Fabricating hydrophobic nanoparticles within mesoporous channel of silica for efficient TSNA removal

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Abstract Based on the synthesis of super hydrophobic silicic xerogel (SG) from methyltrimethoxysilane (MTMS) and dimethyldimethoxysilane (DMDMS), siliceous hydrophobic nanoparticles were fabricated within the mesoporous channels of SBA-15, in order to enhance the efficiency of adsorbing tobacco specific *N*-nitrosamines (TSNA) in aqueous solution. The concentration of precursor solution was adjusted to master the distribution of hydrophobic particles and the mean hydrophobicity of resulting composite, 150% increasing the capacity of SBA-15 in liquid adsorption of TSNA.

Keywords hydrophobic nanoparticles; mesoporous channels of silica; TSNA; liquid adsorption; environment protection

1 Introduction

Tobacco specific nitrosamines (TSNA) exist only in tobacco products, and they cause the potential

risk of genetic mutations to induce tumor for smokers and passive smokers [1-4]. Most of the TSNA in cigarette smoke are transferred from tobacco [5,6], so that reducing the content of TSNA in tobacco is effective to lower the content of the carcinogens in cigarette smoke. At present, one practical method of removing TSNA in tobacco products is to deal with tobacco by water extraction [7]. Therefore, it is possible to use liquid adsorption capturing the harmful substances like TSNA in tobacco extract solution, and the effective sorbent is the key to reduce the harm of tobacco on public health and environment.

In addition to common active carbon, zeolite can be used for liquid adsorption of TSNA [8-10]. However, the microporous channels of zeolite are labored to capture bulky TSNA (0.5-0.9 nm), and what's worse, most of commercial zeolites like NaY or NaA are hydrophilic. Harmful substances such as nitrosamine are mainly oily molecules and their adsorption in tobacco extract solution is inevitably interfered by water [9]. Therefore, new efficient sorbents of trapping TSNA are required having appropriate porous structure and certain hydrophobic to suppress the competition of water. Nowadays, it is common to modify mesoporous silica through alkylation with specific hydrophobic organic silicon reagents. The surface modification of mesoporous materials can be divided into one-pot synthesis and post impregnation methods [11]. One-pot synthesis is simple and able to make organic modifiers distributed more uniformly, but the mesoporous structure of the host will be degraded or damaged more or less due to the interference of organic agent in synthesis [12-14]. In addition, some organic modifiers are inevitably buried inside the channel wall and failed to modify the surface of sorbent [14]. On the contrary, post impregnation is usually able to maintain the favorable structure of mesoporous silica [11], and to adjust the size and surface curvature of channel in case using the optimal organic modifier with required size and functional groups.

Micron-sized super hydrophobic silicic xerogel (SG) has been simply synthesized with

methyiltrimethoxysilane (MTMS) and dimethyldimethoxysilane (DMDMS) [15], and the SG was modified by epitaxial growth of mesoporous silica to prepare a new capturer of *N*-nitrosamines in tobacco solution [16]. However, SG has a very small specific surface area ($4 \text{ m}^2 \text{ g}^{-1}$) though it owns an outstanding liquid adsorption performance in aqueous solution. Therefore, it will be valuable to divide the micron-sized SG into numerous nanoparticles and fabricate them inside the mesoporous channel in order to increase their efficiency of interception and adsorption TSNA in tobacco extract solution. To explore the influence of limited space on the fabrication and liquid adsorption of hydrophobic SG nanoparticles, two hosts are chosen including SBA-15 and MCM-41 mesoporous silica that represent the matrix with wide or narrow mesoporous channel. On the other hand, the silicon source concentration and composition of precursor solution are carefully adjusted to control the distribution of hydrophobic particles in the solid matrix with different geometric confined effects. Liquid adsorption of TSNA in tobacco extract solution is used here to assess the performance of these functional composites [8,10], exploring the fabrication within mesoporous space.

2 Experimental section

2.1. Materials

Cetyltrimethylammonium bromide (CTAB) was the product of Nanjing Chemical (China). Tetraethylorthosilicate (TEOS) and P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) were purchased from Shanghai Wu-lian (China) and Aldrich, respectively. Burley and Virginia type tobacco fibers were bought in market, and other reagents were with AR grade and used as received.

SBA-15 was synthesized according to the recipes of literature [17]. In a typical synthesis, 3 g P123, 90 g HCl (2 M) and 22.5 g H_2O were mixed at 298 K. After P123 was dissolved, 6.38 g TEOS was added into the mixture at 313 K, followed by vigorous stirring for 24 h, and then this

solution was transferred into a teflon bottle and heated statically at 373 K for another 24 h. The solid product was recovered by filtration, washed with distilled water, air-dried and finally calcined at 773 K for 5 h to obtain SBA-15.

MCM-41 was also prepared according to literature [9,18]. 3 g silica aerosol and 1.5 g NaOH were added to 45 g distilled water under stirring and defined as solution A, and solution B was prepared with 4.5 g CTAB and 25 g distilled water. The solution B was added dropwise into solution A at 298 K, and the pH value of mixture was adjusted to 9-11 using HCl solution (2 M). After stirring continuously for an additional 6 h, the gel mixture was heated statically at 403 K for 72 h. The solid was recovered by filtration, washed with distilled water, and air dried. Finally it was calcined at 823 K for 5 h to remove template.

2.2 Synthesis of composited hydrophobic nanoparticles with mixed silanes

0.45 g CTAB and 2.5 g urea were dissolved into certain amount of hydrochloric acid (pH=3.5) and stirred at 303 K for 0.5 h. Then, 1.43 g MTMS and 0.84 g DMDMS were added in the solution and stirred for 0.5 h, forming the precursor solution of super-hydrophobic silicic xerogel (SG). SBA-15 or MCM-41 matrix was put into the solution for impregnation, and after separation, the wet solid and the residual solution were heated at 353 K for 24 h separately. The solid was finally recovered by washed with distilled water, air-dried, giving the sample denoted as SS-r or SM-r, indicating the SG coated in SBA-15 or MCM-41, where r was the volume ratio of hydrochloric acid to two silanes (MTMS+DMDMS) used in the synthesis (Table 1). And their weight increment was carefully measured (Table 2). The residual solution was also heated at 353 K for 24 h to give the solid sample named as SG' [16].

Modification of mesoporous silica with single silane was performed in similar process, but the mixed precursor of MTMS and DMDMS was replaced by 2.39 g MTMS or 2.18 g DMDMS. The

obtained sample was denoted as Sd-n, Sm-n, Md-n or Mm-n, indicating DMDMS or MTMS coated in SBA-15 or MCM-41, respectively, where n was the volume ratio of hydrochloric acid to DMDMS or MTMS.

2.3 Characterization

X-ray diffraction (XRD) pattern of sample was recorded on an XRD-6000 diffractometer (power 40 kV, 40 mA) using Cu-K α radiation in the 2θ range of 0.6-10°. Nitrogen adsorption-desorption isotherm was obtained on a Micromeritics ASAP 2030 volumetric adsorption analyzer at 77 K, for which 100 mg of sample was evacuated at 363 K for 3 h in the degas port prior to test. Specific surface area of sample was calculated by the BET method using adsorption data acquired in the relative pressure range (P/P_0) from 0.04 to 0.2, while the total pore volume was determined from the amount adsorbed at a P/P_0 of about 0.99. The morphology of sample was observed by SEM using a Hitachi S4800 FE-SEM system with 10 kV accelerating voltage and 10 mA of beam current, and TEM analysis was carried out on a JEM-2100 electron microscope operating at 200 kV. Water contact angle was measured using the sessile drop method with a 3 μ L water droplet and a telescopic goniometer (Rame-Hart, Inc., MountainLake, NJ). FTIR spectrum was recorded in the range of 400-4000 cm^{-1} on a NEXUS870 spectrometer, for which the sample was mixed with KBr at a ratio of 3: 97 (w/w) and then pressed as a thin disk for testing. Thermal stability of samples was studied on STA-449F3 instrument working in argon and the temperature rose from 308 K to 1173 K at 10 K min^{-1} .

2.4 Liquid adsorption in tobacco extract solution

Tobacco extract solution was prepared according to industrial processes: 500 g flue-cured tobacco stem (20% long stem and 80% short stem) was submerged into 1150 mL water and the mixture was kept at 348 K for 30 min followed by filtration to separate fiber. On the other hand,

500 g tobacco fines (60% burley tobacco and 40% flue-cured tobacco) were mixed with 3000 mL water at 293 K for 20 min, and then filtrated to remove solid. Two solutions were mixed and enriched in rotary evaporator at 293 K with the rate of 90 r min^{-1} to reach the density of $1.2\text{-}1.22 \text{ g cm}^{-3}$. The obtained tobacco extract solution was stored at 277 K.

50 mg granular adsorbent was added into 10 mL tobacco extract solution in test tube and performed under dynamic and dark condition at 303 K for 1 h. Thereafter it was centrifuged at 3000 rpm for 10 min to separate solid and solution [8,16].

2.5 Determination of TSNA in solution

TSNA content of tobacco extract solution was determined by Applied Biosystems 4000 Q TRAP mass spectrum combined with an Agilent 1200 liquid chromatogram system equipped with a column of CAPCELL PAK C18 MG2 (4.6 mm×150 mm, 3 μm). And the procedure and parameters used in the detection were same as that reported previously [10,19].

3 Results

3.1 Fabricating hydrophobic nanoparticles in mesoporous silica

Fig. 1 presents the low-angle XRD patterns of SS-r and SM-r samples. SBA-15 sample showed three well-resolved XRD peaks indexed to the (100), (110) and (200) diffractions of the 2D hexagonal symmetry ($p6mm$) [17], but SS-4 sample only had one single peak of (100) diffraction with the slightly deviated position along with the obviously lowered intensity (Fig. 1a). As the amount of HCl solution used in the fabrication decreased, the characteristic peak further reduced on the pattern of SS-3 and almost disappeared on SS-2 sample. Clearly, the silicon precursor solution immersed and solidified inside the mesoporous channel of SBA-15 to form nanoparticles blocking the channel, leading to a strongly altered mesoporous structure similar to that modified with 3-aminopropyltriethoxysilane [20]. A different situation was found on MCM-41 sample that had

three well-resolved XRD peaks indexed to the (100), (110) and (200) diffractions of hexagonal symmetry (Fig. 1b). Three coated derivates, SM-4, SM-3 and SM-2 all kept the single peak of (100) diffraction though the peak became weak as less acid was used in the fabrication. No doubt the ordered mesoporous structure of matrix is gradually damaged because of the declined diffraction intensity [21]. The siliceous modifiers inside channel inevitably reduced the scattering among wall of MCM-41, like the influence of carbon deposited in MCM-41 to cause irregular mesoporous structure [22].

Fig. 2 presents the nitrogen adsorption-desorption isotherms of SS-r composites. Parent SBA-15 sample had the typical IV isotherm with a large type H1 hysteresis loop and the narrow pore size distributions, mirroring a one-dimensional cylindrical straight channel [17]. However, the isotherm shape of three SS-r samples dramatically changed and hysteresis loop absent (Fig. 2a). Also, their surface areas sharply decreased from $793 \text{ m}^2 \text{ g}^{-1}$ to less than $100 \text{ m}^2 \text{ g}^{-1}$, and the thicker the concentration of precursor silane solution, the smaller the surface area. The pore volume of SS-r composites changed in the same tendency, too, and among them SS-2 sample exhibited the smallest ($25 \text{ m}^2 \text{ g}^{-1}$, $0.032 \text{ cm}^3 \text{ g}^{-1}$, Table 3) equaling to the 3~4% of that of parent SBA-15. The phenomenon meant the blocked or distorted channel of SBA-15 originating from the import of siliceous species, which is consistent with the results of XRD tests. Unlike the SBA-15 modified with (aminopropyl) triethoxysilane still kept IV isotherm and H1 hysteresis loop though the pore size decreased gradually [20], SS-r samples had the significantly damaged mesoporous structure, and one possible reason is the introduction of MTMS and DMDMS that not only interact with the surface hydroxyl groups of SBA-15, but trigger the polycondensation to form nanoparticles embedded inside channel. As a consequence, their surface area reduced drastically while the most probable pore size decreased from 6 to 3.2 nm (Fig. 2b). A strange phenomenon was observed on SM-r composites

whose isotherms became freak (not shown) and surface area was no more than $10 \text{ m}^2 \text{ g}^{-1}$, similar to that reported on the sample of MCM-48 modified with 3-propylchloridetriethoxysilane [9]. To explore whether the CTAB in precursor solution causes these changes, three SM-r samples were extracted with ethanol for 1h and the resulting composites showed the normal isotherms of IV or I type (Fig. 2c and 2d), meanwhile their surface area rose to $150\text{-}655 \text{ m}^2 \text{ g}^{-1}$ (Table 3). Besides, their pore sizes were close to that of parent MCM-41 (3.5 nm). Through these data, it is inferred that the CTAB micelles might locate inside channels and blocked the pore mouth, hindering the characterization of composite such as XRD test (Fig. S1). These micelles were flexible at ambient temperature but rigid at 77 K [23] so that the adsorption of nitrogen at 77 K was thus hindered. When SBA-15 was modified with single silane MTMS or DMDMS, its surface area decreased quickly from 793 to $6\text{-}26 \text{ m}^2 \text{ g}^{-1}$ while the pore volume lowered from 0.796 to $0.02\text{-}0.05 \text{ cm}^3 \text{ g}^{-1}$ (Table S1). Modification of MTMS made the surface area of MCM-41 declined from 1088 to around $20 \text{ m}^2 \text{ g}^{-1}$ but DMDMS made it further lowered to about $2 \text{ m}^2 \text{ g}^{-1}$ (Table S1).

Fig. 3 displays the TEM images of SBA-15 and MCM-41 before and after hydrophobic modification. SBA-15 sample had a neat and uniform mesoporous structure in which the center distance of adjacent channel was about 6 nm [17]. Nonetheless, SS-3 sample showed a degraded structure whose regularity was considerably declined in which some channels were bended with rough surface, like the distorted channels of the SBA-15 *in situ* incorporated with titanium [24]. According to TEM image, the width of channels of SS-3 was significantly narrowed to about 2~3 nm, and this decrease exceeded that observed on the SBA-15 loaded with bulky organosilicon reagents whose pore size lowered from 6.4 to 4.2 nm [14]. MTMS and DMDMS had small molecular groups like methyl or dimethyl groups, but they dramatically reduced the pore size of SS-3 sample through not only interaction with the silicon hydroxyl on channel wall, but also

condensation polymerization of two silicon sources to form abundant nano-particles inside channel. In contrast, the channel width of SM-3 sample seemed similar to that of parent MCM-41 (Fig. 3e and 3g), though its regularity was slightly lowered accompanied with the channel wall became somewhat fuzzy and the vermiform structure emerged occasionally. Both SS-3 and SM-3 samples exhibited the neat six square channel orifices (Fig. 3f and 3l), implying that they still remained symmetry plane of six-party (p6mm) [20]. This phenomenon is different from that of Ti-modified SBA-15 whose channel orifices were obviously distorted [24], because the structure of SBA-15 is stable enough in this mild post-modification but easily changeable in one-pot synthesis. Another possible reason is the small molecular weight of two kinds of silicon reagents (MTMS and DMDMS). They easily insert and diffuse inside of the wild channel of SBA-15 so that their reactions occurred mainly in channel rather than in pore orifice. It is very hard to exactly measure the size of hydrophobic nanoparticles located inside the mesoporous channel. Yet, they could be introduced into the channels of SBA-15 (about 6 nm) rather than that of MCM-41(3 nm) hence their theoretical size might be 3 nm or more. Also, these particles were guessed to have the size of around 3 nm on the basis of TEM image in Figure 3e.

Fig. 4 presents the FT-IR spectra of SBA-15, SS-3, MCM-41 and SM-3 samples. The bands at around 3434, 1637 and 961 cm^{-1} indicate the presence of -OH groups [25], which were significantly pronounced in SBA-15 and MCM-41 samples but slightly presented in SS-3 and SM-3 composites. It seems that MTMS and DMDM precursors had been consumed in polycondensation to fabricate hydrophobic nanoparticles in mesoporous silica. Furthermore, C-H stretching vibration and bending bands appeared in the spectra of SS-3 and SM-3 samples at 2970 and 1270 cm^{-1} , respectively, illustrating the methyl functional groups that lead to the hydrophobicity of samples [26]. Likewise, the band of Si-C bond at 848 cm^{-1} [27] only appeared in SS-3 and SM-3 samples. The strong peak

near 1080 cm^{-1} and the weak peak near 800 cm^{-1} were assigned to the asymmetric and symmetric bending of Si-O-Si bonds, respectively [27]. SBA-15 and SS-3, or MCM-41 and SM-3, had different shape and intensity of peak, mirroring the mixed silanes had been consumed in the polycondensation to generate Si-O-Si bonds. Fig. 5 illustrates the TG-DSC curves of SBA-15, SS-3, MCM-41 and SM-3 samples. The weight loss under 400 K, which presents the expulsion of water, of hydrophobic SS-3 and SM-3 samples were obviously smaller than that of SBA-15 and MCM-41, respectively. A sharp exothermic peak in DSC curve was observed at 782 K or 880 K for SS-3 or SM-3 sample, due to the oxidation of Si-CH₃ group to Si-OH [25,27]. Thus, it is inferred that the hydrophobic nanoparticles were fabricated in mesoporous silica.

Fig. 6 displays contact angle of SS-r and SM-r samples. Synchronically, the contact angle of all composites gradually decreased with the amount of acid rising, and the value of SS-4 was zero, which means the significant effect of silane solution's concentration on the hydrophobicity of resulting composites. Such influence also emerged on the coating amount (Table 2), especially in the test with glass sheets whose weight increment linearly decreased with the diluted silane solution (Table S2 and Fig. S2). Comparison of Table 2 with Table S2 reveals the effects of other factors on the coating of hydrophobic particles. The coating amount on SM-r was smaller than that of corresponding SS-r sample (Table 2), which ought to be ascribed to the limitation of narrow pore size because MCM-41 has a larger surface area than SBA-15 did (Table 3). Vertically, the hydrophobicity of SM-r samples were superior to that of corresponding SS-r (Fig. 6). The pore size of MCM-41 (3.3 nm) was smaller than that of SBA-15 (6 nm, Table 3) thus two silane agents were difficult to react inside the narrow channel. As the consequence, they were inclined to graft hydrophobic groups on MCM-41, resulting in the improved hydrophobic performance. When MCM-41 was modified with single silane MTMS or DMDMS, its contact angle rose to 120~129°

(Fig. S3) but the loading amount was lower than that of mixed silanes (Fig. S4). Single silane modification dramatically increased the contact angle of SBA-15 to 127~150° (Fig. S3) though its loading amount (less than 40%) obviously was inferior to that of mixed silanes (about 70%, Fig. S4).

3.2 Adsorption of TSNA in tobacco extract solution

Fig. 7 presents the removal of TSNA in tobacco extract solution by two series of hydrophobic modified composites. On the whole, SBA-15 and MCM-41 exhibited the better liquid adsorption of TSNA after the hydrophobic modification. Among them SS-3 sample was the best because it could capture 25.9 % of TSNA in tobacco extract solution, 151% higher than parent SBA-15 (10.3%, Table 4), thanks to the enhanced hydrophobicity inhibiting competitive adsorption of water [9]. Besides, the narrowed channel of SS-3 sample, due to the insertion of hydrophobic nanoparticles, could provide a better geometric confined effect for these target carcinogens. MCM-41 itself showed a better adsorption than SBA-15 because of its inherent smaller pore size, but the improvement of hydrophobic modification became unobvious since SM-3 sample trapped only 6.7% more TSNA than MCM-41 did (Table 4). In addition, the samples modified with single silane were assessed, but all of them had a low removal of TSNA under 10%, even inferior to parent SBA-15 and MCM-41 samples (Table 4).

Different molecular configuration affects the adsorption of three components of TSNA, *N'*-nitrosoanatabine (NAT), 4-(*N*-nitrosomethylamino)-1-(3-pyridyl)-1-butanone (NNK) and *N'*-nitrosonornicotine (NNN), though they all have the functional *N*-nitroso group, N-NO [5]. NNK is a long strip-like molecule with the strength of 1.21 nm and the cross section of about 0.4 nm [10], but NAT and NNN are bulky ones with the cross section of about 0.8 nm. All samples trapped more NAT than NNN or NNK due to the highest NAT content in the tobacco extract solution. As seen in

Table 4, SS-3 sample had a more significant advantage in adsorbing NNN, namely the removal of NNN was enhanced from 1.8% (SBA-15, Table 4) to 20%, though the capture of NNK and NAT were also obviously increased. Nonetheless, the reduction of NNK by SM-3 sample (9.6%, Table 4) was lower than that by MCM-41 (15.8%), which may related to the diluted silane solution used in the modification because a lower NNK reduction (7%, Fig. 7) emerged on SM-4 sample that had been treated with the leaner silane solution (Table 1). MCM-41 lacked cation to attract the N-NO group of NNK hence this wirelike molecule could escape from the channel of sorbents. On the other hand, single hydrophobicity was not strong enough to trap NNK without assistance of geometric confinement, because the hydrophobic sample SG' only showed a weak ability in liquid adsorption of NNK (7.5%, Table 4). Contrarily, when the volume ratio of acid to silanes achieved 3 in the preparation, almost modified composites displayed the best adsorption capacity of TSNA, which may relate to their optimal hydrophobicity consulting the results of contact angle (Fig. 6). Suitable hydrophobicity enables sorbent to suppress the competitive adsorption of water [9, 16], but makes the sorbent immersed in rather than floated on tobacco extract solution so that it can contact fully with TSNA.

4 Discussion

Compared with the SG modified with epitaxial grew mesoporous silica [16], the mesoporous silica coated with hydrophobic nanoparticles has some advantages for liquid adsorption of TSNA. The first is the large surface area thanks to the inherent characters of mesoporous silica. SBA-15 has a surface area over $700 \text{ m}^2 \text{ g}^{-1}$ [9,19], affording a large space for coating hydrophobic nanoparticles. The second is the channel structure supplying the geometric confinement to limit thermal motion of target molecules [9,10], and the third is the hydrophilicity that enables the sorbent immersed in aqueous solution to contact TSNA. The fourth is the mild conditions of

impregnation under 353 K used here, in which the hydrophobic guest nanoparticles can be coated in mesoporous silica host to tailor both surface hydrophobicity and curvature of channel wall. Mesoporous silica SBA-15 did not have movable cation so that its adsorption depended on the weak interaction between TSNA and silicon hydroxyl [9,10]. Coating hydrophobic nanoparticles in mesoporous silica like SBA-15 is actually the multifunctional modification to conquer this drawback. These nanoparticles made the channel surface ups and downs, endowing smooth two-dimensional channel with the disordered multistage aperture (Scheme 1), which is beneficial for intercept of TSNA molecules [9] since the collision between target TSNA and adsorbent is increased. Moreover, the abundant methyl groups of hydrophobic nanoparticles inhibited competitive adsorption of water in aqueous solution and at the same time offered some hydrophobic sites to trap oily TSNA through the rule of similarity [16]. Consequently, SS-r samples exhibited an adsorption efficiency of TSNA significantly superior to SBA-15.

Silicon precursor solution is mixed with host matrix prior to formation of hydrophobic nanoparticles so that the size and distribution of the guests are enviably affected by the porous structure of host. Tiny spherical particles were faintly visible on the external surface of SM-3 but absent on the SEM image of SS-3 composite (Fig. S5). Together with the contact angle measured on the two samples (Fig. 6), it is inferred that the major nanoparticles were embedded inside the channel of SBA-15, but located on the external of MCM-41 probably due to its narrow channel. The limited nano-space may impede the polycondensation between MTMS and DMDMS, but further study is required to explore this impact.

Although SM-r had a similar adsorption capacity of TSNA to SS-r samples in tobacco extract solution (Fig. 6, Table 4), their advantage were different in comparison with their parent. The capacity of SS-3 sample (25.9 %) was 150% higher than that of SBA-15 (10.3%) since the better

geometric confined effect and proper hydrophobicity provided by the embedded hydrophobic nanoparticles. However, MCM-41 showed a better performance (16.5%) than SBA-15 did because of its inherent smaller pore size to offer a tighter geometric constraints for the target [9,10], hence the capacity of SM-3 sample (23.2%) was 41% higher than that of MCM-41. Hydrophobic nanoparticles on the external surface of MCM-41 inhibited the competitive adsorption of water more or less, which is beneficial for TSNA to enter mesoporous channel and improve the liquid adsorption.

Those samples modified with single silane were just grafted some small molecular groups on the surface of host, and those groups like methyl and siloxane bridge (Si-O-Si) groups were reported to be 0.2 and 0.26 nm respectively [28]. Unlike SS-r samples with big hydrophobic nanoparticles occupied channel, these groups seem unable to provide an optimal geometric confinement and surface curvature for capture of TSNA carcinogens. In contrast, their high hydrophobicity (120~150°, Fig. S3) made them float on the surface of solution rather than immerse in it therefore all of them exhibited a relatively lower removal of TSNA than corresponding SS-3 or SM-3 sample, even inferior to SBA-15 and MCM-41 (Table 4). Proper hydrophobicity is important for liquid adsorption of TSNA in aqueous solution [9]. Hydrophobic adsorbent can reduce competitive adsorption of water, but it will float on solution failing to contact with TSNA [16]. Although the hydrophobicity of composite was gradually improved as the silanes precursor solution was concentrated (Fig. 6), the optimal adsorption of TSNA emerged on those prepared with the acid to silanes ratio of 3 (Fig. 7), which provides a valuable clue for functionalization of mesoporous silica.

5 Conclusion

Hydrophobic nanoparticles were successfully fabricated in mesoporous silica SBA-15 to prepare

TSNA trapper in tobacco extract solution, and the volume ratio of 3 of hydrochloric acid (pH=3.5) to silanes was proven to be the optimal, which 150% increases the adsorption capacity of SBA-15 in tobacco extract solution.

Pore structure of host matrix affects the distribution of guest nanoparticles, and the majority of them located inside the channel of SBA-15 but on the external of MCM-41. The intrinsic structure of MCM-41 hinders the formation of hydrophobic nanoparticles inside its channel so that SBA-15 seemed to be the better host.

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Table 1 The composition of precursor solution to coat hydrophobic particles.

	CTAB (g)	Urea (g)	MTMS (g)	DMDMS (g)	V _{MTMS} (mL)	V _{DMDMS} (mL)	V _{Mix} (mL)	V _{HCl} (mL)	V _{HCl} : V _{Mix} (n)
1	0.46	2.5	1.43	0.84	0.965	1.497	2.5	5	2
2	0.46	2.5	1.43	0.84	0.965	1.497	2.5	7.5	3
3	0.46	2.5	1.43	0.84	0.965	1.497	2.5	10	4

Table 2 The weight increase of samples after coated with hydrophobic particles.

Samples	M ₀ (g)	M ₁ (g)	△M (g)	Loading (%)
SS-2	0.1057	0.1782	0.0725	68.6
SS-3	0.1048	0.1762	0.0714	68.1
SS-4	0.1050	0.1719	0.0669	63.7
SM-2	0.1053	0.1634	0.0581	55.2
SM-3	0.1052	0.1506	0.0454	43.2
SM-4	0.1055	0.1438	0.0383	36.3

Table 3 The textural properties of mesoporous silica samples.

Sample	S _{BET} ^a (m ² g ⁻¹)	S _{micro} ^b (m ² g ⁻¹)	V _p ^c (cm ³ g ⁻¹)	V _{micro} ^d (cm ³ g ⁻¹)	D _p ^e (nm)
SBA-15	793	138	0.796	0.054	6.0
SS-2	25	-	0.032	-	3.2
SS-3	51	-	0.068	-	3.2
SS-4	78	-	0.139	-	3.4
MCM-41	1088	-	0.672	-	3.3
SM-2	2	-	-	0.004	-
SM-3	6	-	-	0.003	-
SM-4	10	6.8	-	0.003	-
SM-2*	150	15	0.108	0.004	3.54
SM-3*	242	-	0.164	-	3.30
SM-4*	655	-	0.370	-	3.30

[a] S_{BET}, BET surface area; [b] S_{mic}, micropore area; [c] V_p, total pore volume; [d] V_{mic}, micropore volume; [e] D_p, BJH mesopore diameter calculated from the adsorption branch.

* This sample was extracted with ethanol at room temperature for 1h.

Table 4 Residual TSNA in the tobacco extract solution adsorbed by porous sorbents.

Samples	NNN ^a (nmol g ⁻¹)	Cut (%)	NAT ^b (nmol g ⁻¹)	Cut (%)	NNK ^c (nmol g ⁻¹)	Cut (%)	TSNA (nmol g ⁻¹)	Reduced (%)
Control	0.127	-	0.268	-	0.055	-	0.450	-
[#] Control	0.130	-	0.141	-	0.082	-	0.352	-
SBA-15	0.125	1.8	0.232	13.4	0.047	14.9	0.404	10.3
SS-3	0.102	20.0	0.189	29.4	0.042	22.8	0.333	25.9
MCM-41	0.112	12.0	0.218	18.8	0.046	15.8	0.376	16.5
SM-3	0.108	15.1	0.188	29.8	0.050	9.6	0.346	23.2
SG'	0.124	2.4	0.233	13.1	0.051	7.3	0.408	9.3
[#] Sm-2	0.126	2.6	0.132	6.4	0.083	0	0.341	3.3
[#] Sm-3	0.122	6.1	0.124	12.0	0.083	0	0.328	6.8
[#] Sm-4	0.124	4.3	0.127	9.8	0.073	10.6	0.324	7.9
[#] Sd-2	0.125	3.5	0.134	4.5	0.080	2.9	0.339	3.7
[#] Sd-3	0.124	4.8	0.132	6.0	0.079	3.5	0.335	4.9
[#] Sd-4	0.127	2.2	0.131	6.8	0.080	2.9	0.338	4.1
[#] Mm-2	0.126	3.0	0.135	3.8	0.083	0	0.345	2.1
[#] Mm-3	0.125	3.5	0.131	7.1	0.077	5.9	0.333	5.4
[#] Mm-4	0.125	3.9	0.132	6.0	0.075	8.8	0.332	5.8
[#] Md-2	0.131	0	0.135	3.8	0.078	4.7	0.345	2.0
[#] Md-3	0.122	6.1	0.134	4.9	0.081	1.2	0.337	4.4
[#] Md-4	0.122	6.1	0.128	9.0	0.076	7.1	0.326	7.4

^a NNN is *N*'-nitrosonornicotine.^b NAT is *N*'-nitrosoanatabine.^c NNK is 4-(*N*-nitrosomethylamino)-1-(3-pyridyl)-1-butanone.[#]Those samples are adsorbed the corresponding letter solution. **Scheme 1** Hydrophobic nanoparticles within mesoporous channel of silica along with the adsorption of TSNA

Caption of Figures

Fig. 1. Low-angle XRD patterns of (a) SBA-15 and (b) MCM-41 samples. .

Fig. 2. The N₂ adsorption isotherm of (a, b) SBA-15 and (c, d) MCM-41 composites.

Fig. 3. TEM images of (a, b, c) SBA-15 and (d, e, f) SS-3 and (g, h, i) MCM-41 and (j, k, l) SM-3 samples.

Fig. 4. FT-IR spectra of SBA-15, SS-3, MCM-41 and SM-3 samples.

Fig. 5. The TG-DSC plot of (a) SBA-15 and SS-3, (b) MCM-41 and SM-3 samples.

Fig. 6. Contact angle images of (a) SM-2, (b) SM-3, (c) SM-4, (d) SS-2, (e) SS-3 and (f) SS-4 samples.

Fig. 7. Adsorption of TSNA by SS-r (a) and SM-r samples in tobacco extract solution.

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