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ARTICLE TYPE

Stereoselective adsorption utilizing L-phenylalanine imprinting chiral ordered mesoporous silica

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L-phenylalanine imprinting chiral ordered mesoporous silica (L-Phe-COMS) was facile synthesized in the presence of amino acid phenylalanine by combining tetraethyl orthosilicate and quaternized aminosilane silica sources. The obtained COMS was favoured with MCM-41-type structure, narrow pore size distribution, and high specific surface area characterized by powder X-ray diffraction and N_2 adsorption experiments. The imprinting chirality of COMS was disclosed by mixed and separate L- and D-phenylalanine adsorption on the L-Phe-COMS with a stereoselective adsorption capacity up to 3.24. In addition, six racemic mixtures including amino acids and drugs were explored to test the stereoselective adsorption capacity of L-Phe-COMS. The imprinting chiral ordered mesoporous silica take advantages of straightforward synthesis approach and robust stereoselective adsorption capacity, making it a processing candidate for chiral adsorption and separation.

Introduction

Recently, chiral ordered mesoporous silica (COMS) materials have become the hotspot and provide a new approach to obtain pure enantiomers because of high surface area, large pore volume, decorating accessibility of the pore wall or the framework, high thermo stability and so on.[1-4] Currently, COMS are mainly synthesized by achiral silica source, and combining chiral surfactants or achiral surfactants.[5-7] COMS materials have also been previous developed in our laboratory,[8] which was synthesized using the chiral anionic surfactant as a single template. However, there are some defects in the synthesis by chiral surfactants, for example, most of the chiral surfactants are complicated to synthesize, sometimes even multiple surfactants or chiral molecules are needed as inducers in the procedure.

Amino acids are pH-sensitive zwitterionic surfactants as the inducers and display the properties of anionics at high pH. Toshiyuki *et al*. demonstrated that a simple amino acid monomer can promote the formation of silica, resulting in preparation of the well-ordered silica nanospheres.[9] Furthermore, with their simple structures and the ready availability of both enantiomers, amino acids provide an inexpensive approach for resolution studies and have been used either as the racemate for resolution or as the chiral selector for resolution of racemic mixtures of several other compounds.[10] Coronas *et al*. reported the COMS imprinting with amino acids arginine, histidine, isoleucine, and proline exhibiting enantioselectivity.[11,12] Meanwhile, L-phenylalanine (L-Phe) has been successfully applied to the chiral chromatographic separation as chiral selector in mobile phase.[13-15] Moreover, phenylalanine is a well-known α–amino acids that all of human essential them possessing the L-configuration. Phenylalanine containing of benzene and amino, carboxylic acid moieties facilitate the formation of COMS through non-covalent multiple interactions with silica resource and surfactants added involving of electrostatic interaction and hydrophobic interaction.[16,17]

However, there have been few reports to utilize the COMS imprinting with L-Phe in the stereoselective adsorption so far. In this work, L-Phe imprinting COMS (L-Phe-COMS) was synthesized in basic media by combining tetraethyl orthosilicate and quaternized aminosilane (as a templating reagent role) silica source together with amino acid L-phenylalanine. L-Phe-COMS showed a stereoselective adsorption capacity up to 3.24 for D,L-phenylalanine. The possible mechanisms of synthesis and stereoselective adsorption were also discussed in this work.

Experimental

Synthesis of L-phenylalanine imprinting chiral ordered mesoporous silica

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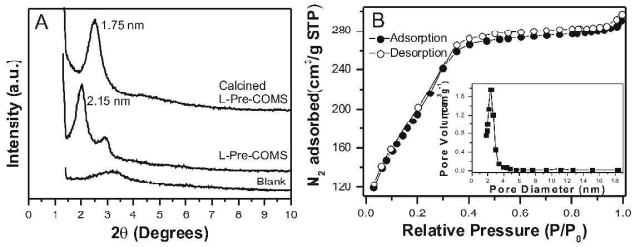


Fig.1 (A) Low-angle XRD patterns of blank (without L-phenylalanine), $_L$-Phe-COMS and calcined $_L$-Pre-COMS and (B) N_2 adsorption-desorption isotherms of calcined $_L$-Phe-COMS and the inset is corresponding BJH pore size distribution.

$_L$-Phe-COMS were generally prepared using tetraethyl orthosilicate （TEOS） as the main silica source and the N-3-[3- (trimethoxysilyl) propyl]-N-octadecyl-N,N-dimethylammonium chloride (C_{18}-TMS) as the initiator, with the molar composition of TEOS:C_{18}-TMS:$_L$-phenylalanine:H_2O:NaOH = 6:1:2:1000:4. Typically, 0.605 g of $_L$-phenylalanine was dissolved in 47.58 mL ultrapure water at constant temperature, then 2.637 g C_{18}-TMS, 3.337 g TEOS were added stepwise and the mixture was stirred at constant temperature. The apparent pH value was about 11 until the end of the synthesis. The resulting mixtures were poured into Teflon-kettle and maintained at 80 ˚C for 24 h. The product was then washed by deionized water for several times till the pH value decreased approximately to 7.0, washed by ethanol three times, centrifuged at 3000 rpm, and the precipitate was dried at 80 ˚C overnight. Finally, the COMS material was obtained by calcination at 650 ˚C for 8 hours to remove the organic materials. For comparison purposes, samples were also prepared without $_L$-phenylalanine (blank COMS). The major material source is described in the Electronic Supplementary Information (ESI). The materials prepared were characterized by FTIR, SEM, TEM, XRD and nitrogen sorption; the details of instruments are shown in the ESI. The stereoselective adsorption capacity of $_L$-phenylalanine adsorbed by $_L$-Phe-COMS was studied. The stereoselective adsorption of other racemic amino acids ($_{DL}$-phenylalanine, $_{DL}$-alanine, $_{DL}$-lysine and $_{DL}$-tryptophan) and drugs (naproxen and chlorpheniramine maleate) were also studied. The experiment procedure in detail is represented in the ESI.

Stereoselective adsorption experiments

10 mg $_L$-phenylalanine were dissolved by 10 mL ultrapure water in seven round flasks and 40 mg $_L$-Phe-COMS were added to the solution respectively. Residuals were collected at different time intervals (0 h, 12 h, 24 h, 36 h, 48 h, 60 h and 72 h) to determine unabsorbed $_L$-phenylalanine. Control experiments were preformed with blanks containing no $_L$-phenylalanine under the same conditions as for the mixed solution described above. The adsorption kinetics of $_D$-phenylalanine in $_L$-Phe-COMS was further performed to determine the stereoselective adsorption capacity. Afterward, the suspensions were analyzed by circular dichroism spectra (CD) analysis.

To further investigate stereoselective adsorption ability of this materials, 10 mg $_{D,L}$-phenylalanine, $_{D,L}$-alanine and $_{D,L}$-lysine were dissolved in 10 mL ultrapure water, $_{DL}$-tryptophan, naproxen and chlorpheniramine maleate were dissolved in 10 mL methanol, respectively; and then 40 mg $_L$-Phe-COMS was added to the above solutions. Finally, the residual was collected after 72 hours to determine the unabsorbed molecules by CD analysis.

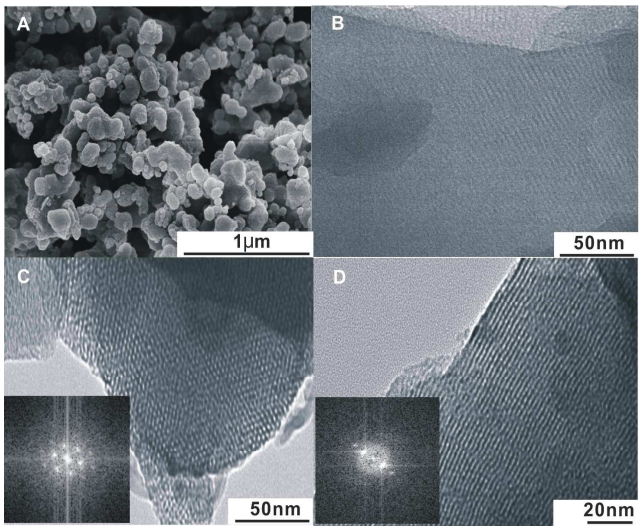


Fig.2 (A) SEM of $_L$-Phe-COMS; (B) TEM of template-unremoved COMS; (C) TEM of $_L$-Phe-COMS and FFT (parallel to the pore channels) and (D) TEM of calcination $_L$-Phe-COMS (perpendicular to the pore channels).

Results and discussion

Characterization of the prepared L-Phe-COMS

FT-IR was performed to validate the removal of organic materials. Peaks in 2921.43 cm^{-1} and 2848.92 cm^{-1} are the bending vibrations of -C-H in C_{18}-TMS belongs to organic materials and the absence of the two peaks in $_L$-Phe-COMS indicates the complete removal of organic materials (Fig.S1A). The spectrum of $_L$-Phe-COMS show the successful formation of silica skeleton due to the emerging of stretching vibration (1124.43 cm^{-1}) and bending vibration (850.78 cm^{-1}) of -Si-O-Si-. The XRD patterns of COMS prepared with L- forms of phenylalanine (Fig. 1A) show four characteristic peaks (at 2.1°, 3.5°, 4.0°, and 5.3°) of MCM-41 hexagonal structure, which could be indexed as (100), (110), (200), and (210).[18] In addition, the material retained its XRD order upon calcination. However, an evident contraction was obtained from 2.15 to 1.75 nm (d-spacing values obtained from Bragg's law). The XRD pattern of a blank material prepared without phenylalanine is included for comparison, revealing that this material did not possess the MCM-41-type structure.

N_2 adsorption-desorption isotherms and corresponding pore size distribution of extracted mesoporous materials are shown in Fig.1. The BJH pore diameters were in the narrow range from 2.3 nm to 2.5 nm, and the values of BET surface area (m^2/g) and pore volume (cm^3/g) were 730 and 0.47, respectively obtained by N_2 relative pressure arranging from 0.05 to 0.20. N_2 adsorption-desorption isotherms is assigned to a type-IV with the absence of hysteresis loop consistent with pore diameters below approximately 4 nm of MCM-41 materials,[19] which suggested the mesoporous structure of $_L$-Phe-COMS. SEM image of $_L$-Phe-

COMS as-obtained showed the irregular nanoparticles (Fig.2A). TEM image of template-unremoved COMS (Fig.2B) clearly exhibited the existence of ordered mesopore and the ordered mesoporous feature still existed in the calcined $_L$-Phe-COMS (Fig.2C, D). Hexagon channels were distinctly observed by Fig.2D different from Fig. 2B. Furthermore, insets of Fig.2 C and D are fast Fourier transform (FFT) diffractograms of along directions perpendicular (C) and parallel (D) to the channels axis which are assigned to two orientations of *p*6mm plane of feature characteristics MCM-41 materials.

Samples	L-Phe	NaOH	C_{18}.TMS	TEOS	H_2O	Initial temperature (℃)	Reaction time (h)
COMS-1	2	2	1	6	1000	25	24
COMS-2[a]	2	4	1	6	1000	25	24
COMS-3	2	8	1	6	1000	25	24
COMS-4	2	4	1	3	1000	25	24
COMS-5	2	4	1	9	1000	25	24
COMS-6	2	4	1	6	1000	0	24
COMS-7	2	4	1	6	1000	50	24
COMS-8	2	4	1	6	1000	25	12
COMS-9	2	4	1	6	1000	25	36

[a]Note: COMS-2 was marked as $_L$-Phe-COMS

Table 1 Effect of $_L$-phenylalanine, C_{18}-TMS, TEOS and H_2O on preparation of $_L$-Phe-COMS

Effect of $_L$-phenylalanine, C_{18}-TMS, TEOS and H_2O on preparation of $_L$-Phe-COMS

For optimum preparation of $_L$-Phe-COMS, COMS-n (n = 1-9) were synthesized by different molar rations of precursors as shown in Table 1 with the same procedure described above. To investigate the effect on mesoporous pore order, in which the COMS-2 was marked as $_L$-Phe-COMS in this work. It was observed that sodium hydroxide concentration significantly affected the mesoporous order. The XRD of COMS-1 in Fig.S2 showed lower mesoporous order than that of COMS-2, which may result from the faster TEOS polymerization and slower arrangement of ordered pore structure into the silica framework when in the weak alkaline environment. Appropriate amounts of OH^- , which compressed double electric layer and weakened the interaction among the charged surfactants arranged the surfactants more tightly and promoted the surfactant molecules aggregating into the micelles. Furthermore, the tightly-arranged surfactants could promote the silica aggregation on the micelles. However, the crippling interaction among the organic-inorganic compounds resulted from overwhelming OH^- existed in the micelles decreased the mesoporous order (Fig.S2, COMS-3). The silicon polymerization could be also inhibited and unfavourable monomer form started to exist with excessive OH^- , under which circumstances would be difficult to obtain solid product and mesoporous structure. Overall, the amounts of OH^- played a key role in morphology and mesoporous order. The ratio of C_{18}-TMS / TEOS also had an effect on mesoporous order. Silica skeleton was difficult to form due to the inadequate TEOS when the ratio was high (Fig.S3, COMS-4), whereas higher ratio would affect the formation of micelles and decrease the mesoporous order. It was showed that higher initial temperature was favourable of mesoporous order (Fig.S4, COMS-6). However, mesoporous order would be reduced over the highest temperature due to micelles order decreasing (Fig.S4, COMS-7).

Appropriate reaction time played a role in mesoporous order which was observed from Fig.S5 (COMS-8, and COMS-9).

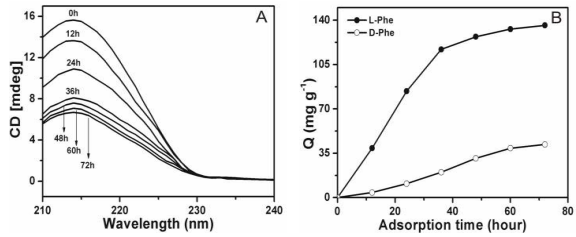


Fig.3 (A) CD spectra of the residual $_L$-phenylalanine(initial concentration of 1.0 mg ml^{-1}) adsorbed on 40 mg of $_L$-Phe-COMS after 0 h, 12 h, 24 h, 36 h, 48 h, 60 h, 72 h. (B)The kinetic curves of $_L$-phenylalanine, $_D$-phenylalanine (initial concentration of 1.0 mg ml^{-1}) adsorbed on 10 mg of $_L$-Phe-COMS, respectively.

Under alkaline condition, the electrostatic interaction between solvated silicate anions and cationic surfactant assemblies (often referred to the organic template), combined with the hydrophobic interactions of the nonpolar surfactant tails, drives the formation of mesostructured silica.[16] It was deduced that hydrolyzed C_{18}-TMS surfactant molecule condensed to form the positively charged dimers. In addition, both negatively charged amino acid molecules and silica species had an electrostatic interaction with the dimers under basic conditions, and the dimers further organized into micelles due to the hydrophobic interaction of the nonpolar surfactant tails (C_{18}-TMS). Meanwhile, the silica species combined with the C_{18}-TMS by covalent bond and formed the silica skeleton. Therefore, the mesostructured silica was formed and the chirality was transferred from the micelles into the ordered mesoporous silica.

In summary, C_{18}-TMS participated in both the formation of silica skeleton (as silica source) and chiral pore channel (as a kind of positively charged surfactant). Besides, amino acids had an electrostatic interaction with positively charged surfactant and also took part in the formation of chiral pore channel.

Stereoselective adsorption of L-phenylalanine on L-Phe-COMS

In this work, we take the advantages of unique structural features of $_L$-Phe-COMS and imprinting chirality as a robust adsorbent for stereoselective adsorption capacity.The stereoselective adsorption capacity of $_L$-Phe-COMS for $_L$-phenylalanine was investigated by first. The CD spectra of the $_{DL}$-Phe solution adsorbed by $_L$-Phe-COMS and blank COMS (obtained without $_L$-Phe), respectively, which indicated the $_L$-Phe molecule resulted in the stereoselective adsorption. Furthermore, it was observed that the

concentration of L-phenylalanine in the solution decreased time-dependent (Fig.3A). Over half of L-phenylalanine (1.0 mg mL^{-1}) was adsorbed on 40 mg of L-Phe-COMS after 72 hours. The concentration of L-phenylalanine in the solution can be obtained from the equation (1):

$$\theta = 100[\theta]lc/M \quad (1)$$

Where, θ (deg) is the experimental ellipticity, $[\theta]$ (deg cm^2 $dmol^{-1}$) is the molar ellipticity, l is the wavelength and c (g mL^{-1}) is the concentration of L-phenylalanine M is the molar mass of test molecule. Adsorption amount can be calculated by the standard curve method according to the θ against C. The adsorption capacity of L-phenylalanine on L-Phe-COMS after 72 hours is as high as 140 mg g^{-1}. To further investigate the stereoselective adsorption capacity of L-Phe-COMS, adsorption of D-phenylalanine was also performed in the same way as L-phenylalanine. The kinetics curves of L-phenylalanine and D-phenylalanine showed a stereoselective adsorption capacity of L-Phe-COMS to the two enantiomers (Fig.3B).

The stereoselective adsorption factor between L-phenylalanine and D-phenylalanine in solution interacted with L-Phe-COMS for 72 hours can be calculated from the equation (2):

$$\alpha = Q_{L-phe}/Q_{D-phe} \quad (2)$$

Where, α is the stereoselective adsorption factor, $Q_{L\text{-}Phe}$ and $Q_{D\text{-}Phe}$ are the adsorption capacity of L-phenylalanine and D-phenylalanine respectively. The stereoselective adsorption factor was 3.24 according to the equation (2), which indicated the efficient stereoselective adsorption capacity of L-Phe-COMS for the two enantiomers.

After the chiral recognition of L-Phe-COMS was identified, this chirality imprinting ordered mesoporous solid silicate as-made was further explored to separate other racemic mixtures. Fig.4 showed stronger chiral recognition ability of L-Phe-COMS for amino acids (D,L-phenylalanine, D,L-alanine, D,L-tryptophan, and D,L-lysine) than that of some racemic drugs (chlorpheniramine maleate and naproxen). Chlorpheniramine maleate and naproxen were hardly absorbed on calcined L-Phe-COMS resulting from both no amino acid groups and larger molecular size. In comparison to alanine, long alkyl chain hamper effective absorption of lysine on L-Phe-COMS. Thus, L-form of the guests simultaneous with suitable molecular size and benzene group were appropriate for stereoselective adsorptive separation of racemic guests. The observed above results showed high adsorption capacity and selective stereoselective separation of racemic guests was favoured by chirality imprinting microenvironment.

Preliminary mechanism on stereoselective adsorption of L-Phe-COMS

The stereoselective adsorption mechanism of the L-Phe-COMS could be illustrated in view of COMS formation process. Differential stereoselective adsorption may result from the molecule chirality imprinted in the pore channel as shown in Scheme 1. In this experiment, the chirality transferred from the L-phenylalanine to the silica skeleton enabled more stereoselective adsorption of L-phenylalanine than D-phenylalanine. Supramolecule formed in the synthesis also had an effect on stereoselective adsorption. During the synthesis of L-Phe-COMS , C_{18}-TMS and its dimers or trimmers had an electrostatic

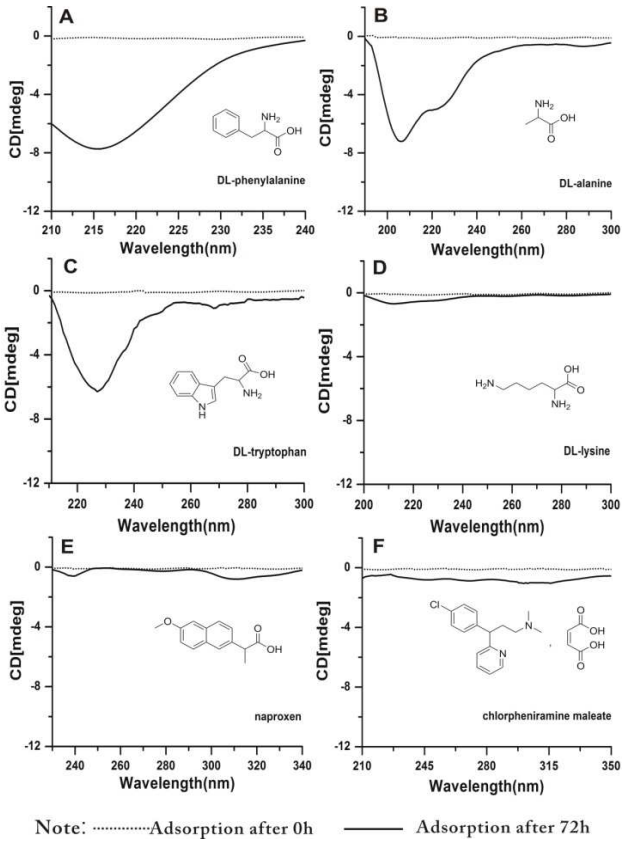
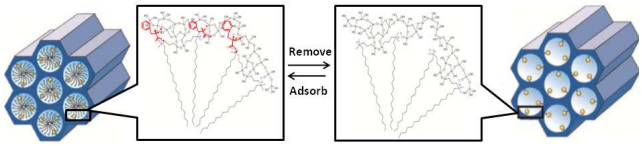


Fig.4 Stereoselective adsorption of racemic mixtures with a initial concentration of 0.5 mg ml^{-1} adsorbed on 10 mg of L-Phe-COMS: (A) D,L-phenylalanine; (B) D,L-alanine; (C) D,L-tryptophan; (D) D,L-lysine; (E) racemic naproxen and (F) racemic chlorpheniramine maleate

interaction with the L-phenylalanine and formed the micelles. Meanwhile, the head group of C_{18}-TMS was dragged and twisted by L-phenylalanine, thus formed the chiral pore channel. Consequently, the stereoselective recognition ability of L-Phe-COMS may result from not only the chirality imprinted in the pore channel, but also the chiral pore channel formed by the twisted micelle which was constituted by the L-phenylalanine and C_{18}-TMS. [17]



Scheme 1 A representative represent for L-Phe-COMS with ordered MCM-41type structure before and after remove the chiral introducer and adsorb the target molecule

Conclusion

In summary, L-phenylalanine imprinting chiral ordered mesoporous silica (L-Phe-COMS) was straightforward synthesized by combining tetraethyl orthosilicate and quaternized aminosilane silica source together with L-phenylalanine as a chiral imprinted reagent. The obtained L-Phe-COMS showed several features such as highly ordered mesoporous structure, narrow pore size distribution arranging from 2.3 nm to 2.5 nm,

large specific surface area of 730 $cm^2 g^{-1}$ and high pore volume of 0.47cm^3g^{-1}. C_{18}-TMS participated in the formation of the chiral pore channel (as a kind of positively charged surfactant) as well as silica skeleton (as silica source). Amino acids take part in the formation of chiral pore channel through a similar electrostatic interaction with positively charged surfactant. An exceptional stereoselective adsorption capacity up to 3.24 for $_L$-phenylalanine over $_D$- phenylalanine was obtained by using of $_L$-Phe-COMS in aqueous solution. Unique structural features and stereoselective adsorption capacity of CMOS make it an alternative candidate for multitude of applications involving asymmetric catalysis and enantiomeric separation.

Acknowledgement

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References

1. S. MacQuarrie, M. P. Thompson, A. Blanc, N. J. Mosey, R. P. Lemieux and C. M. Crudden, *J. Am. Chem. Soc.,* 2008, **130**, 14099.
2. S. Polarz and A. Kuschel, *Adv. mater.,* 2006, **18**, 1206.
3. G. Zhu, D. Jiang, Q. Yang, J. Yang and C. Li, *J. Chromatogr. A,* 2007, **1149**, 219.
4. G. Zhu, H. Zhong, Q. Yang and C. Li, *Micropor. Mesopor. Mater.,* 2008, **116,** 36.
5. A. Gabashvili, D. D. Medina, A. Gedanken and Y. Mastai, *J. Phys. Chem. B,* 2007, **111**, 11105.
6. X. Wu, S. Ji, Y. Li, B. Li, X. Zhu, K. Hanabusa and Y. Yang, *J. Am. Chem. Soc.,* 2009, 131, 5986.
7. X. Liu, W. Zhuang, B. Li, L. Wu, S. Wang, Y. Li and Y. Yang, *Chem. Commun.,* 2011, 47, 7215.
8. B. Di, L. Cheng, Q. Jiang, M. Su, W. Hao, *New J. Chem.* 2013,37, 1603.
9. T. Yokoi, Y. Sakamoto, O. Terasaki, Y. Kubota, T. Okubo and T. Tatsumi, *J. Am. Chem. Soc.,* 2006, **128**, 13664.
10. R. Bhushan and S. Dixit, *Biomed. Chromatogr.,* 2012, **26**, 962.
11. S. Lacasta, V. Sebastian, C. Casado, A. Mayoral, P. Romero, A. Larrea, E. Vispe, P. Lopez-Ram-de-Viu, S. Uriel and J. Coronas, *Chem. Mater.,* 2011, **23**, 1280.
12. C. Casado, J. Castán, I. Gracia, M. Yus, A. Mayoral, V. Sebastián, P. López-Ram-de-Viu, S. Uriel, and J. Coronas, *Langmuir*, 2012, **28**, 6638.
13. R. Bhushan and S. Tanwar, *J. Chromatogr. A,* 2010, **1217**, 1395.
14. Z. F. Zhang, G. L. Yang, D. X. Wang, G. J. Liang and Y. Chen, *J. Liq. Chromatogr. Related Technol.,* 2004, **27**, 813.
15. J. D. Senra, L. F. B. Malta, P. M. N. Ceva-Antunes, R. J. Correa and O. A. C. Antunes, *J. Braz. Chem. Soc.,* 2007, **18**, 1367.
16. J. Fan, S. W. Boettcher, C.-K. Tsung, Q. Shi, M. Schierhorn and G. D. Stucky, *Chem. Mater.,* 2008, **20**, 909.
17. Z. Guo, Y. Du, Y. Chen, S.-C. Ng and Y. Yang, *J. Phys. Chem. C,* 2010, **114**, 14353.
18. C. Kresge, M. Leonowicz, W. Roth, J. Vartuli, J. Beck, *nature* 1992,**359(6397**),710.
19. Q. Huo, D. I. Margolese, G. D. Stucky, *Chemistry of Materials* 1996, **8 (5)**, 1147.

Figure legends

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