Preparation of Silica Monoliths with Macropores and Mesopores and of High Specific Surface Area with Low Shrinkage using a Template Induced Method

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In this study we report a new method for the synthesis of a silica monolithic column bed with bimodal pores (throughpores and mesopores). The template induced synthesis method was used to direct bimodal pores simultaneously instead of the usual post base-treating method. Block polymer Pluronic F127 was chosen as a dual-function template to form hierarchically porous silica monolith with both macropores and mesopores. This is a simplification of the method of monolithic column preparation. Poly(ethylene glycol) was used as a partial substitute for F127 can effectively prevent shrinkage during the monolith aging process without losing much surface area (944 m^2/g to 807 m^2/g). More importantly, the resultant material showed a much narrower mesopore size (centered at 6 nm) distribution than that made using only F127 as the template reagent, which helps the mass transfer process. The solvent washing method was used to remove the remaining organic template, and it was proved to be effective enough. The new synthesis method makes the fabrication of the silica monolithic column (especially capillary column) much easier. All the structure parameters indicate that monolith PFA05 prepared by the above method is a good material for separation, with the merits of much higher surface area than usual commercial HPLC silica particles, suitable mesopore volume, narrow mesopore size distribution, low shrinkage and it is easily prepared.

Key Words : Silica monolith, Bimodal pores, Low shrinkage, Separation material, High surface area

Introduction

Silica monoliths with macropores (or throughpores) and mesopores, which were first introduced by Nakanishi and Soga,[1] have attracted much attention in the separation field. Compared to traditional particulate packings, this novel structure enables high efficiency and low backpressure simultaneously. The bimodal pores silica monolith is usually fabricated by a two step method in which the hydrolysis and condensation of alkoxysilane in the presence of polyethyleneglycol forms a silica skeleton with macropores. Then treatment of the silica skeleton with base results in the formation of mesopores. Numerous reports have demonstrated the effectiveness of this kind of silica monolith in HPLC and CEC.[2-6]

Nevertheless, the two step manufacturing process is complicated, and cannot be easily reproduced.[7] The key problem is the mesopore formation in the silica gel. It is usually achieved by post-gelation treatments using solvent-exchange (usually using aqueous ammonium hydroxide solution) and aging.[8-10] This results in a wide variation in mesopore size. The total mesopore volume [11] is usually larger than the pore volume normally used in chromatography (usually about 1 cm^3/g), The specific surface area S$_{BET}$ is usually about 170-370 m^2/g.

To precisely control the mesopore size distribution and simplify the manufacturing process, Nakanishi, K. *et al.*[12] reported the preparation of macroporous silica with tailored mesopores. The size of the mesopores was controlled by making use of base coming from the hydrolysis of urea, which was added in the initial mixture. The mesopores are obtained merely by heating the whole gelation mass instead of using the post-solvent-exchange method with aqueous ammonium hydroxide solution. By this method, the mesopore size can be controlled to 8 nm and the total volume is 4.47 cm^3/g.[13] The resulting specific surface area is a little lower than that prepared by the two-step procedure.[14]

The development of monolithic capillary columns for μ-HPLC and capillary electrochromatography has been the subject of much research in recent years.[15] However, this research has mostly focused on the monolith applications, and there has been little evolution on the monolithic material itself.[16,17] More importantly, the specific surface area has not further improved and the bimodal pores structure can not be optimized, which directly affects its chromatographic performance. Therefore, a new synthetic strategy is needed to improve the mesopore structure with appropriate pore volume (usually about 1cm^3/g for separation), higher surface area and narrower pore size distribution. Thus separation will improve and much higher column efficiency can be expected.

In the present paper we report a simple one-pot method using the surfactant-templated strategy for the preparation of a silica monolith containing macropores and mesopores, with the merit of *anti*-shrinkage, which is appropriate for monolithic capillary columns, and also cladded monolithic

columns. In this work, block polymer Pluronic F127 was used as a dual-function template to form a hierarchically porous silica monolith with both macropores and mesopores. The surfactant-templated mesoporosity can result in nearly three times the surface area than that of previously reported base-treated silica monoliths. The resulting porous material is characterized with high surface area (800-1000 m²/g), suitable pore volume (usually about 1 cm³/g) and narrow pore size distribution (centered at about 6 nm). These are desirable properties for separation. However, bimodal pore monoliths can easily shrink during aging.[14,18] This shrinkage is a disadvantage in monolithic capillary column fabrication. A range of preparation conditions were explored to deal with the shrinkage of the monolith during the aging procedure and fused-silica capillaries (ID = 100 μm or 250 μm) were used to evaluate shrinkage. When the shrinkage factors are understood, the size of the silica monolith column can be controlled to meet specific needs. Thus monolithic column with both macropores and mesopores can be expected to be an important development in the separation field.

Experimental

Materials and Reagents. Tetramethoxysilane (TMOS) obtained from the Chemical Factory of Wuhan University (Wuhan, China), was used as a silica source. Poly(ethylene glycol) (Mw 10000) was obtained from Merck (Darmstadt, Germany). Acetic acid (AR) was purchased from Shanghai General Chemical Reagent Factory (Shanghai, China). Poly(alkylene oxide) block polymer (abbreviated as EO106PO70EO106, F127) was a gift from BASF (USA). Water was distilled from a quartz apparatus. Fused-silica capillary (ID = 100 μm or 250 μm) was purchased from Hebei Reafine chromatography Company.

Preparation of the Bimodal Pore Silica Monolith. All the monoliths were prepared by the sol-gel method from a starting composition shown in Table 1. Hydrolysis and poly-condensation were conducted by mixing a homogeneous solution of F127 (or its mixture) and aqueous acid solution with TMOS under vigorous stirring in an ice bath. After stirring for 30 min, the resultant transparent solutions were transferred to a PTFE vessel or a fused-silica capillary, and then sealed. The samples were allowed to gel at various temperatures (shown as Table 1) for 24 h. It can be observed

(from the PTFE vessel) that the gelation took place after 1 h. The wet gels were subsequently aged at the same temperature with the seals still in place for 24 h. Next, the wet gel pieces immersed in an appropriate amount of aqueous external solvent were then transferred to an autoclave filled with distilled water to be treated at 120 °C for 1 h. They were then cooled to room temperature. To remove the organic constituents from the wet gel, the pieces of aged gel were then immersed in distilled water and stirred washing by an agitator for half an hour, then rinsed with methanol, finally evaporation-dried at 40 °C. For purposes of comparison, PFA05C was then calcined at 560 °C for 8 h.

Characterization. The macroporous morphology was examined by an SEM (S-3400N, Hitachi Co. Japan, with Au coating) and FE-SEM (S-4800N, Hitachi Co. Japan, without coating).

Nitrogen adsorption-desorption measurements at 77 K using ASAP 2020 (Micromeritics, USA) were performed to obtain mesopore size distributions. Samples were out-gassed under vacuum at 150 °C for at least 8 h prior to each measurement. Specific surface areas were calculated by the BET method. For pore size distributions, adsorption branch was used in the BJH calculation.

Results and Discussion

In this work the amount of the template addition (PEG and F127) was fixed at 1.15 g while varying other synthesis parameters. All the silica samples were successfully prepared *via* sol-gel processing, and the as-synthesized samples exhibit monolithic shape with white color and glossy surface with no cracks observable. The dimensions of the resulting monolith depended on the mold used. All the silica monolith specimens exhibited co-continuous morphology of silica gel skeletons and macropores (as shown in Figures 1-6). For the samples FA, FA01Et and PFA05 the mean through pore size is approximately 2 μm which corresponds to the size of interstitial voids in a conventional column packed with 5 μm spherical particles.[19] The porosity measurement results of the bimodal pore silica monoliths are listed in Table 2.

F127 Acting as a Dual-Function Template. Sample PA, using PEG as the only template, has a co-continuous porous morphology (shown in Figure 1), but the mesopores of PA proved to be too small to use as a chromatographic material directly as shown in Table 2. Block polymer F127 was chosen to use as the only template reagent in sample FA and

Table 1. Starting composition of sample gels

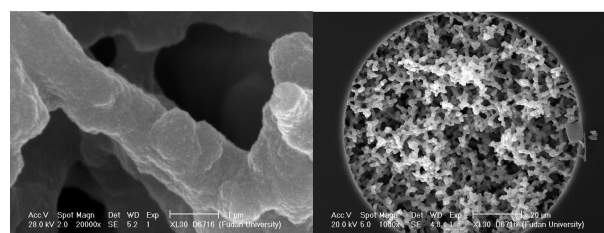| Sample	TMOS (mL)	0.01 M HAc aq (mL)	F127 (g)	PEG (g)	T_Gelling (°C)
PA	4.0	10	/	1.15	40
FA	4.0	10	1.15	/	40
FA6	6.0	10	1.15	/	40
FA01Et	4.0	10(containing 10% ethanol)	1.15	/	45
PFA05	5.0	10	0.57	0.57	40
PFA05C	5.0	10	0.57	0.57	40

Figure 1. SEM photographs of capillary monolithic column PA (I.D. = 100 μm).
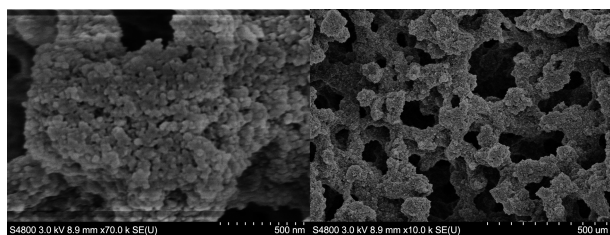
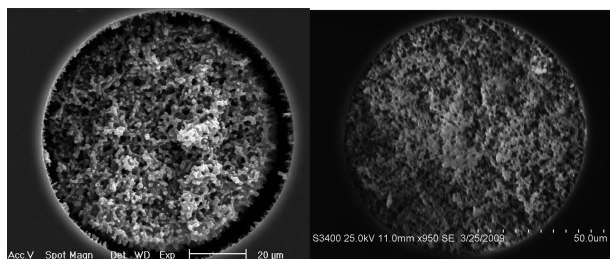**Figure 2.** FE-SEM photographs of dried FA silica monolith.

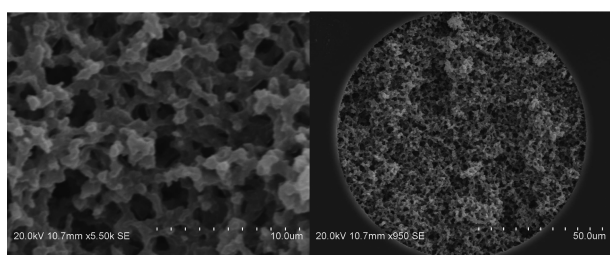**Figure 3.** SEM photographs of monolithic capillary column (100 μm) of FA (left) and FA6 (right).

Figure 4. SEM photographs of dried silica monolith FA01Et and its capillary column (100 μm).
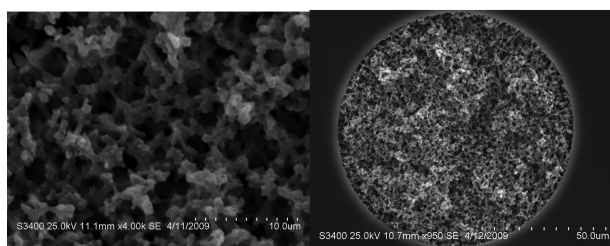

Figure 5. SEM photographs of dried PFA05 silica monolith and its capillary column (100 μm).

Figure 6. SEM and FE-SEM photographs of dried PFA05 silica monolith and its capillary column (250 μm).

Table 2. Porosity measurement results of the bimodal pore silica monolith

Sample	S_{BET} (m^2/g)	Pore size (nm)	Total pore volume^a (cm^3/g)
PA	646	2.5	0.6
FA	944	6.0	1.3
FA01Et	16	22	0.1
PFA05	807	6.4	0.9
PFA05C	924	5.7	0.9

^{a}Pore size distribution calculated on the adsorption branch of the isotherm. Taken as the maximum in the pore size distribution curve.

Figure 7. Nitrogen adsorption/desorption isotherm plots of samples PA, PFA05 and FA.

its co-continuous macropore morphology is shown in Figure 2. The through pore is in an appropriate size of about 2-3 μm.

Figure 7 shows the nitrogen adsorption and desorption isotherms for the silica monolith FA which exhibits a typical type IV curve with a H1 hysteresis loop and a well-defined step at approximately $P_s/P_0 = 0.5$-0.9. This is a typical result for a mesoporous material.

The bimodal pore structure obtained can be attributed to the block co-polymer F127 which has two functions in the formation of the silica monolith. It acts as both a phase separation agent directing the macropores and also a self-assembling template directing mesopores during the poly-
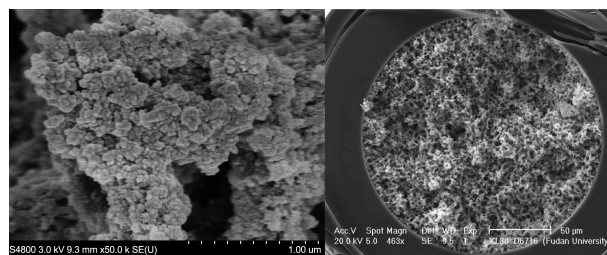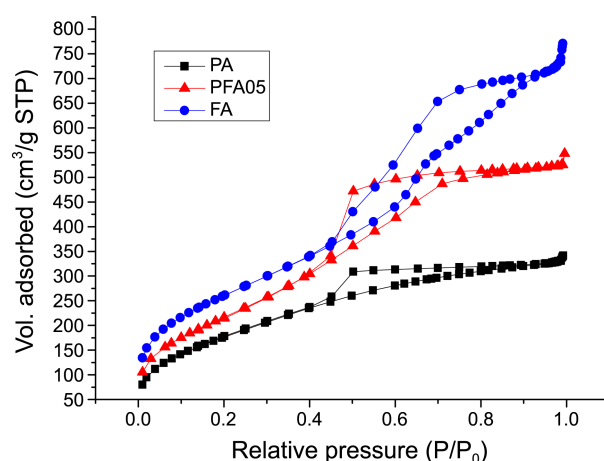
condensation process. The pore size distribution calculated from the adsorption branch of the isotherms based on Barrett-Joyner-Halenda (BJH) model, as shown in Figure 8, gave a broad peak centered at 6 nm. This could be attributed to the micelles of F127 being a little distorted by the methanol hydrolyzed by TMOS. When the concentration of F127 in the initial solution is above the critical micelle concentration (CMC, for F127 the CMC value is 0.076 g·L^{-1} at 40 ᵒC),[20] the F127 micelles appear. However, in a sealed space, with the methanol hydrolyzed from TMOS present in the initial solution, the distorted F127 micelles and free F127 monomers are present together in solution. As a result, the FA silica monolith shows no obvious XRD signals in the region 2θ ranging from 1ᵒ to 10ᵒ where ordered mesoporous silica materials generally show Brag lines. We propose the
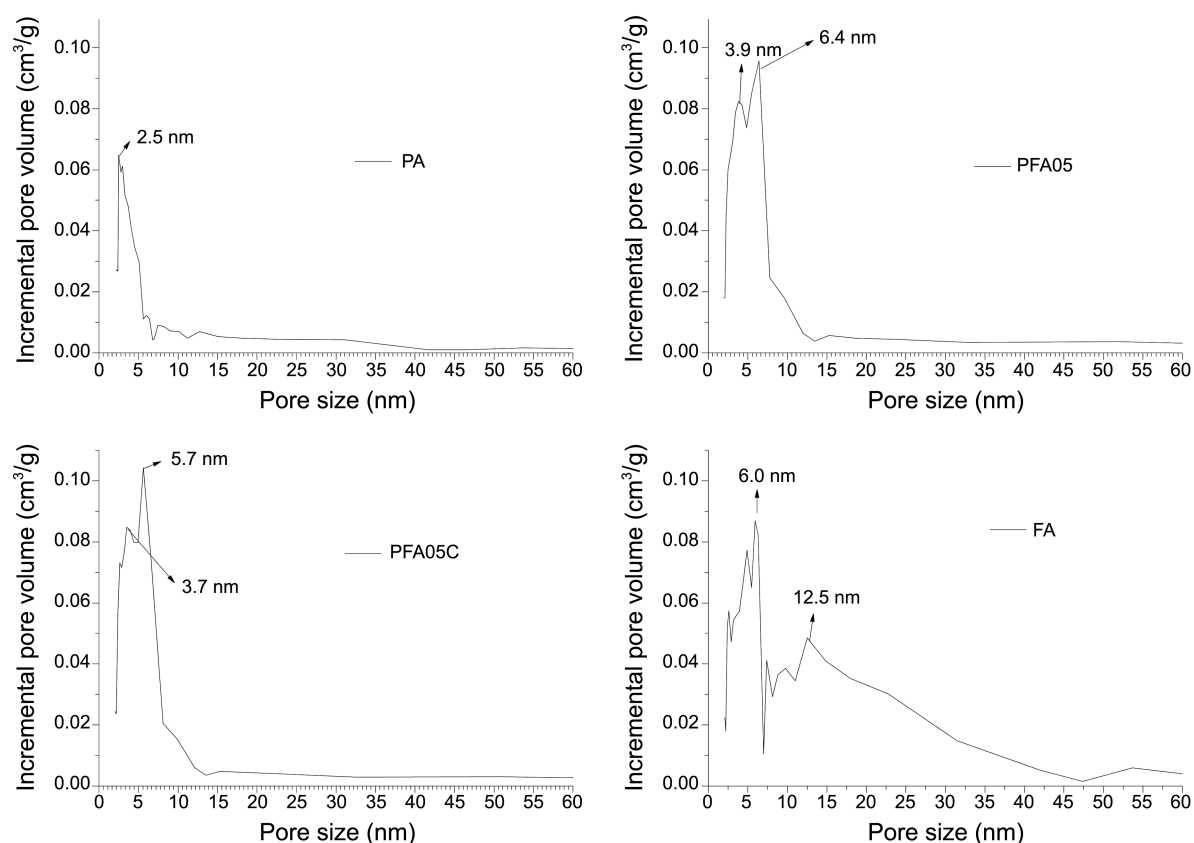
Figure 8. Pore size distribution curves of samples PA, PFA05, PFA05C and FA.

silica initially interacts with F127 micelles, which corresponds to the self-assembling process, and the aggregation of which is further controlled by the hydrogen-bonding of other F127 linear monomers directing the phase separation. Therefore, the bimodal pore system is formed spontaneously in a closed condition.

The specific surface area was calculated to be 944 m^2/g using Brunauer-Emmett-Teller (BET) method, it is nearly three times higher than that of usual commercial HPLC materials. The total pore volume was 1.26 cm^3/g. The FA monolith is proven to be a bimodal pore silica monolith with both interconnected macropores in the micrometer range and internal mesopores in the nanometer range, and all the structure characterization results indicate FA is a good material for separation.

However, when the FA type was used to make a monolithic capillary column, an obvious shrinkage was observed after the aging process (Figure 3). This was more obvious than the PA with PEG as template. Therefore, A PTFE heat-shrinkable enveloping tube can be used instead.

The shrinkage occurs because that FA material characterized with high surface area has more mesopores than PA. Therefore, to form a same volume, the FA needs more silica source than the PA. There are two ways to reduce the shrinkage. One is adding more silica source. However, only adding the silica source as FA6 listed in Table 1, induced a very dense structure losing the advantage of high permeability usually associated with the monolith structure (Figure

3). The other way is to sacrifice a moiety of mesopores and specific surface area. This should prevent the further condensation during the aging and hydrothermal process. Accordingly, the samples FA01Et and PFA05 were thus successfully prepared. These kinds of monolithic materials are especially fit for using as μ-HPLC and CEC column.

***Anti*-Shrinkage Silica Monolith.**

Using Organic Additive: Wan, Y. *et al.*[21] reported that lyophilic organics can aid or oppose the formation of micelles. At high concentration, agents such as short-chain alcohols can enhance the solubility of monomeric surfactants, thus suppressing micellization and raising CMC values of nonionic surfactants. In this study, different amounts of ethanol were added to the HAc aqueous solution as the organic additive before the TMOS hydrolysis. It can be observed that, when the ethanol is added at a low concentration (5%), the shrinkage of the final product in a 100 μm capillary is not obvious. When the ethanol concentration was raised to 10% (marked as FA01Et), no shrinkage can be observed even after the hydrothermal process, and a perfect co-continuous structure was obtained as shown in Figure 4. This can be interpreted as: at the 10% concentration, ethanol enhances the solubility of F127 in the initial solution, which suppressing micellization of F127, more monomeric F127 lead to a decrease in the number of micelles directing mesopore formation on the silica skeleton, thus the monolith shrinkage caused by large numbers of mesopores can be reduced.

However, the effect of ethanol on *anti*-shrinkage is limited. When the capillary was changed to a wider internal diameter (ID = 250 μm), the shrinkage could not be avoided. Furthermore, when the concentration of ethanol was above 10%, the gelation could be observed to be more and more difficult. This observation indicates that the ethanol has another effect which does have a distinct influence on the reaction kinetics. This especially affects the hydrolysis rates, and the as-synthesised monolith product is in fact not stable enough in the aging process. In case of removing the template reagent and drying at a high temperature (> 150 °C), the monolith FA01Et tended to proceed to a further polycondensation. The mesopores thus collapsed, and the final dry product therefore lost its high specific surface area (only 16 m²/g).

Adding Silica Source: As described above, F127 has two functions in the formation of the silica monolith, it acts as not only a phase separation agent but also a mesopore template during the polycondensation process. However, fixing the amount of silica, more mesopores mean greater tendency for shrinkage. Therefore, sacrificing a moiety of mesopores is a strategy to reduce the shrinkage. Consequently, 50% of the total mass of structure-directing reagent was replaced by PEG (MW = 10000) instead (W_{PEG}/W_{F127} = 1/1), to reduce the numbers of mesopores. Here PEG acts mainly as the phase separating agent.

Changing the constituent of the structure-directing reagent proved not to be enough. Therefore the amount of silica source TMOS was also increased from 4 mL to 5 mL. PFA05 was thus successfully prepared as listed in Table 1 and its macropore structure was shown in Figures 5 and 6. Both 100 μm and 250 μm capillary monolithic columns exhibited perfect co-continuous morphology, and no shrinkage was observed indicating an obvious *anti*-shrink effect.

The PFA05 monolith appeared a similar morphology with that of FA. The through pore size is about 2-3 μm, and the skeleton size is about 1 μm. Figure 7 shows the nitrogen adsorption and desorption isotherms for the silica monolith PFA05, which exhibits a typical type IV curve with a H1 hysteresis loop, and a well-defined step at approximately P_s/P_0 = 0.4-0.9. This behavior is typical of a mesoporous material. The pore size distributions calculated from the adsorption branch of the isotherms based on Barrett-Joyner-Halenda (BJH) model, are shown in Figure 8. Compared to the monolith of FA, PFA05 gave a narrower peak centered at 6.4 nm, and the mesopore size is comparable to that of commercial silica particles, therefore is appropriate for chromatographic use. The specific surface area was calculated to be 807 m²/g using Brunauer-Emmett-Teller (BET) method, it is a little lower than that of FA, but is still much higher than the surface areas of usual commercial HPLC materials. The total pore volume was found to be 0.91 cm³/g.

Monolith PFA05 is proven to be also a bimodal pore silica monolith with both interconnected macropores in the micrometer range and internal mesopores in the nanometer range. It is a good material for separation with the merit of low-shrinkage, especially suitable for making a capillary column used in μ-HPLC and CEC by *in-situ* method.

To prevent a further shrinkage during a long calcination process, the organic constituents in the wet gel can be removed by the washing method as described in the experimental. For comparison, the residual monolith PFA05 was calcined at 560 °C for 8 h (marked as PFA05C), no cracks were seen but a little shrinkage of the monolith was observed. Nitrogen adsorption-desorption measurement results were shown in Table 2. The total pore volume exhibited no change besides the specific surface area showing a slight increase, which indicates that the mesopore structure is stable enough. The template removal method by solvent washing is highly efficient. Therefore, the calcination step in the silica monolith preparation can be avoided, which represents a simplification in monolith preparation.

Conclusions

In this study, a new simple template induced synthesis method for bimodal (macropores and mesopores) pores silica monolith showed a co-continuous porous morphology was reported. F127 acts as two functions template in the formation of silica monolith: one is a phase separation agent directing the macropores in micrometer range, and the other is a self-assembling template directing mesopores in nanometer range during the polycondensation process. Although the concentration of F127 used was above its CMC value with the methanol hydrolyzed from TMOS coexisting in the sealed space, the F127 micelles were distorted and in fact were concurrent with free F127 monomer. As a result, no obvious XRD signals can be observed as ordered mesoporous materials generally show. The resulting porous material is characterized with a much higher surface area (944 m²/g) than usual commercial HPLC silica particles, proper mesopore volume (1.3 cm³/g), but a broad mesopore size distribution (centered at 6.4 nm). The obtained through pore size of about 2-3 μm is corresponded to the size of interstitial voids in a conventional column packed with 5 μm spherical particles, however, it showed a tendency to shrink during the monolith aging process.

The addition of 10% ethanol as an organic additive to enhance the solubility of F127 and thereby decrease the numbers of mesopores showed a limited *anti*-shrinkage effect, but the resultant monolith appeared not stable enough at high temperature.

Using poly(ethylene glycol) as a partial substitute for F127 followed with adding a silica source can effectively prevent the shrinkage with minimal lose of surface area (944 m²/g to 807 m²/g) , which can make the fabricating of silica monolithic column as well as capillary monolithic column much easier. More importantly, the resultant material showed a much narrower mesopore size distribution (centered at 6 nm) than that of using only F127 as the template reagent, which is in favours the mass transfer process.

The solvent washing method was used in the final organic template removing process. Nitrogen adsorption-desorption measurement results showed that the total mesopore volume

remained unchanged after the calcination process (0.9 cm^3/g), which indicated that the solvent washing method is effective, and can simplify monolith preparation.

All the structure parameters indicating that monolith PFA05 with bimodal pores is a good material for separation, with the merits of much higher surface area than usual commercial HPLC silica particles, suitable mesopore volume, narrow mesopore size distribution, *anti*-shrinkage and easy preparation. It is a new material especially suitable for making a capillary column used in μ-HPLC and CEC by in-situ method.

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