



# One-step synthesis of hydrophobic mesoporous silica ellipsoidal particles with a bimodal mesopore system

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## ABSTRACT

Highly CH<sub>3</sub>-functionalized mesoporous silica ellipsoidal particles with bimodal mesopore structure were prepared via a one-step route using polymethylhydrosiloxane (PMHS) and tetraethoxysilane (TEOS) with triblock copolymer P123 as template under acidic conditions. N<sub>2</sub> adsorption-desorption, XRD, HRTEM, SEM and <sup>29</sup>Si MAS NMR were used to characterize the obtained material. The introduction of PMHS into the synthetic system led to the formation of a bimodal mesopore system consisting of framework mesopores of ~7.2 nm and textural mesopores of ~29.4 nm. The two scale pores were directly observed in HRTEM images and indirectly proved by the two-step increase in N<sub>2</sub> adsorption-desorption isotherm. Also, PMHS played an important role in morphology controlling and organic functionalization, ensuring monodisperse ellipsoidal particle morphology and high CH<sub>3</sub> functionalization degree of the mesoporous silica product. Subjected to removing highly diluted nonylphenol from aqueous solution, the hydrophobic bimodal mesoporous silica ellipsoidal particles showed high adsorption performance.

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## 1. Introduction

Hierarchical porous materials with two or more levels of porosity have attracted significant attention owing to their important role in the systematic study of structure–property relationships and their technological promise in applications such as catalysis, adsorption and separation [1]. Such materials can improve the diffusion of guest molecules through the inorganic network of pores and channels, as the larger pores allow for better molecular accessibility, whereas the smaller pores provide high surface areas and large pore volumes [2].

Commonly, the pores in different sizes are derived from the templates of different length scales. The macropores can be obtained from colloidal particles or poly(dimethylsiloxane) (PDMS) molds, the mesopores can be from surfactant templates, and the micropores can be produced from some structure-directing agents such as tetramethylammonium hydroxide (TMAOH), tetraethylammonium hydroxide (TEAOH), and tetrapropylammonium hydroxide (TPAOH). Most of the hierarchical porous materials can be synthesized by using mixed templates [3].

Up to now, various types of mesoporous silica materials with a bimodal pore size distribution have been reported. Sun et al. [4] presented a method by means of which particles of a primary mesoporous material, e.g. MCM-41, were crosslinked using triblock copolymer assemblies as templating agents to form a material with independently controlled bimodal pore structure. Zhao et al. [5] have prepared mesoporous silica spheres with bimodal pore structure from silica/hyperbranched polyester using a simple sol-gel process. Mixed hydrocarbon/fluorocarbon templating has been employed to generate hierarchical pore systems [6,7]. Areva et al. [6] reported on their one-pot aerosol synthesis of spherical core-shell silica nanoparticles with bimodal porosity by using the non-ionic triblock copolymer F127 and the cationic fluorocarbon surfactant IC-11. Xing et al. [7] presented a facile synthetic approach to well-defined bimodal porous silica using mixed cetyltrimethylammonium chloride (CTAC) and 1,1,2,2-tetrahydro-perfluorodecylpyridinium chloride (HFDePC) as templates.

Organic-functionalized mesoporous silica materials have been widely used in many applications because such hybrid materials possess the dual characteristics of inorganic supports and organic groups, and their surface properties can be easily modified to meet special applications. In recent years, organic-functionalized bimodal mesoporous silica materials have been rarely developed. Yang et al. [8] reported on the synthesis of phosphonic acid

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functionalized mesoporous organosilicas with bimodal nanostructure by a post-synthesis treatment method. Gong et al. [9] found that the co-presence of some organosiloxanes and a specific surfactant could improve the assembly of organic-functionalized MSU-X with a bimodal pore size distribution. In their later study, they investigated the synthesis of silica with disordered bimodal mesopore structure. The organic-functionalized mesoporous silica with a bimodal pore size distribution was synthesized from organotrialkoxysilane and TEOS in the first step. Then the incorporated organic groups were removed using programmed calcination and pure silica with disordered bimodal mesopore structure was obtained [10].

Organic-functionalized bimodal mesoporous silica materials not only have tailored surface properties due to their organic features, but also can improve the diffusion of guest molecules through the bimodal mesopore structure. Unfortunately, the research on the synthesis of such materials has been seldom reported so far. In the present work, an alternative one-step synthetic method is provided for the preparation of highly  $\text{CH}_3$ -functionalized bimodal mesoporous silica ellipsoidal particles simply by co-condensation of two different silica precursors PMHS and TEOS in the presence of P123 as template. PMHS had a great impact on the mesostructure, morphology and functionalization. So-obtained hydrophobic bimodal mesoporous silica was used as adsorbent for removal of highly diluted nonylphenol from aqueous solution.

## 2. Experimental

### 2.1. Synthesis

Polymethylhydrosiloxane (PMHS) and tetraethoxysilane (TEOS) were employed as silica precursors and triblock copolymer P123 was used as templating agent.

In a typical synthesis, 2 g of P123 was completely dissolved in 15 mL of deionized water and 30 mL of a 2 mol/L HCl solution at 40 °C. 2.21 g of TEOS and 2.21 g of PMHS were added together to the above solution under vigorous stirring. After 24 h of stirring at 40 °C, the reaction mixture was allowed to age at 100 °C for another 24 h under quiescent conditions. Then the white precipitate was recovered by filtration, washed with deionized water, and dried at 80 °C. Finally, the template inside the as-synthesized material was removed by Soxhlet extraction with ethanol for 48 h.

### 2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a D8 Advance Bruker AXS diffractometer using  $\text{Cu K}\alpha$  radiation.  $\text{N}_2$  adsorption–desorption isotherms were measured at 77 K on a Micromeritics Tristar 3000 Sorptometer. The samples were degassed at 353 K and under a vacuum of  $10^{-6}$  Torr for at least 12 h prior to the measurement. The specific surface areas were calculated using the multiple-point Brunauer–Emmett–Teller (BET) method. The pore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) model. The pore channels were observed by high-resolution transmission electron microscopy (HRTEM) images on JEOL JEM-2010. Field emission scanning electron microscopy (FESEM) images were obtained on LEO 1530VP.  $^{29}\text{Si}$  MAS NMR experiments were performed on a Varian Infinityplus-300 spectrometer using 7.5 mm probe under magic-angle spinning.

### 2.3. Adsorption of nonylphenol in aqueous solution

In typical adsorption experiments, 10 mg (or 15 mg) of the adsorbent was added into 50 g (or 55 g) of an aqueous solution of

nonylphenol with an initial concentration of 4.9 ppm. After adsorption with stirring for a given time, the supernatant solution was separated by millipore filter (0.22  $\mu\text{m}$ ) and the residual nonylphenol was analyzed using a Shimadzu UV-3150PC spectrophotometer at 278 nm.

## 3. Results and discussion

### 3.1. Bimodal mesopore structure determination

Fig. 1 shows the  $\text{N}_2$  adsorption–desorption isotherm and the corresponding BJH pore size distribution of the obtained hydrophobic bimodal mesoporous silica ellipsoidal particles. There are two obvious capillary condensation steps at relative pressure ( $P/P_0$ ) ranges of 0.6–0.8 and 0.8–1.0 in the isotherm, indicating the formation of bimodal mesopore structure. The corresponding BJH pore size distribution is bimodal with two clear peaks at 7.2 and 29.4 nm, further showing bimodal mesoporosity. Moreover, the BET surface area and total pore volume are 574  $\text{m}^2/\text{g}$  and 2.50  $\text{cm}^3/\text{g}$ , respectively. Based on the structural characterization results, the synthesized material possessed excellent textural properties including bimodal mesoporosity, high specific surface area and extremely large pore volume.

The small-angle XRD pattern of the hydrophobic bimodal mesoporous silica ellipsoidal particles as shown in Fig. 2 only consists of a single broad (1 0 0) diffraction peak corresponding to the  $d$ -spacing of 11.5 nm. By contrast, the XRD pattern of SBA-15 mesoporous silica generally showed four well-resolved peaks indexable as (1 0 0), (1 1 0), (2 0 0), and (2 1 0) reflections associated with  $p6mm$  hexagonal symmetry. It is possible that the bimodal mesopore structure and the introduction of a large number of methyl groups directly led to the formation of the broad (1 0 0) diffraction peak.

To further elucidate the bimodal mesopore characteristics, the detailed texture was investigated by HRTEM technique. Fig. 3a depicts a direct image of the wormhole-like homogeneous structure of the obtained bimodal mesoporous silica ellipsoidal particles. Small wormhole-like mesopores and large irregular-shaped mesopores can be observed in Fig. 3b, which is in good agreement with the above  $\text{N}_2$  adsorption–desorption results.

According to the literature [11], the polymerization of silica might lead to the introduction of an attractive force between surfactant micelles and thus played an important role in the micellar packing in a 2D hexagonal mesostructure because oligomeric/polymeric silica could adsorb on the EO palisade layer

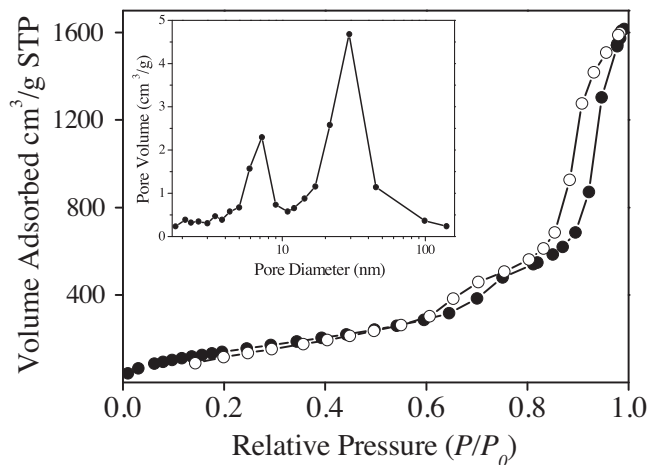
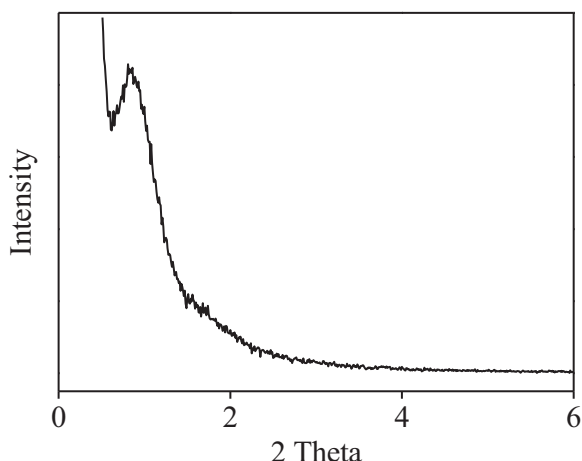


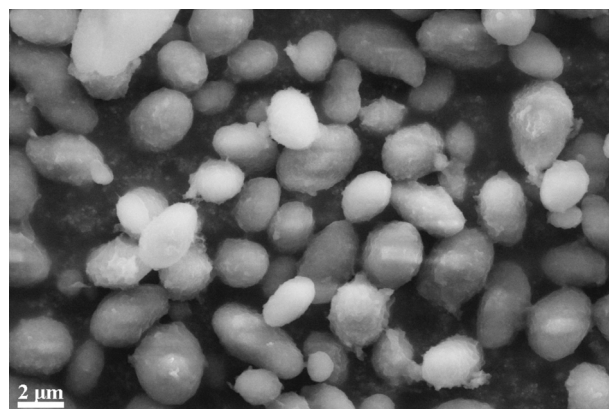
Fig. 1.  $\text{N}_2$  adsorption–desorption isotherm of the hydrophobic bimodal mesoporous silica ellipsoidal particles. Inset: BJH pore size distribution of the sample.



**Fig. 2.** Powder XRD pattern of the hydrophobic bimodal mesoporous silica ellipsoidal particles.

of the micelles and had the ability to bridge to another micelle. In the present work, however, the addition amount of TEOS adopted in the synthesis is much less than that needed in the formation of a well-ordered hexagonal mesochannel array in the presence of triblock copolymer P123. An inadequate amount of TEOS might weaken the attractive force between surfactant micelles significantly and was unfavorable to the self-assembly of the hybrid micelles to a 2D hexagonal mesostructure.

Hydrogen-containing silicone oil PMHS is distinctive in molecular structure, possessing a long chain structure of repeating unit  $[\text{CH}_3(\text{H})\text{SiO}]_n$ . The introduction of PMHS, which contains a large number of hydrophobic groups, into the synthetic system induced a strong interfacial tension between oil phase and water phase, and thus flexible PMHS molecular chains showed a tendency to form loops in aqueous solution in order to decrease the interfacial tension. Meanwhile, the Si-H groups in PMHS could be hydrolyzed into Si-OH groups under the weak catalysis of HCl. The Si-OH groups in PMHS would co-condense with the hydrolyzate of TEOS with the result that hybrid (P123-siliceous species) micelles could not pack in a 2D hexagonal mesostructure under the action of a weakened attractive force. The hybrid micelles might be arranged end to end along the flexible PMHS molecular chains to form tortuous tubules with a diameter of about 7 nm after the

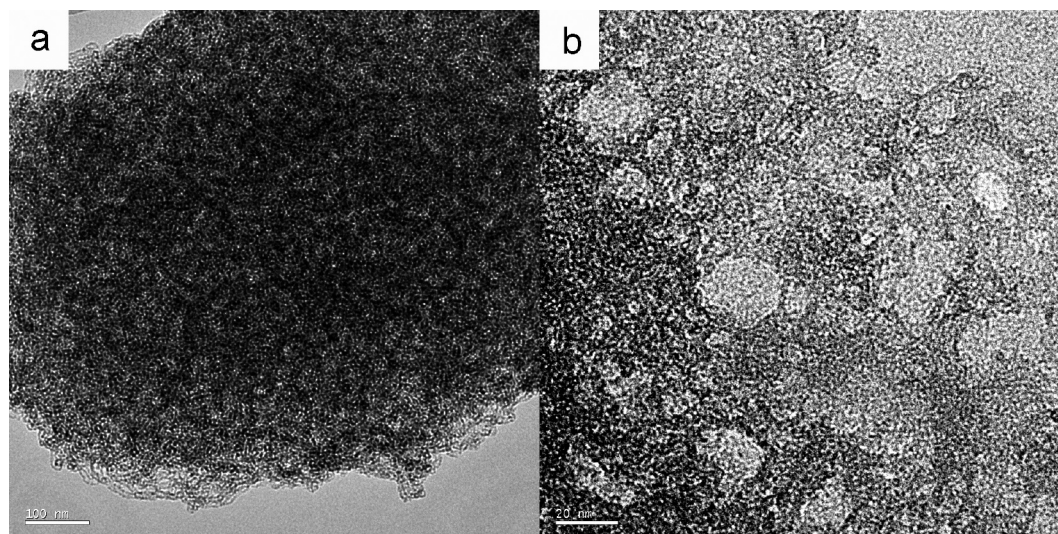


**Fig. 4.** SEM image of the hydrophobic bimodal mesoporous silica ellipsoidal particles.

removal of P123 template, which led to the formation of small wormhole-like mesopores. These tortuous tubules interwove to form the resulting ellipsoidal particles. Owing to the fact that P123 is the only templating agent adopted in the synthesis, the formation of large irregular-shaped mesopores might be attributed to toroidal bend of flexible PMHS molecular chains in aqueous solution. Therefore, PMHS not only was a silicon source, but also played a crucial role in the formation of bimodal mesopore structure.

### 3.2. Particle morphology

**Fig. 4** shows the particle morphology of the obtained material. Clearly, the material consists mainly of monodisperse ellipsoidal particles with a relatively uniform particle size of  $\sim 2 \mu\text{m}$ . As is known, pure siliceous SBA-15 generally possesses a fiber-like morphology, so it can be speculated that the addition of PMHS into the synthetic system had a great influence on the morphology of the produced silica. Previous research has shown that when a nonspherical inclusion of a liquid is suspended into another immiscible liquid, it evolves into a spherical shape due to interfacial tension. In our study, PMHS is absolutely immiscible with water due to its long chain structure of repeating unit  $[\text{CH}_3(\text{H})\text{SiO}]_n$ . Thus, the introduction of PMHS into acidic aqueous solution led to the formation of a nonionic surfactant–oil–water



**Fig. 3.** HRTEM images of the hydrophobic bimodal mesoporous silica ellipsoidal particles: (a) low-magnification image and (b) high-magnification image.



dispersion system, in which the oil phase was composed of PMHS molecular chains and triblock copolymer P123 played roles as templating agent and solubilizer. Due to the strong interfacial tension, the numerous  $\text{CH}_3$  groups evenly distributed in PMHS molecular chains should be enriched inside the oil phase because of their hydrophobic trait and outside the oil phase were the hydrophilic Si–OH groups under the weak catalysis of HCl. Also, the Si–OH groups on the surface of hybrid (P123-siliceous species) micelles would co-condense with the Si–OH groups in PMHS with the result that the hybrid micelles got close to the oil phase and self-assembled end to end along the flexible PMHS molecular chains to form tortuous tubules after the removal of P123 template, which interwove to form the resulting ellipsoidal particles.

### 3.3. $^{29}\text{Si}$ MAS NMR

Solid-state  $^{29}\text{Si}$  MAS NMR can provide information about the silicon environment and  $\text{CH}_3$  functionalization degree [12]. Fig. 5 depicts the  $^{29}\text{Si}$  MAS NMR spectrum of the hydrophobic bimodal mesoporous silica ellipsoidal particles, which displays five main resonance signals at  $-36$ ,  $-56$ ,  $-66$ ,  $-101$  and  $-111$  ppm, corresponding to  $D^2$  [ $\text{CH}_3(\text{H})\text{-Si}(\text{OSi})_2$ ],  $T^2$  [ $\text{CH}_3\text{-Si}(\text{OSi})_2(\text{OH})$ ],  $T^3$  [ $\text{CH}_3\text{-Si}(\text{OSi})_3$ ],  $Q^3$  [ $\text{Si}(\text{OSi})_3(\text{OH})$ ] and  $Q^4$  [ $\text{Si}(\text{OSi})_4$ ], respectively. It is well-known that with NaOH as the catalyst, the active Si–H groups in PMHS could be rapidly hydrolyzed to form Si–OH groups which would come into the subsequent co-condensation with the hydrolyzate of TEOS. Because of the weaker catalysis of HCl and the strong interfacial tension between oil phase and water phase induced by the introduction of PMHS, the incomplete hydrolysis of Si–H groups took place and led to the existence of the  $D^2$  resonance signal.

The  $(D+T)/(D+T+Q)$  ratio calculated from the normalized peak areas is 61.1%, namely, the  $\text{CH}_3$  functionalization degree of the hydrophobic bimodal mesoporous silica ellipsoidal particles is as high as 61.1%, which exceeds the conventional methyl group loading of 10% (in molar) in mesoporous silica framework by one-step synthesis. Thus, the introduction of PMHS into the synthetic system realized high  $\text{CH}_3$  functionalization degree of the obtained material.

### 3.4. Adsorption of nonylphenol in aqueous solution

Alkylphenolic chemicals such as nonylphenol, which are biodegradation products of alkylphenol polyethoxylate resin, have

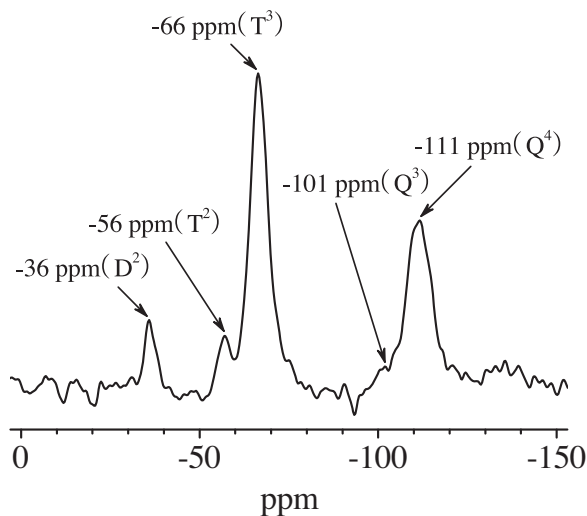


Fig. 5.  $^{29}\text{Si}$  MAS NMR spectrum of the hydrophobic bimodal mesoporous silica ellipsoidal particles.

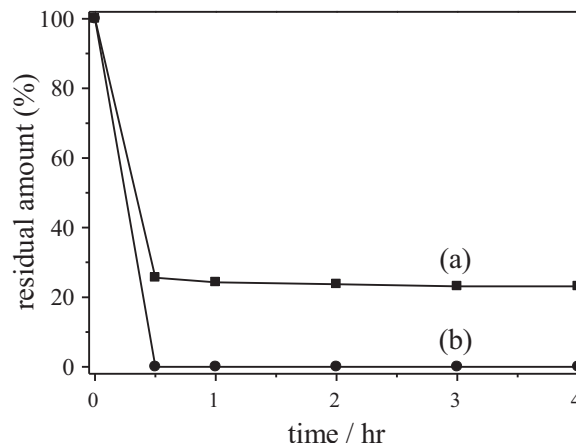


Fig. 6. Time courses of nonylphenol concentrations in aqueous solution during the adsorption with different amounts of the hydrophobic bimodal mesoporous silica ellipsoidal particles: (a) 10 mg of adsorbent/50 g of an aqueous solution of nonylphenol (4.9 ppm) and (b) 15 mg of adsorbent/55 g of an aqueous solution of nonylphenol (4.9 ppm).

been found to be the major oestrogenic contaminants to induce feminizing effects in fish [13]. Nonylphenol in aqueous solution even at a very low concentration (parts per million, ppm) could cause serious environmental pollution problems. Adsorption-based processes may lead to one of the most efficient routes for removal of toxic substances. The fundamental and great challenge is developing highly efficient adsorbents. Recent research has revealed that organic functional groups, grafted on porous inorganic substrates, could greatly improve the sorption efficiency of the inorganic materials due to their high affinity to a certain class of toxic contaminants [14].

In this work, we investigated the performance of the obtained hydrophobic bimodal mesoporous silica ellipsoidal particles as adsorbent for removal of highly diluted nonylphenol from aqueous solution. Fig. 6 shows the time courses of nonylphenol concentrations in aqueous solution during the adsorption with different adsorbent amounts. At first, 10 mg of the adsorbent was added into 50 g of an aqueous solution of nonylphenol (4.9 ppm). Obviously, the highest adsorption efficiency reaches 76.9% as shown in Fig. 6a. In order to further improve the adsorption capacity, an increment adsorbent amount was adopted. 15 mg of the adsorbent was added into 55 g of an aqueous solution of nonylphenol (4.9 ppm). It can be observed in Fig. 6b that highly diluted nonylphenol was totally removed within 1 h by the obtained hydrophobic adsorbent. The excellent adsorption performance might be attributed to the bimodal mesopore structure and the grafting of a large number of methyl groups. The system with bimodal mesoporosity could facilitate the faster mass transfer of nonylphenol molecules to the adsorption sites in ellipsoidal particles. The grafting of a large number of methyl groups could effectively improve the adsorption by hydrophobic interaction. Moreover, Inumaru et al. [15,16] have investigated the molecular selective adsorption of alkylanilines and alkylphenols on alkyl-grafted MCM-41. They gave evidence of novel organic–inorganic cooperative molecular recognition in the nanostructure and held that alkyl-grafted MCM-41 recognized hydrophobic and hydrophilic groups of such molecules simultaneously through the inorganic walls and the organic moiety in the nanostructure and thus achieved high adsorption selectivity. Therefore, in this work, the total adsorption of nonylphenol might be attributed to the bimodal mesopore structure and the organic–inorganic cooperative molecular recognition in the nanostructure.

#### 4. Conclusions

A one-step synthesis route is provided for the preparation of hydrophobic bimodal mesoporous silica ellipsoidal particles by co-condensation of PMHS and TEOS in the presence of triblock copolymer P123 as template under acidic conditions. The addition of PMHS had a great influence on the meso-structure and morphology of the produced silica, leading to the formation of bimodal mesopore structure and monodisperse ellipsoidal particle morphology. Also, the introduction of PMHS into the synthetic system realized high CH<sub>3</sub> functionalization degree of the produced silica. Thus-obtained hydrophobic bimodal mesoporous silica ellipsoidal particles could be used as an effective adsorbent for removal of organic pollutant nonylphenol at a very low concentration (ppm) from aqueous solution.

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#### References

- [1] D.B. Kuang, T. Brezesinski, B. Smarsly, J. Am. Chem. Soc. 126 (2004) 10534–10535.
- [2] X.H. Cai, G.S. Zhu, W.W. Zhang, H.Y. Zhao, C. Wang, S.L. Qiu, Y. Wei, Eur. J. Inorg. Chem. 2006 (2006) 3641–3645.
- [3] F.Q. Zhang, Y. Yan, Y. Meng, Y.L. Xia, B. Tu, D.Y. Zhao, Micropor. Mesopor. Mater. 98 (2007) 6–15.
- [4] J.H. Sun, Z.P. Shan, T. Maschmeyer, J.A. Moulijn, M.O. Coppens, Chem. Commun. (2001) 2670–2671.
- [5] Y.B. Zhao, J.H. Zou, W.F. Shi, L.X. Tang, Micropor. Mesopor. Mater. 92 (2006) 251–258.
- [6] S. Areva, C. Boissière, D. Grosso, T. Asakawa, C. Sanchez, M. Lindén, Chem. Commun. (2004) 1630–1631.
- [7] R. Xing, H.J. Lehmler, B.L. Knutson, S.E. Rankin, Langmuir 25 (2009) 6486–6492.
- [8] Q.H. Yang, J. Yang, J. Liu, Y. Li, C. Li, Chem. Mater. 17 (2005) 3019–3024.
- [9] Y.J. Gong, D. Wu, Y.H. Sun, Z.D. Zhang, H.G. Zhu, D.Y. Zhao, Chin. Chem. Lett. 12 (2001) 747–750.
- [10] Y.J. Gong, L. Mu, T. Dou, Petrol. Sci. 4 (2007) 94–99.
- [11] K. Flodström, H. Wennerström, V. Alfredsson, Langmuir 20 (2004) 680–688.
- [12] Q. Gao, W.J. Xu, Y. Xu, D. Wu, Y.H. Sun, F. Deng, W.L. Shen, J. Phys. Chem. B 112 (2008) 2261–2267.
- [13] K. Inumaru, J. Kiyoto, S. Yamanaka, Chem. Commun. (2000) 903–904.
- [14] D.J. Yang, B. Paul, W.J. Xu, Y. Yuan, E.M. Liu, X.B. Ke, R.M. Wellard, C. Guo, Y. Xu, Y.H. Sun, H.Y. Zhu, Water Res. 44 (2010) 741–750.
- [15] K. Inumaru, Y. Inoue, S. Kakii, T. Nakano, S. Yamanaka, Chem. Lett. 32 (2003) 1110–1111.
- [16] K. Inumaru, Y. Inoue, S. Kakii, T. Nakano, S. Yamanaka, Phys. Chem. Chem. Phys. 6 (2004) 3133–3139.