarchical Porous Silica Materials with a Trimodal Pore System Using Surfactant Templates

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Hierarchical Porous Silica Materials with a Trimodal Pore System Using Surfactant Templates

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Hierarchical porous materials have attracted significant attention owing to their important role in the systematic study of structure–property relationship and their technological promise in applications.¹ Also, well-defined multimodal mesopore systems are needed for the elucidation of fundamental aspects of sorption theory such as diffusion and hysteresis. Ideally, such materials should possess adjustable and well-defined macropores and tunable, interconnected mesopore types of different size (between 2 and 50 nm in size) in the macropore walls. On all length scales, the larger pores should be connected through the smaller pores. Furthermore, the material has to be accessible through a facile, well-established sol–gel templating method. Recent studies mainly described the fabrication of bimodal pore systems with macropores and one type of well-defined mesopores,^{2,3} while here we address trimodal pore morphologies with bimodal mesoporosity. The macroporosity can be easily introduced by using colloidal particles,^{3–5} and a suitable strategy to achieve an adjustable hierarchical mesoporosity within the macropore walls is to add mixtures of ionic with nonionic surfactants of different block lengths, thus leading to pores of corresponding sizes.^{6–8} However, this mixing strategy itself does not necessarily result in the desired bimodal mesopore distribution, because often the small surfactant just acts as a co-templating agent for the larger one, just leading to a monomodal pore size.^{6,7,9} Also, in certain cases one mesopore type is created as interparticulate space, e.g. by using cetyltrimethylammoniumchloride and Pluronics surfactants.⁸ Moreover, bimodal and trimodal mesoporous materials may show a nonuniform pore structure.^{2,10–14} To the best of our knowledge, there are no reports on porous silica possessing a trimodal pore structure with a well-defined pore size and morphology on all three length scales. Here, we describe the preparation and characterization of such a material by using poly(styrene) (PS), a novel block copolymer, and an “ionic liquid” (IL) as templates, the latter two possessing optimized templating properties. ILs were reported to exhibit a unique templating behavior, based on the distinct polarizability of the headgroups, leading to highly ordered pore systems.³ In particular, ILs showed a significantly stronger tendency toward self-aggregation and tolerance toward perturbations in supramolecular templating.^{3,15} This distinct property of ILs was therefore expected to help to avoid phase separation with the polymer within the sol–gel process. The block copolymer used in this study, (poly(ethylene-co-butylene)-block-poly(ethylene oxide), “KLE”), $[\text{H}(\text{CH}_2\text{CH}_2)_{0.67}(\text{CH}_2(\text{CH})\text{CH}_2\text{CH}_3)_{0.33}]_{100}(\text{OCH}_2\text{CH}_2)_{86}\text{OH}$, was reported to produce highly ordered spherical mesopores of ca. 14 nm in size in a broad concentration regime.¹⁶

A facile synthetic procedure was developed, in which the PS latex sphere, the block copolymer, and an ionic liquid (1-hexadecyl-3-methylimidazolium-chloride, $\text{C}_{16}\text{mimCl}$, prepared with high purity in our lab) were used as templates to produce macropores and large and small mesopores, respectively.^{15–17}

Tetramethyl orthosilicate (TMOS) was added to a solution of KLE in ethanol and ionic liquid under stirring, followed by the

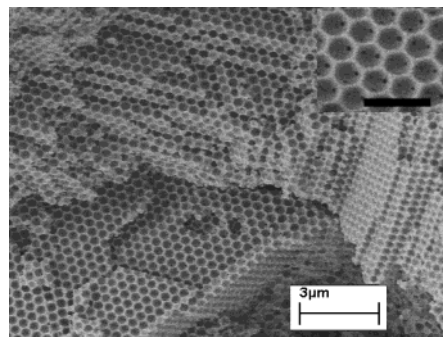


Figure 1. Scanning electron microscopy (SEM) image of the trimodal porous silica material after removal of the templates by calcination. The inset is the high magnification SEM image, the scale bar is 1000 nm.

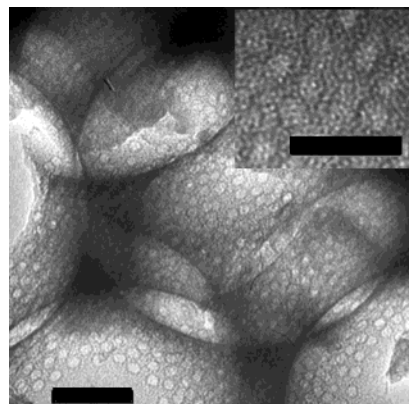


Figure 2. Transmission electron microscopy (TEM) image of the trimodal porous silica materials after removal of the templates by calcination (scale bar = 100 nm). The inset is a TEM image with a scale bar of 50 nm.

addition of an appropriate amount of 0.01 M HCl and stirring for 30 min. The molar ratio of the reactants is 1 TMOS: 1.96×10^{-3} KLE: $0.077 \text{ C}_{16}\text{mimCl}$: 7.35×10^{-4} HCl: 2.5 EtOH: 4.1 H_2O . To a suspension of PS (560 nm particles) in ethanol (0.3 g PS in 1 mL EtOH) was added 1 mL of the precursor solution. The mixture was aged at room temperature, and the resulting material was calcined at 550 °C for 5 h in air. SEM (Zeiss DSM 940, Figure 1) reveals that the material represents a 3D macroporous structure with long-range order and interconnecting windows of ca. 80 nm.

The macropore size is ca. 360 nm with a wall thickness of 100 nm. TEM images (Zeiss EM 912 Ω , Figure 2) show that the inorganic wall texture of the macroporous silica contains two distinguishable types of pores of different sizes. The large spherical mesopores (ca. 12 nm) are attributable to KLE, and the small elongated mesopores (2–3 nm), to the $\text{C}_{16}\text{mimCl}$ surfactant, respectively.^{3,16} More importantly, the smaller mesopores are located between the larger mesopores, thus excluding the possibility of phase separation of KLE and the IL. The synthesis fails with other ionic surfactants such as CTAB (cetyltrimethylammonium bromide).

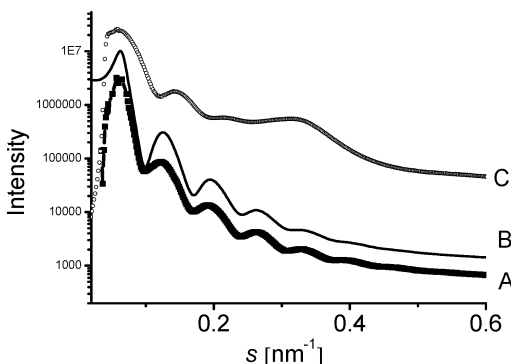


Figure 3. Small-angle X-ray scattering (SAXS) patterns. (A) Mesoporous silica obtained from KLE. (B) Simulation of A. (C) Trimodal porous silica. $s = 2/\lambda \sin \theta$, $\lambda = 0.154 \text{ nm}$.

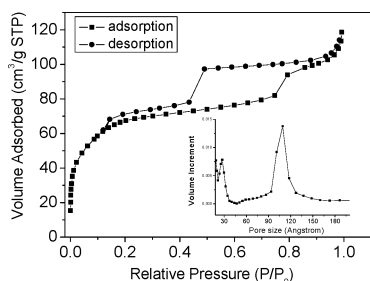


Figure 4. N_2 adsorption-desorption isotherms of the synthesized trimodal porous materials. Inset: pore size distribution (adsorption branch).

The SAXS pattern of the trimodal porous silica (Cu $K\alpha$ rotating anode instrument) (Figure 3 C) shows a series of interferences, the ones below $s = 0.3 \text{ nm}^{-1}$ caused by the KLE mesopore structure (Figure 3 A, B). These interferences are attributable to a distorted cubic system of spherical pores of ca. 12 nm in the trimodal silica (14 nm for monomodal KLE silica) and were analyzed based on the Percus-Yevick hard-sphere approach for their mutual arrangement (for details see Supporting Information).¹⁸ The broad peak at $s = 0.27\text{--}0.40 \text{ nm}^{-1}$ represents the short-range ordering of the small mesopores (distance ca. 3.5 nm), confined between the larger mesopores, thereby confirming the absence of phase separation. The KLE mesopores are smaller than in the monomodal porous KLE silica, which could be a consequence of the interaction of $\text{C}_{16}\text{mimCl}$ with the KLE headgroups.

The SAXS results are confirmed by N_2 sorption (Micromeritics Tristar 3000, Figure 4). The BET surface area is $244 \text{ m}^2 \text{ g}^{-1}$, and the mesoporosity, $0.169 \text{ cm}^3 \text{ g}^{-1}$. Including macropores, the total porosity amounts to be ca. $0.33 \text{ cm}^3 \text{ g}^{-1}$, substantially exceeding the porosity of previous reported systems, e.g. from PS and P123 surfactant [$46 \text{ m}^2 \text{ g}^{-1}$, $0.053 \text{ cm}^3 \text{ g}^{-1}$].² The deviation between the porosity and the initial content in organic matter is attributable to the significant shrinkage during calcination. The pore size distribution (BJH approach) is bimodal (3 and 11 nm) and in accordance with TEM and SAXS. Thus far, we do not have an explanation for the (reproducible) deviation of the adsorption and desorption branches at small p/p_0 , but we speculate that it is due to contraction of the macropore morphology upon pressure changes. The pronounced hysteresis is a consequence of the mesopores being connected through smaller mesopores (2.5 nm).

The present materials represent a significant progress compared to previously reported trimodal porous silica: First, the pores are

well-defined in size and shape on all three length scales. Second, no phase separation is observed, with the small mesopores being located in the walls of the respective larger pores. It is noteworthy that the small ionic liquid template can be added in comparatively large amounts without interfering with the block copolymer mesostructure. The latter observation can be explained by the distinct templating behavior of the KLE polymer and the $\text{C}_{16}\text{mimCl}$ ionic liquid.^{3,9,15} It was recently demonstrated that KLE has optimized templating properties compared to block copolymers of the pluronics family (e.g., F127) with respect to higher stability of the mesostructure and better regularity in terms of the pore size and lattice.¹⁶ Therefore, the KLE mesopore structure tolerates substantial amounts of smaller surfactants added to the precursor solution. Similarly, the $\text{C}_{16}\text{mimCl}$ IL produces mesostructures with higher regularity compared to standard ionic surfactants such as CTAB, owing to the special polarizability of the headgroup.^{9,15}

In summary, the present work shows a general methodology for the preparation of hierarchically ordered porous silica with a well-defined macropore structure and bimodal mesoporosity, using suitable types of novel surfactant templates. In a separate study, the material is used to address fundamental aspects of sorption theory, the elucidation and clarification of “pore blocking” and “cavitation”, which might occur for larger mesopores connected through smaller connecting mesopores (from IL). The size of the latter is easily controllable by our facile templating procedure, using suitable types of ILs. In addition, this material is an ideal candidate with which to study the diffusion of liquids through model pore morphologies, for instance, spin diffusion NMR techniques.

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Supporting Information Available: SAXS analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Yang, P.; Deng, T.; Zhao, D.; Feng, P.; Pine, D.; Chmelka, B. F.; Whitesides, G. M.; Stucky, G. D. *Science* **1998**, *282*, 2244–2246.
- (2) Sen, T.; Tiddy, G. J. T.; Casci, J. L.; Anderson, M. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 4649–4653.
- (3) Zhou, Y.; Antonietti, M. *Chem. Commun.* **2003**, 2564–2565.
- (4) Wijnhoven, J. E. G. J.; Vos, W. L. *Science* **1998**, *281*, 802–804.
- (5) Kuang, D.; Xu, A.; Zhu, J.; Kang, B. *New J. Chem.* **2002**, *26*, 819–821.
- (6) Tian, B.; Liu, X.; Zhang, Z.; Tu, B.; Zhao, D. *J. Solid State Chem.* **2002**, *167*, 324–329.
- (7) Song, M. G.; Kim, J. Y.; Cho, S. H.; Kim, J. D. *Langmuir* **2002**, *18*, 6110–6115.
- (8) Suzuki, K.; Ikari, K.; Imai, H. *J. Am. Chem. Soc.* **2004**, *126*, 462–463.
- (9) Smarsly, B.; Kuang, D.; Antonietti, M. *Colloid Polym. Sci.* **2004**, *282*, 892–900.
- (10) Sun, J.; Shan, Z.; Maschmeyer, T.; Moulijn, J. A.; Coppens, M. O. *Chem. Commun.* **2001**, 2670–2671.
- (11) Yuan, Z.; Blin, J.; Su, B. *Chem. Commun.* **2002**, 504–505.
- (12) Suzuki, K.; Ikari, K.; Imai, H. *J. Mater. Chem.* **2003**, *13*, 1812–1816.
- (13) Smätt, J. H.; Schunk, S.; Lindén, M. *Chem. Mater.* **2003**, *15*, 2354–2361.
- (14) Huerta, L.; Guillem, C.; Latorre, J.; Beltrán, A.; Beltrán, D.; Amorós, P. *Chem. Commun.* **2003**, 1448–1449.
- (15) Zhou, Y.; Antonietti, M. *Adv. Mater.* **2003**, *15*, 1452–1455.
- (16) Thomas, A.; Schlaad, H.; Smarsly, M.; Antonietti, M. *Langmuir* **2003**, *19*, 4455–4459.
- (17) Goodwin, J. W.; Hearn, J.; Ho, C. C.; Ottewill, R. H. *Colloid Polym. Sci.* **1974**, *252*, 464–471.
- (18) Smarsly, B.; Göltner, C.; Antonietti, M.; Ruland, W.; Hoinkis, E. *J. Phys. Chem. B* **2001**, *105*, 831–840.

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