Microchimica Acta (2019) 186: 331
https://doi.org/10.1007/s00604-019-3441-6

ORIGINAL PAPER

Polyhedral oligomeric silsesquioxane grafted silica-based core-shell microspheres for reversed-phase high-performance liquid chromatography

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Received: 16 January 2019 / Accepted: 13 April 2019 / Published online: 6 May 2019

Abstract

Polyhedral oligomeric silsesquioxane (POSS) was used to modify spherical silica to fabricate core-shell POSS@SiO_2 microspheres. The material was characterized by Fourier transform infrared experiments, scanning electron microscopy, thermogravimetric analysis and elemental analysis. The material was also used as a stationary phase for HPLC separation. The POSS@SiO_2 column exhibits a reverse-phase liquid chromatography (RPLC) retention mechanism. The column efficiency of alkylbenzenes reaches 67,200 plates·m^{-1}. The POSS@SiO_2 column was also utilized for separation of basic anilines and polycyclic aromatic hydrocarbons. Compared with the commercial C8 column, the POSS@SiO_2 column exhibits enhanced separation selectivity. The column was also used for the separation of synthetic cytokinins 6-benzylaminopurine and 6-furfurylaminopurine in bean sprout after extraction. In addition, the methacrylate groups on the surface of the POSS@SiO_2 microsphere were further functionalized so as to facilitate the fabrication of versatile stationary phases with various separation mechanisms.

Keywords POSSs · Stationary phase · Fabrication · Separation · Post-modification · Ionic liquids · Bean sprout

Introduction

Polyhedral oligomeric silsesquioxane (POSS) is a rigid, structurally defined nano-structured material (diameter: 1–3 nm) consisting of an inorganic "core" and an organic "shell". The molecular formula of POSSs can be expressed as $(RSiO_{1.5})_n$ ($n = 8, 10, 12$) [1–3]. The inorganic "core" of POSSs is of the basic structure of Si-O-Si. The organic R "shell" can be designed as either inactive alkyl, cycloalkyl, aryl groups or active alcohol, alkenyl, acrylate, epoxyalkyl groups [4, 5].

POSSs have been approved to be with the merits of good pH tolerance [6], excellent thermal stability [7, 8], oxidation and wear resistance [9, 10], as well as flame retardancy [11]. They can easily be grafted on the surface of matrix materials via covalent bonds or self-assembly so as to improve their surface properties [12–16]. One of the important applications of POSS reagents is for preparation of hybrid capillary monolithic columns for high-performance liquid chromatography (HPLC) or capillary electrochromatography (CEC) [17–22]. The POSS-based monolithic columns exhibit the merits of ease of preparation, wide pH stability as well as high column efficiency [23–26]. Wu et al. prepared a POSS-based ionic liquid hybrid monolithic column via photoinitiated polymerization of 1-butyl-3-vinylimidazolium-bis[(trifluoromethyl)sulfonyl]imide and POSS methacrylate-substituted (POSS-MA). The column was applied for CEC separation of various aromatic anilines, phenols and alkylbenzenes [20]. With mixed glycidyl-POSS (EP-POSS) and N-phenylaminopropyl-POSS (PA-POSS) as both the crosslinker and monomer, dual POSSs polymerization hybrid monolithic column was designed by Wang et al. for separation of small molecules with mutually-mediated mechanisms. Alkylbenzene ketones, alkylbenzenes, phenolic acids,

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Electronic supplementary material The online version of this article (https://doi.org/10.1007/s00604-019-3441-6) contains supplementary material, which is available to authorized users.

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amino acids and nucleic acid bases were successfully separated via hydrophilic interaction liquid chromatography (HILIC), reverse-phase liquid chromatography (RPLC) or mixed-mode retention mechanisms [21]. With octavinyl-modified POSS (Ov-POSS) and methacrylic acid as the crosslinker and monomer, S-amlodipine (S-AML) imprinted star-shaped coating material was fabricated by Liu and coauthors. Under the optimal conditions, the column efficiency for AML reaches 54,000 plates·m^{-1} with the best resolution of 33 [22]. Zou and coauthors successfully prepared four hybrid capillary monolithic columns by using POSS-epoxy and 1,12-diaminododecane (DADD), 1,10-diaminodecane (DAD), 1,6-diaminohexane (HDA) or 1,8-diaminooctane (DAO). The monolithic columns show highly ordered three-dimensional skeleton structures. The column efficiency can reach 140,000 plates·m^{-1} [27]. In our group, highly cross-linked hybrid monolithic column using POSS-MA and dipentaerythritol penta−/hexa-acrylate was fabricated. The column exhibits high stability and good separation selectivity. The column efficiency can reach 511,000 plates·m^{-1} [28]. Although POSS reagents play important roles in preparation of hybrid monolithic columns, however, to the best of our knowledge, the development of novel kinds of core-shell HPLC stationary phases with POSSs as the shell materials has not been reported so far.

Spherical silica gel is a commonly used matrix material for fabrication of HPLC stationary phases and also widely used for preparation of core-shell materials [29–31]. It possesses the merits of regular spherical units, facilely controlled size and pore structure, good mechanical strength as well as special surface chemistry for versatile post-modifications [32]. However, besides the inherent disadvantage of narrow pH working window (usually 3–7), the silanol groups on the surface of silica gel can't be completely modified via silane reagents due to the steric hindrance [33–35]. The residual silanol groups can produce irreversible adsorption especially for the basic analytes. Thus, tailing peaks are easily observed accompanying with reduced column efficiency during HPLC separation.

POSS was exploited for grafting spherical silica via thiol-ene click reaction. As the representative POSS reagent, POSS-MA was firstly used. With the fabricated POSS@SiO$_2$ core-shell microspheres as the stationary phases, the HPLC performances of the packed column were evaluated. The separation efficiencies of the column were further compared with the commercially available C8 column. Most importantly, the methacrylate groups on the surface of the core-shell microspheres can be further functionalized so as to prepare versatile stationary phases with multiple retention mechanisms.

Experimental

Chemicals and reagents

Spherical silica porous particles (5 μm, 100 Å) were purchased from Fuji Silysia Chemical (Kasugai, Japan, www.fujisilysia.com). POSS-MA was provided by Sigma-Aldrich (St. Louis, MO, USA, www.sigmaaldrich.com). EF-C8 column (150 mm × 4.6 mm i.d., 5 μm, 120 Å) was obtained from Galak Chromatography Technology (Wuxi, China, http://galaktech.bioon.com.cn). Dimethylphenylphosphine (DMPP) and (3-mercaptopropyl)trimethoxysilane (MPS) were obtained from Aladdin Industrial Corporation (Shanghai, China, www.aladdin-e.com). 1-Vinyl-3-carboxymethylimidazolium bromide (VCI·Br) was from Chengjie Chemical (Shanghai, China, www.shyfhx.com). 2,2-Azoisobutyronitrile (AIBN), uracil and uridine were from J&K Scientific (Beijing, China, www.jkchemical.com). Adenosine, inosine, biphenyl, anthracene, o-terophenyl, m-terphenyl and triphenylene were provided by Tokyo Chemical Industry (Shanghai, China, www.tcichemicals.com). Benzene, toluene, ethylbenzene, n-propylbenzene and n-butylbenzene were supplied by Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China, http://tjguangfu.bioon.com.cn). 2,6-dimethylaniline, aniline, diphenylamine and triphenylamine were supplied by Tianjin Kemiou Chemical Reagent (Tianjin, China, www.chemreagent.com). HPLC-grade acetonitrile (ACN) and methanol were from Shanghai Xingke Biochemistry (Shanghai, China, www.cincgrp.com). Water was purified with a Millipore Milli-Q system (Molsheim, France, www.merckmillipore.com).

Instruments

Scanning electron microscope (SEM) pictures were obtained by using a Japan Electron Optics Laboratory JSM-7500 SEM system (Tokyo, Japan, https://www.jeol.co.jp/en/). Fourier transform infrared (FT-IR) experiments were measured on a Bruker Vertex 70 spectrometer (Ettlingen, Germany, www.bruker.com). Thermogravimetric analysis was carried out on a Perkin-Elmer TGA/SDTA851E system (Boston, USA, http://www.perkinelmer.com). Elemental analysis data were obtained from Thermo Fisher Scientific Flash EA1112 system (Milano, Italy, www.thermofisher.com). HPLC experiments were performed on an Elite P230II system (Dalian Elite Analytical Instrument, Dalian, China, www.elitehplc.com).

Fabrication of POSS@SiO$_2$ core-shell microspheres

POSS@SiO$_2$ core-shell microspheres were synthesized with two-steps. Firstly, spherical silica gel (3.0 g) was suspended in anhydrous toluene (35 mL). Then, MPS (3.5 mL) was further added and the suspension was refluxed at 110 °C for 24 h under nitrogen atmosphere. The MPS-modified silica (SIL-MPS) was cooled to room temperature and thoroughly washed by toluene/methanol, dried under vacuum, ready for further usage.

For fabrication of POSS@SiO_2 core-shell microspheres, SIL-MPS (3.0 g) was placed in a reaction flask containing 35 mL of methanol. Then, POSS-MA (4.5 g) and DMPP (catalyst, 0.3 g) were further added into the above suspension. After further stirring at 60 °C for 1 day under nitrogen atmosphere, the POSS@SiO_2 core-shell microspheres were obtained. They can be directly used for column packing after thoroughly washed by methanol.

Fabrication of 1-vinyl-3-carboxymethylimidazolium bromide (VCI·Br) modified POSS@SiO_2 core-shell microspheres

For fabrication of VCI-POSS@SiO_2 core-shell microspheres, POSS@SiO_2 microspheres (3.0 g) were firstly suspended in 25 mL methanol. Then, 4.5 g VCI·Br and 100 mg AIBN were further added, followed by refluxing at 60 °C for 2 days under nitrogen protection. Finally, the fabricated VCI-POSS@SiO_2 core-shell microspheres were cooled to room temperature, repeatedly washed by methanol & methanol/water (1:1, v/v), dried under vacuum, ready for column packing.

Preparation the bean sprout extraction sample

The bean sprouts (25 g) were purchased from the local market. Firstly, the bean sprouts were homogenized with a juicer, followed by centrifuging for 15 min at 15,000 rpm. Then, 16% lead acetate solution (2.0 mL) was slowly added to the above supernatant under stirring. After centrifuging for 15 min again, the supernatant was lyophilized for 12 h, redissolved in 20 mL of methanol and then filtered by 0.45 μm filter membrane. The sample was lyophilized again, redissolved in 20 mL water, for usage. The sprinkled sample was made by mixing equal bean sprout extraction sample and standard 6-benzylaminopurine (6-BA) and 6-furfurylaminopurine (KT) (each 20 $\mu g \cdot mL^{-1}$). An aliquot of 5 μL of samples was further used for direct HPLC analysis.

Results and discussion

Fabrication and characterization of POSS@SiO_2 core-shell microspheres

The typical strategy for fabrication the POSS@SiO_2 core-shell microspheres is illustrated in Fig. 1, with two steps. Firstly, MPS was used to functionalize the spherical silica gel so as to obtain thiol modified microsphere SIL-MPS. Then, with methanol as the solvent, POSS-MA was directly grafted on the surface of SIL-MPS via thiol-ene click reaction for 24 h at 60 °C. The catalyst for preparation of the POSS@SiO_2 core-shell microspheres is crucial important. Both DMPP and AIBN were selected for initiating the click reaction. When AIBN was used as the catalyst, POSS-MA easily self-polymerized and formed tiny fragments (Fig. S1A, see Electronic Supplementary Material; ESM). However, when DMPP was selected as the catalyst, more homogeneous polymerization can be observed which benefits for subsequent HPLC separation (Fig. S1B, see ESM).

To verify the successful fabrication of the POSS@SiO_2 core-shell microspheres, FT-IR was firstly used. The FT-IR spectra are shown in Fig. S2 (see ESM). In the spectrum of SIL-MPS, the band at 980 cm^{-1} attributing to the free silanol groups on silica completely disappears, which can verify the successful modification of the silica with MPS. The presence of band 1730 cm^{-1} in the spectrum of POSS@SiO_2 core-shell microspheres belongs to the stretching vibration absorption of C=O bonds in POSS-MA. The band at 700 cm^{-1} belongs to the vibration absorption of formed C-S bonds. The elemental analysis results demonstrate that the contents of C, H and O of SIL-MPS are 9.8, 2.2 and 1.6%, respectively. For POSS@SiO_2 microspheres, the contents of C, H and O increase into 14.0, 2.8 and 4.4%, respectively. These results can preliminary verify the successful fabrication of the POSS@SiO_2 core-shell microspheres.

Moreover, thermogravimetric analysis was also used to characterize the POSS@SiO_2 core-shell microspheres. From Fig. 2a, we can see the endothermic mass loss aggravates at about 300 °C for POSS@SiO_2 core-shell microspheres. Additional 2.1 and 8.0% weight loss are observed compared with bare silica and MPS modified silica at 700 °C, respectively. These results indicate the acceptable thermostability of the POSS@SiO_2 core-shell microspheres. These results also provide further evidence of the successful fabrication of the core-shell microspheres. SEM picture shows that POSS-MA was homogeneously grafted on the surface of spherical silica gel simultaneously dotted with tiny POSS particles (Fig. 2b) which is obviously different with the bare silica gel (Fig. 2c).

Retention mechanism

The POSS@SiO_2 core-shell microspheres were packed into a 150 mm × 4.6 mm stainless column so as to evaluate its retention mechanism and chromatographic performances. Firstly, the retention mechanism of the POSS@SiO_2 column was studied with a series of hydrophobic alkylbenzenes. As shown in Fig. 3, as the concentration of ACN in the mobile phase system increases to 90%, the retention of benzene, toluene, ethylbenzene, n-propylbenzene and n-butylbenzene sharply decreases which represents typical RPLC retention mechanism.

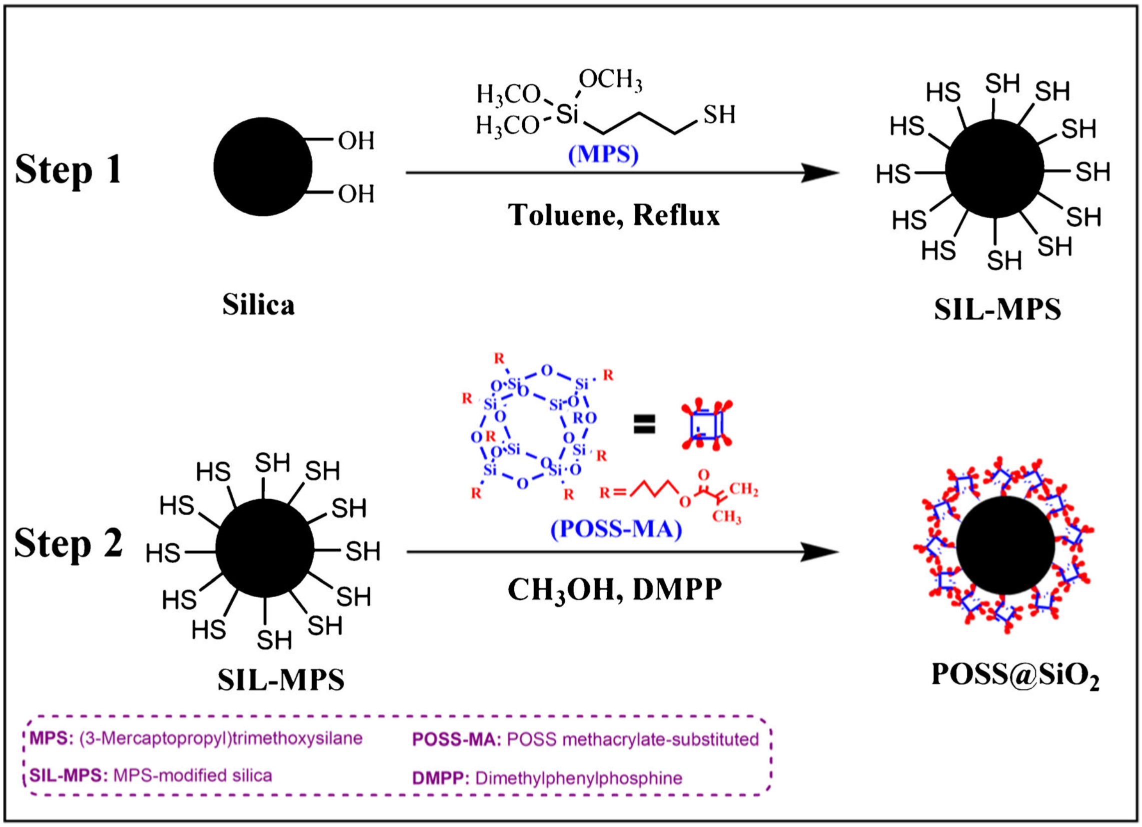

Fig. 1 Scheme for fabrication of the POSS@SiO$_2$ core-shell microspheres. Step 1: MPS functionalizes the silica gel to obtain thiol-modified silica SIL-MPS. Step 2: POSS-MA grafts SIL-MPS with DMPP as the catalyst. Toluene and CH_3OH: solvents

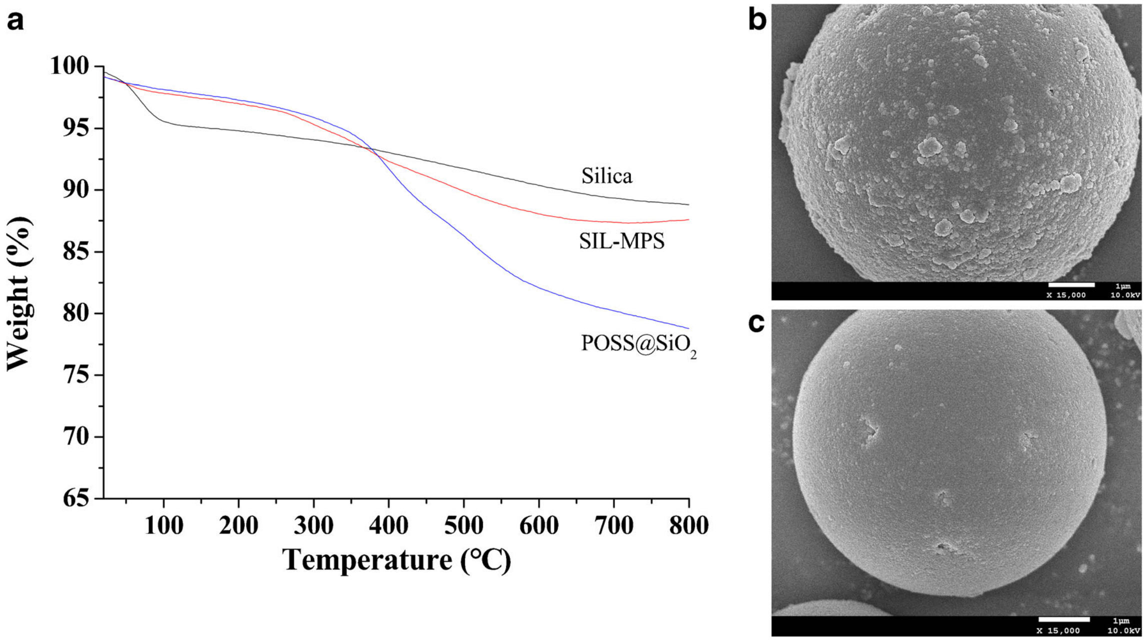

Fig. 2 Thermogravimetric curves of Silica, SIL-MPS and POSS@SiO$_2$ core-shell microspheres (**a**); SEM pictures of the POSS@SiO$_2$ core-shell microsphere (**b**) and bare silica (**c**) with the magnification of 15,000 ×

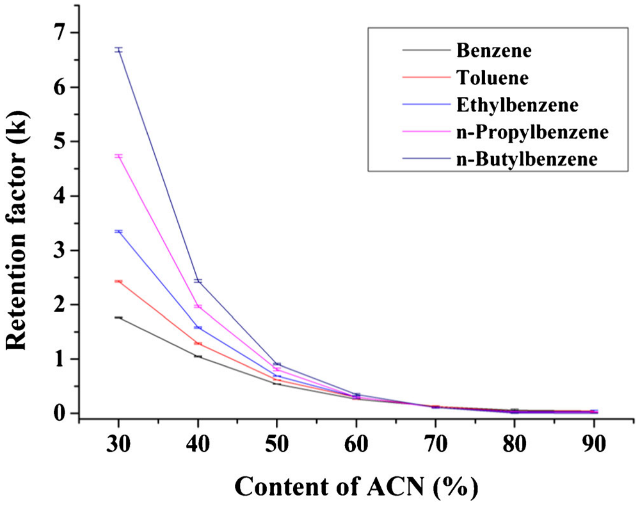

Fig. 3 Effect of ACN content of the mobile phase on the retention of alkylbenzenes. Conditions: mobile phase, ACN/H_2O with corresponding volume fractions; flow-rate, 1.0 mL·min^{-1}; detection wavelength, 214 nm

Separation of alkylbenzenes

For evaluating the chromatographic performances of the POSS@SiO_2 column, n-butylbenzene, n-propylbenzene, ethylbenzene, toluene and benzene were firstly used as the test samples. The separation chromatogram is shown in Fig. 4a. With ACN/H_2O (40:60, v/v) as the mobile phase, baseline separation of these compounds can be achieved within 6 min. The column also displays high column efficiencies and reach 62,700 ± 1700–67,200 ± 2500 ($n = 3$) plates·m^{-1}. Furthermore, the peaks also indicate with good symmetry and the tailing factors for these compounds range from 1.05 to 1.15.

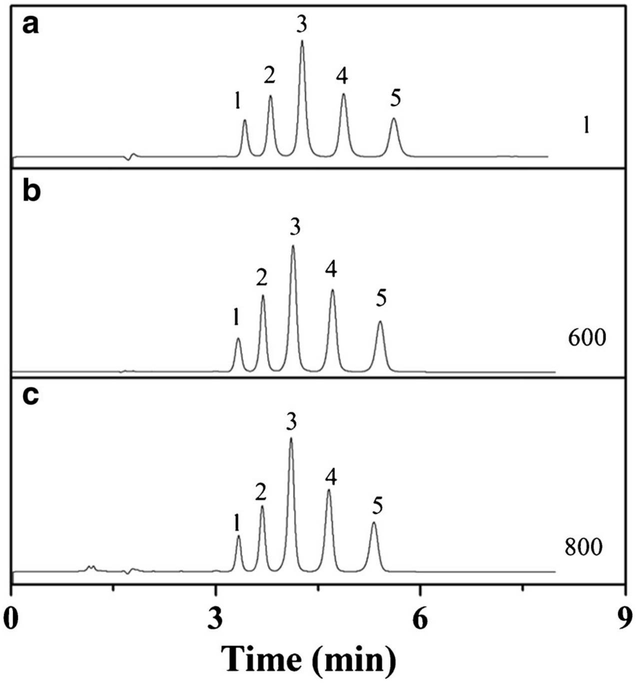

Fig. 4 Separation chromatograms of alkylbenzenes on POSS@SiO_2 column (**a**) and its stability after continuous injection for 600 (**b**) and 800 (**c**) times. Conditions: mobile phase, ACN/H_2O (40:60, v/v); flow-rate, 1.0 mL·min^{-1}; detection wavelength, 214 nm. Analytes: 1. benzene; 2. toluene; 3. ethylbenzene; 4. n-propylbenzene; 5. n-butylbenzene

We further investigated the stability of the POSS@SiO_2 column by using alkylbenzenes. After the column was continuously used for 600, 800 times, the separation profiling of these substances are not significantly changed. These results indicate the good stability of the POSS@SiO_2 core-shell stationary phases (Fig. 4b and c).

Separation of polycyclic aromatic hydrocarbons

The separation performance of the POSS@SiO_2 column was also tested with polycyclic aromatic hydrocarbons biphenyl (Log P: 3.71), anthracene (Log P: 4.03), o-terophenyl (Log P: 5.38), m-terphenyl (Log P: 5.38) and triphenylene (Log P: 5.03). With ACN/H_2O (40:60, v/v) as the mobile phase, the five test compounds can be baseline-separated within 11 min (Fig. 5a). A commercial EF-C8 column was also used to separate the above compounds. With the same chromatographic conditions, the column demonstrates strong retention for these compounds and the retention time prolongs to more than 200 min (Fig. 5b). By further increasing the ratio of ACN in the mobile phase to ACN/H_2O (68:32, v/v), as shown in Fig. 5c, the total separation time is almost the same as that in Fig. 5a. However, the resolution of o-terophenyl (peak 3) and m-terphenyl (peak 4) is only 1.14.

The C8 column displays typical RPLC retention mechanism. Thus, the elution orders of polycyclic aromatic hydrocarbons on C8 column are agreed with their hydrophobicity. The Log *P* values of o-terophenyl (peak 3) and m-terphenyl (peak 4) are both 5.38. Therefore, they were poorly separated with the present conditions on C8 column (Fig. 5c). For comparison, the elution order of triphenylene is reversed with o-terophenyl and m-terphenyl on the POSS@SiO_2 column which probably attributes to the relatively strong π-π interaction between triphenylene and the POSS shell materials. Furthermore, the POSS@SiO_2 column also exhibits different separation selectivity (Fig. 5a).

Separation of basic anilines

The separation performance of the POSS@SiO_2 column was also evaluated with basic anilines. The results were also compared with that via the commercially available C8 column. Figure 6a is the typical chromatogram for separation of 2,6-dimethylaniline, aniline, diphenylamine and triphenylamine with ACN/H_2O = 40:60 as the mobile phase. The four compounds are baseline-separated within 10 min with the tailing factors of 1.18, 1.18, 0.97 and 0.92, respectively. Figure 6b is the chromatogram for separation of these compounds on the

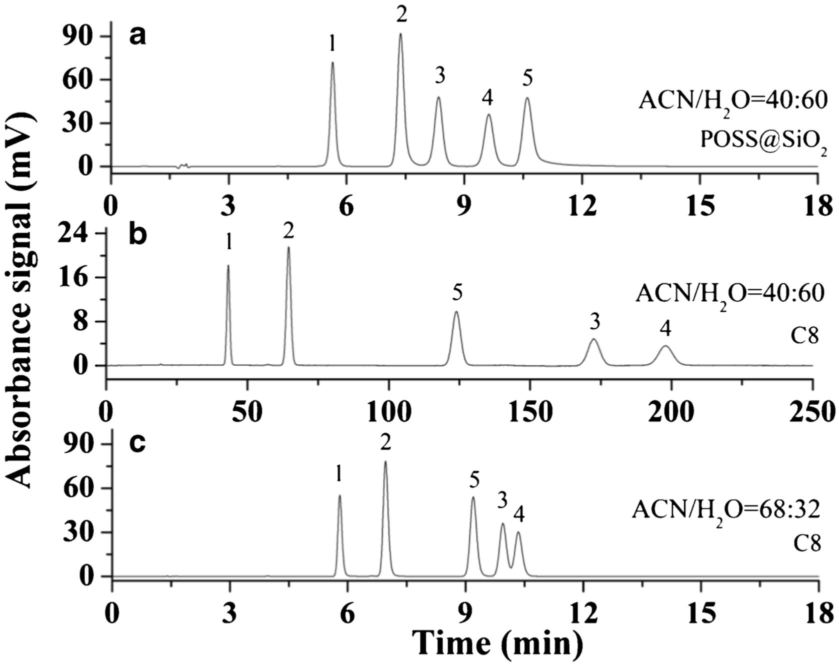

Fig. 5 Separation chromatograms of polycyclic aromatic hydrocarbons on POSS@SiO_2 column (**a**) and commercially available C8 column (**b**, **c**). Conditions: mobile phase, ACN/H_2O (40:60, v/v) for (**a** and **b**), ACN/H_2O (68:32, v/v) for (**c**); flow-rate, 1.0 mL·min^{-1}; detection wavelength, 254 nm. Analytes: 1. biphenyl; 2. anthracene; 3. o-terophenyl; 4. m-terphenyl; 5. triphenylene

C8 column with the same conditions. The anilines display strong retention and the peak of triphenylamine can't be observed up to 120 min. By further increasing the ACN content of the mobile phase to ACN/H_2O = 72:28, as shown in Fig. 6c, triphenylamine (peak 4) almost displays the same retention time as that in Fig. 6a. However, 2,6-dimethylaniline (peak 1) and aniline (peak 2) stack together with the tailing factors of 1.65, 1.27 and 1.13, respectively. Obviously, the POSS@SiO_2 column demonstrates different separation selectivity and improves the peaks shapes for basic anilines.

Analysis of plant growth regulators in bean sprout

Bean sprouts are the traditional Chinese food which are mainly cultured from mung or soya beans. To accelerate the growing of bean sprouts, synthetic cytokinins, such as 6-BA and KT, are often illegally utilized as the plant growth regulators [36]. However, such bean sprouts are detrimental to the health of the human body and can cause many diseases. Therefore, rapid and effective detection for the residues of 6-BA and KT in bean sprout is vital important for the food safety.

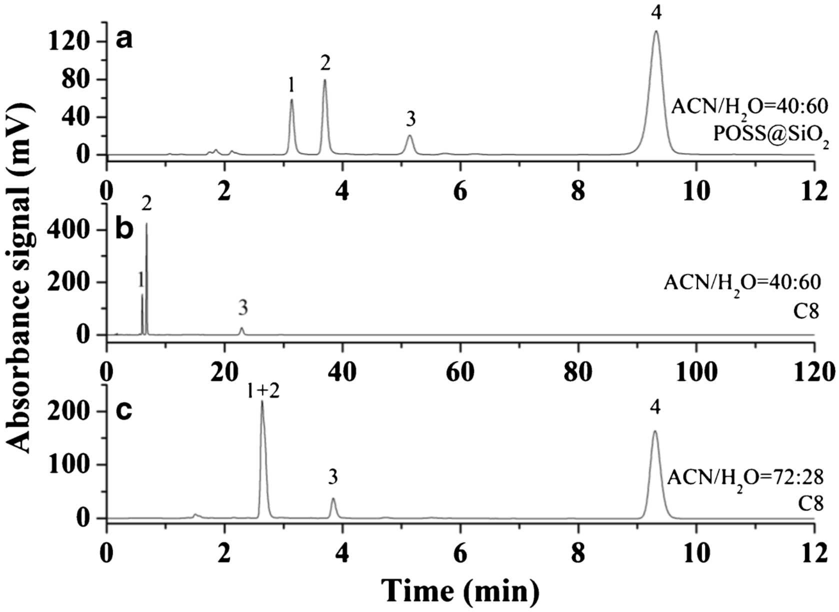

Fig. 6 Separation chromatograms of anilines on POSS@SiO_2 column (**a**) and commercially available C8 column (**b**, **c**). Conditions: mobile phase, ACN/H_2O (40:60, v/v) for (**a**, **b**), ACN/H_2O (72:28, v/v) for (**c**); flow-rate, 1.0 mL·min^{-1}; detection wavelength, 214 nm. Analytes: 1. 2,6-dimethylaniline; 2. aniline; 3. diphenylamine; 4. triphenylamine

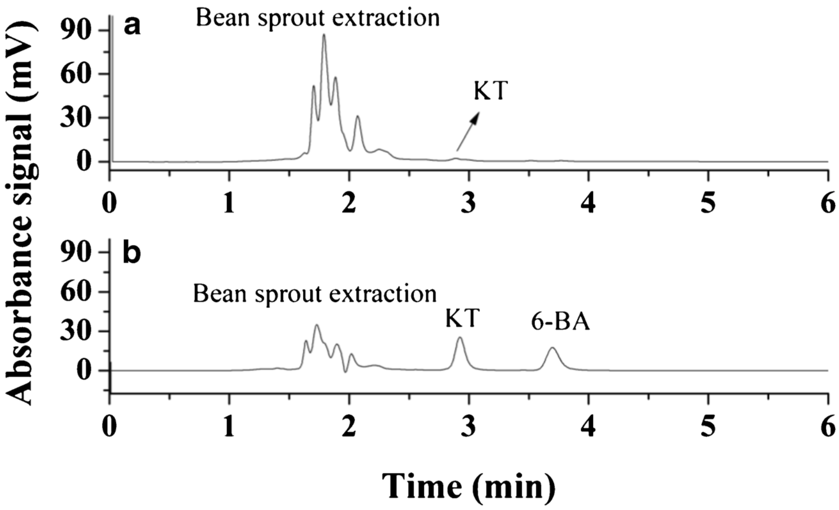

Fig. 7 Separation chromatograms of bean sprout extraction (**a**) as well as that sprinkled with 6-BA and KT (**b**). Conditions: mobile phase, ACN/H_2O (40:60, v/v); flow-rate, 1.0 mL·min^{-1}; detection wavelength, 214 nm

Figure 7a is the typical chromatogram for separation of the bean sprout extraction with ACN/H_2O (40:60, v/v) as the mobile phase. The main components of the sample are presented in around 1.5–2.4 min. Figure 7b is the chromatogram of the bean sprout extraction sprinkled with 6-BA and KT standards. The two standards display symmetric peak shapes and are well separated with the matrix of the bean sprout. Furthermore, based on the retention time, KT can be detected from the bean sprout extraction. These results further demonstrate the potential application of the POSS@SiO_2 column for real sample analysis.

Polyhedral oligomeric silsesquioxane on silica (POSS@SiO_2) core-shell microspheres further post-modification

The development of versatile customizable stationary phases is crucial for comprehensive applications in real sample analysis. One of the important merits of the POSS@SiO_2 core-shell microspheres is that numerous methacrylate groups still exist on the surface of the POSS shell materials. Thus, it provides a route for fabrication of versatile stationary phases with multiple retention mechanisms. For example, a zwitterionic ionic liquid VCI·Br was further used to functionalize the POSS@SiO_2 core-shell materials. The synthesis route is illustrated in Fig. S3 (see ESM). The new VCI-POSS@SiO_2 core-shell microspheres were further verified via FT-IR (Fig. S4, see ESM) and thermogravimetric analysis (Fig. S5, see ESM).

When it was further modified by VCI·Br, the hydrophilicity of the VCI-POSS@SiO_2 core-shell microspheres is obviously increased. As shown in Fig. 8a, both RPLC and HILIC retention mechanisms can be observed from the VCI-POSS@SiO_2 column. Thus, successful separation of hydrophilic uracil, adenosine, uridine and inosine can be achieved (Fig. 8b).

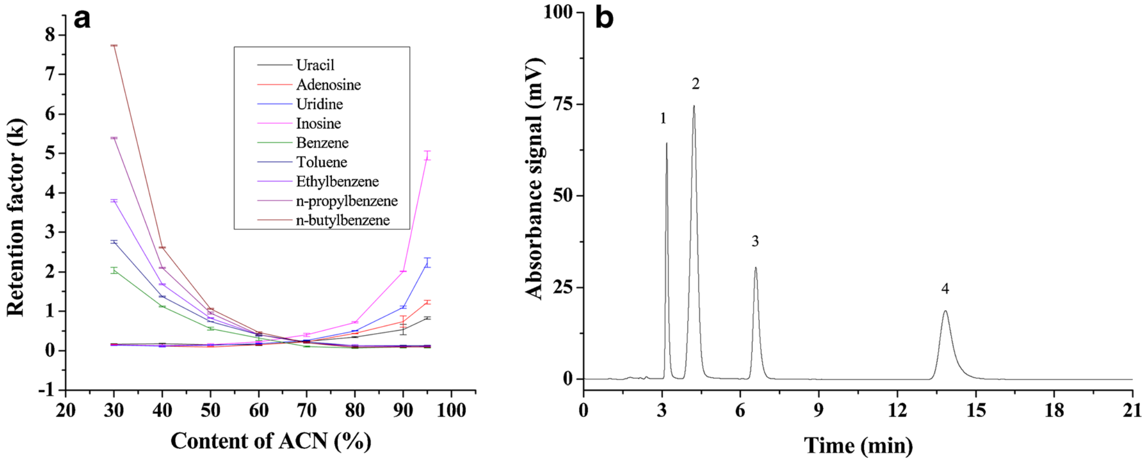

Fig. 8 Effect of ACN content of the mobile phase on the retention of alkylbenzenes, nucleosides and nucleic acid bases on VCI-POSS@SiO_2 column (**a**) and it was further used for separation of nucleosides and nucleic acid bases (**b**). Experimental conditions: mobile phase, ACN/H_2O with corresponding volume fractions for (**a**), ACN/H_2O (90/10, v/v) for (**b**); flow-rate, 1.0 mL·min^{-1}; detection wavelength, 254 nm. Analytes: 1. uracil; 2. adenosine; 3. uridine; 4. inosine

Conclusions

In conclusion, polyhedral oligomeric silsesquioxane on silica ($POSS@SiO_2$) core-shell microspheres were fabricated and further exploited as stationary phase for HPLC. The packed $POSS@SiO_2$ column exhibits high column efficiency and enhanced separation selectivity via RPLC. In addition, the $POSS@SiO_2$ core-shell microspheres can be further functionalized so as to fabricate versatile stationary phases with multiple retention mechanisms. In our future research, new stationary phases based on $POSS@SiO_2$ microspheres will be designed and fabricated, especially those suitable for analysis of complex biological samples.

Acknowledgements Financial supports from National Natural Science Foundation of China (21675039) and Young Talent of Hebei Province are gratefully acknowledged.

Compliance with ethical standards The author(s) declare that they have no competing interests.

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