

# A method for the preparation of transparent mesoporous silica sol–gel monoliths containing grafted organic functional groups

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Transparent, crack-free mesoporous silica sol–gel monolith **2** was prepared from the hydrolysis of  $\text{Si}(\text{OMe})_4$  in MeOH containing ethylene glycol ( $\text{HOCH}_2\text{CH}_2\text{OH}$ ). Gradual exposure of the product monolith **1** to MeOH/ $\text{H}_2\text{O}$  and then  $\text{H}_2\text{O}$  helps prevent cracking of the monolith. Direct reaction of chelating diamine  $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$  with **1** gave diamine-grafted monolith **3**. Imprint-grafting of monolith **1** with the  $\text{Cu}^{2+}$  complex  $\text{Cu}[\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OMe})_3]_4^{2+}$  yielded monolith **5** grafted with the monoamine ligand  $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{O}-)_3$  (APS). BET studies showed that the average pore size in amine-imprint-grafted **5** was *ca.* 47 Å with a specific surface area of  $232 \text{ m}^2 \text{ g}^{-1}$ , and the total pore volume was  $0.24 \text{ cm}^3 \text{ g}^{-1}$  for all pores of the gel which were less than 174 Å.

## Introduction

Porous silica sol–gel materials are of intense current interest. The sol–gel reaction between  $\text{Si}(\text{OR})_4$  and  $\text{H}_2\text{O}$  at or near room temperature, and the mesopores of 20–500 Å in many silica sol–gel materials, allow grafting or encapsulation of a variety of functional groups. Such materials have been widely studied in many areas of chemistry such as catalysis and green chemistry,<sup>1</sup> separation,<sup>2</sup> sensors,<sup>3</sup> electrochemistry,<sup>4</sup> and organic synthesis.<sup>3a,5</sup> Sol–gel processing requires a delicate balance of a number of variables including the nature and ratios of starting materials, pH, temperature, and aging and drying times.<sup>6</sup> Mesoporous silica sol–gels have larger pores and pore/silica volume ratios, and these materials usually exist as powders.<sup>1d,2a,c</sup> MCM-41 powders of, *e.g.*, 100 nm particles in size have been prepared with surfactant templates to give a hexagonal array of pores. These powders have been grafted with many organic functional groups and used for, *e.g.*, toxic metal separation.<sup>1d,2a,c</sup> Binders are often used to make pellets from these mesoporous powders.<sup>7</sup>

Mesoporous silica sol–gel materials in the form of monoliths are highly desirable. Such monoliths may be optically transparent in the visible region, and their mesopores allow grafting of organic functional groups for a variety of applications such as optical sensing. However, it is a challenge to prepare crack-free transparent monoliths of mesoporous sol–gel silica.<sup>6,8–11</sup> Mesoporous silica monoliths have been prepared from liquid crystal polymer templates, and calcination has been subsequently used to remove the templates.<sup>8</sup> Direct hydrolysis of a mixture of  $\text{Si}(\text{OR})_4$  and functionalized trialkoxysilanes  $\text{RSi}(\text{OR})_3$ , followed by supercritical drying of the wet gels, has yielded monolithic aerogel cylinders.<sup>9</sup> These monoliths are often opaque.<sup>8c,9</sup> Polymers such as polydimethylsiloxane (PDMS) or poly(methyl methacrylate)

(PMMA) have been added to optical silica monoliths to enhance their physical strength.<sup>12,13</sup> In the preparation of  $\text{SiO}_2$ –PMMA composite glasses, methyl methacrylate monomer diffuses into the open pores of preformed silica and polymerizes inside.<sup>10a,13</sup> In addition to the aforementioned materials, silica monolithic thin films have also been reported.<sup>14</sup>

We have recently developed a procedure to prepare transparent, crack-free silica sol–gel monoliths without organic polymers, and our work shows that numerous experimental parameters need to be carefully controlled to yield such monoliths. Organic ligands were subsequently grafted through the reactions between  $\text{L}-(\text{CH}_2)_n-\text{Si}(\text{OMe})_3$  and the hydroxyl  $\text{Si}-\text{OH}$  groups in the pores of a pre-formed sol–gel monolith to give organic–inorganic hybrid monoliths that have potential as a metal ion sensor. The preparation of the silica sol–gel monoliths and subsequent ligand grafting processes are reported here.

## Experimental

### General

The chemicals used in this study, including  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (Mallinckrodt, analytical reagent),  $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$  [3-aminopropyltrimethoxysilane (APS), Aldrich, 97%],  $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$  [*N*-[3-(trimethoxysilyl)propyl]ethylenediamine, Aldrich, 97%],  $\text{Si}(\text{OMe})_4$  [tetramethyl orthosilicate (TMOS), Aldrich, 98%], MeOH (Mallinckrodt, 99.9%), and ethylene glycol ( $\text{HOCH}_2\text{CH}_2\text{OH}$ , Fisher, Certified), were used as received. Distilled water was used in the preparation of all gels and aqueous  $\text{CuCl}_2$  solutions. Distilled water was also used in gel washing. Gels used in these experiments were prepared in bulk; the following procedures are for the preparation of a single monolith. Amounts of reagents were increased stoichiometrically to give the desired number of monoliths. The sol–gel monoliths were stored in distilled water before use.

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### Preparation of a blank sol-gel monolith (gel 2)<sup>15</sup>

MeOH (225  $\mu$ l, 5.55 mmol), Si(OMe)<sub>4</sub> (225  $\mu$ l, 1.53 mmol), and ethylene glycol (115  $\mu$ l, 2.06 mmol) were mixed with stirring in a small glass vial (diameter = 13.4 mm). The stir bar was removed and 50 mM NaOH (135  $\mu$ l, 6.75  $\mu$ mol) was added to this mixture. Gelation was complete within *ca.* 3 min. The freshly prepared gel was covered with MeOH, and the vial was capped and allowed to stand for *ca.* 18 h. The MeOH was then removed, and the gel was allowed to shrink for 8 h in air to *ca.* 10.8 mm (diameter)  $\times$  4 mm (thickness). The monolith was again covered with MeOH and allowed to stand overnight to give gel 1. In the subsequent procedures to make monoliths 2–4, the size of the monoliths did not change.

After 24 h the MeOH solution was decanted and replaced stepwise with 75% MeOH, 50% MeOH, 25% MeOH, and finally pure water to avoid monolith cracking. The water above the gel was changed several times before use to give blank gel 2.

### Preparation of gel 3, a monolith grafted with diamine ligand H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH(CH<sub>2</sub>)<sub>3</sub>Si(O<sup>-</sup>)<sup>15</sup>

To gel 1 covered with MeOH (1.5 ml) prepared by the aforementioned method was added H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH(CH<sub>2</sub>)<sub>3</sub>-Si(OMe)<sub>3</sub> (37.5  $\mu$ l, 0.172 mmol). The vial was then capped and placed on a mechanical shaker overnight. Deionized water (1 ml) was added to the solution above the gel, and the vial was again placed on the mechanical shaker overnight. The supernatant solution was decanted and replaced stepwise with 75% MeOH, 50% MeOH, 25% MeOH, and finally pure water. The gel was allowed to stand in water overnight. To ensure that the diamine ligand had grafted completely to the sol-gel monolith, 50 mM CuCl<sub>2</sub> solution (1.5 ml) was added to the original supernatant solution. This solution did not exhibit the intense blue color of the Cu<sup>2+</sup> : ligand complex, indicating that the grafting procedure was successful and the ligand was covalently bound to the sol-gel monolith. The water above the gel was changed several

times prior to use to give gel 3. The preparation of gel 3 is shown in Scheme 1.

### Preparation of gel 5, a monolith imprint-grafted with APS [NH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>Si=]<sup>15</sup>

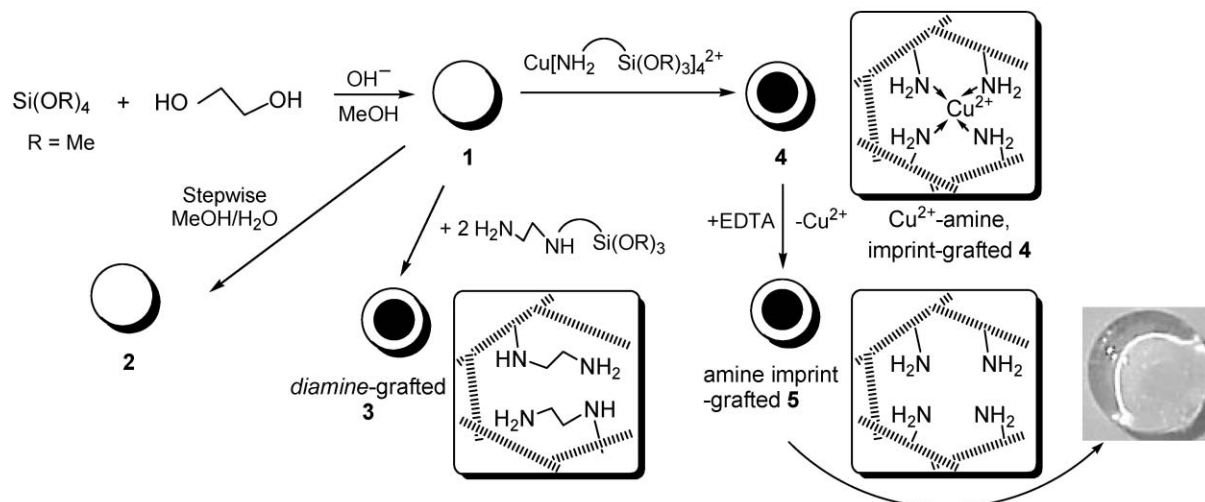
H<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>Si(OMe)<sub>3</sub> (30.0  $\mu$ l, 0.172 mmol) was added to CuCl<sub>2</sub> (6.79 mg, 0.0398 mmol) dissolved in MeOH (1485  $\mu$ l) to give a blue solution of Cu[H<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>Si(OMe)<sub>3</sub>]<sub>4</sub><sup>2+</sup> complex. This solution was added to gel 1 and placed on a mechanical shaker overnight. A blue monolith 4 with a colorless supernatant was observed within 18 h. The supernatant solution was decanted and replaced stepwise with 75% MeOH, 50% MeOH, 25% MeOH, and finally pure water to avoid gel cracking. To remove Cu<sup>2+</sup>, 0.100 M EDTA (disodium salt, 3 ml) was added to the gel, which was then placed on a mechanical shaker. This EDTA solution was changed several times. When the gel appeared colorless, the EDTA solution was replaced with water, and the gel was washed with water several times to give 5. A schematic of the gel preparation is given in Scheme 1.

### Brunauer–Emmett–Teller (BET) surface area and pore size distribution measurement for 5<sup>16</sup>

The BET studies were performed with the use of a Quantachrome Corporation Nova 1000 Gas Sorption Analyzer using N<sub>2</sub> gas adsorption. The sample was ground into a powder and dried at 100 °C for at least 24 h. The powder was subsequently evacuated under vacuum, and then cooled to -196 °C using liquid nitrogen before the BET analysis. The adsorption portion of the N<sub>2</sub> gas adsorption-desorption isotherms was used to calculate the pore size distribution of the sol-gel monoliths.

### <sup>29</sup>Si solid-state NMR characterization of powders of 2 and 5

<sup>29</sup>Si magic-angle-spinning (MAS) solid-state NMR experiments were performed on a Varian-Inova 400 MHz spectrometer operating at a frequency of 79.43 MHz. The samples (2 and 5) were ground into a powder, and the NMR spectra



**Scheme 1** Schematic of the preparation of blank 2, diamine-grafted 3, and amine-imprint-grafted 5. A photo of 5 (bottom right) is shown. For a photo of 4 see the Table of Contents.

were recorded with a 5.5 kHz spin rate and 1800–5300 scans.  $^{29}\text{Si}$  chemical shifts were referenced to tetramethylsilane. All spectra were collected under ambient conditions.

### Scanning electron microscopy (SEM) characterization of the surface of monolith 5

A Hitachi S-4700 FEG-scanning electron microscope was used for the SEM studies. The samples were ground into a powder and dried at 100 °C for at least 24 h before SEM studies were carried out.

## Results and discussion

### Preparation of mesoporous sol–gel monoliths

The sol–gel process involves the hydrolysis and polycondensation of alkoxide precursors such as  $\text{Si}(\text{OR})_4$  at room temperature to yield inorganic glasses.<sup>1–6</sup> Sol–gels are particularly well suited for use as substrates in optical analysis partly because they are transparent in the visible region.<sup>3,6,10a</sup> The porosity of the final glass product is easily varied, allowing the incorporation of organic functional groups into the glass matrix and supporting the fast transport of small molecules throughout the gel interior. There are two main methods for the incorporation of organic functional groups into a sol–gel glass: doping and grafting.<sup>3a–c</sup> Chemical doping is highly versatile because organic molecules (or biological species) containing the functional groups are simply encapsulated within the matrix of the gel by engineering the gel porosity.<sup>1a,3a–c,17</sup> These doped gels are prepared by the hydrolysis of a mixture of  $\text{Si}(\text{OR})_4$  and the organic molecules containing functional groups to give, e.g., porous  $\text{SiO}_2$  thin films doped with the molecules. However, since the organic molecules are not chemically bound to the gel interior, they often leach out over time. In the grafting technique, organic functional groups are covalently bound to the sol–gel matrix, and therefore reagent leaching is not expected in the chemically grafted gels.<sup>1a,2,18</sup> The organic molecules usually contain the  $-\text{Si}(\text{OR})_3$  group, and grafting occurs through a condensation reaction with hydroxyl groups  $\text{HO}-\text{Si}\equiv$  on the sol–gel surface.

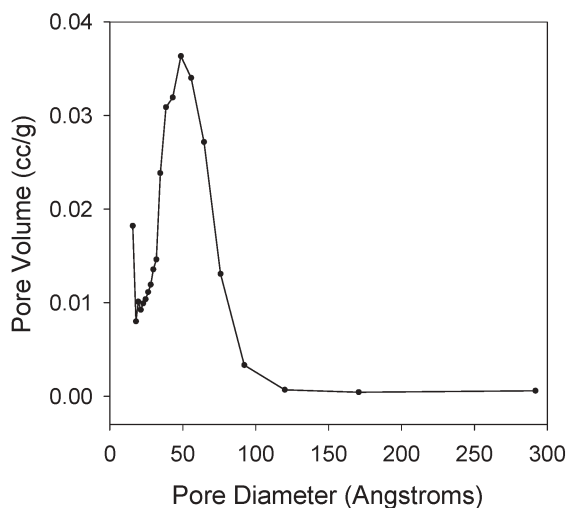
During the drying period in the formation of sol–gel glasses, a pressure gradient in the liquid phase of the gel is produced, leading to different rates of shrinkage within the siloxane network.<sup>10b</sup> When the exterior of the gel shrinks at a faster rate than the interior of the gel, tensile stresses arise that lead to fracture of the network. Cracking of the glass often occurs because the stress in the gel network exceeds its strength.<sup>10</sup> In purely inorganic systems, this cracking may be prevented by increasing the aging time so the gel develops adequate strength to reduce cracking during the drying stage, increasing the pore size to decrease capillary pressure, or by the addition of chemical additives which may decrease capillary stress or allow for faster drying.<sup>6a,10</sup> However, crack prevention is often much more difficult in inorganic–organic hybrid materials, because the network is not composed exclusively of  $-\text{Si}-\text{O}-\text{Si}-$  bonds.

Pore sizes in the mesoporous range are usually required to graft organic functional groups in the monoliths. Preparation of mesoporous sol–gel monoliths has been a major challenge, as such materials with relatively large pores easily crack.

We have found that the direct hydrolysis of a mixture of  $\text{Si}(\text{OMe})_4$  and an organic functional compound such as  $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$  as starting materials yield poor quality gels. A new approach was thus developed in which a purely inorganic, mesoporous sol–gel monolith was first prepared, and an organic functional compound was then added at a later stage after gelation was complete.

Several methods were used in an attempt to prepare crack-free, ligand-grafted sol–gel monoliths prior to the development of the current procedure to give blank, mesoporous monolith **2** and ligand-grafted monoliths **3** and **5**. These earlier studies led to cracking of the monoliths. Monoliths **2–5** described here are in comparison strong and colorless. A variety of variables in the gel preparation were investigated and optimized, including the ratios of starting materials, effects of catalysts and additives, and the conditions during the grafting, aging, and drying steps. The formation of a purely inorganic sol–gel monolith, followed by the addition of the organic functional compound after gelation is complete, seems to be the most important factor in crack prevention. Another key component of the current approach is the use of ethylene glycol. It perhaps acts as a nonsolvent or porogen, and leads to mesopores throughout the bulk of the gel. Ethylene glycol was easily removed during the subsequent  $\text{MeOH}-\text{H}_2\text{O}$  washes after the monoliths were formed. Without ethylene glycol, the pores in the monoliths were found to be too small to be grafted with amine ligands by the procedures in the current work. The current approach to mesoporous  $\text{SiO}_2$  is different from some recent approaches where a surfactant was usually used and subsequently removed through calcination or extraction to give mesoporous powders.<sup>1d,2a–c</sup> Another important step in the approach here is the stepwise exposure of the newly-formed, mesoporous monolith **1** and amine-grafted **3** and **5** in  $\text{MeOH}$  by 75%  $\text{MeOH}$ , 50%  $\text{MeOH}$ , 25%  $\text{MeOH}$ , and finally pure water. In the case of **1**, this step yields **2**. If **1** was used to graft the amine groups, this gradual  $\text{MeOH}$  to  $\text{H}_2\text{O}$  conversion was conducted after the grafting. This step helped reduce surface tension when a monolith prepared in the organic solvent methanol was then placed in water. The monoliths could then be used in aqueous solutions. *Without this step of gradual exposure to water, the monoliths often crack.* Finally adequate aging and slow drying at ambient temperature and pressure also appear to aid in crack prevention.

The diamine ligand  $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$  was directly grafted to blank monolith **1** to give monolith **3**, after the gradual  $\text{MeOH}-\text{H}_2\text{O}$  exposure. This chelating amine ligand in the monoliths was found to bind/remove  $\text{Cu}^{2+}$  ions from aqueous solutions, as we observed with the amine-grafted granulars.<sup>18</sup> The chelation of the two N atoms in the diamine ligand enhances metal binding.<sup>19</sup> For the monoamine  $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$ , recent work has shown that imprint-grafting using, e.g., the preformed  $\text{Cu}^{2+}$  complex  $\text{Cu}[\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OMe})_3]_4^{2+}$  significantly enhances subsequent selectivity of the amine-grafted gels for  $\text{Cu}^{2+}$  binding.<sup>20</sup> The imprint-grafting approach was thus used in the current work to graft the monoamine  $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{O}-)_3$  on monolith **1** to give **4**.  $\text{Cu}^{2+}$  ions in the imprint-grafted gels were subsequently removed by washing the monoliths with an EDTA solution to give monolith **5**.<sup>21</sup>



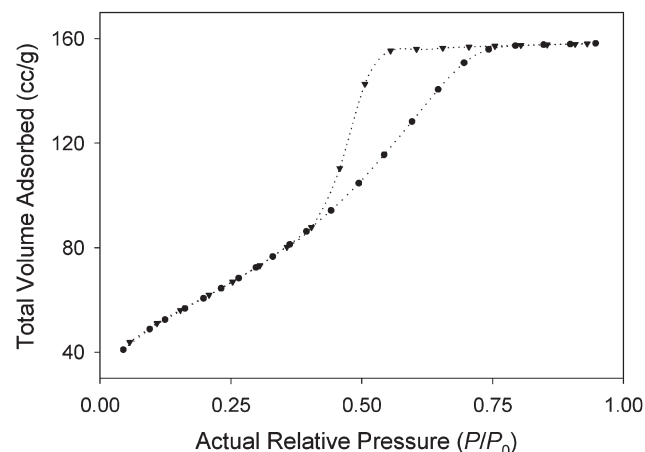
**Fig. 1** BET pore size distribution for monolith **5**. The average pore diameter is *ca.* 47 Å.

### BET surface area and pore size distribution measurements<sup>16</sup>

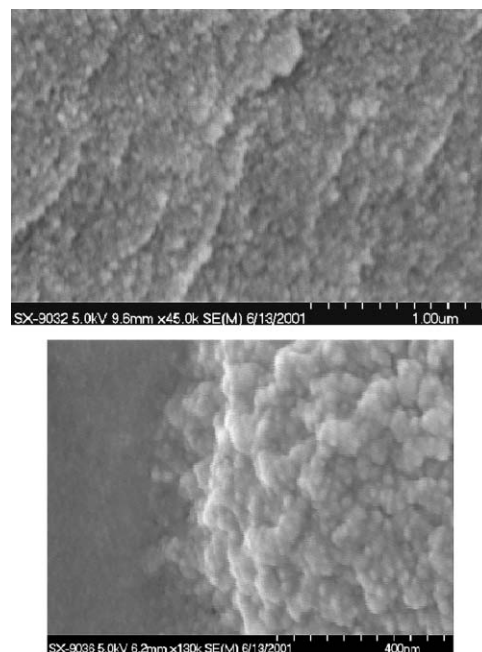
BET gas adsorption experiments indicate that monolith **5** is mesoporous with an average pore diameter of *ca.* 47 Å. A plot of pore volume as a function of pore diameter (Fig. 1) indicates that monolith **5** has a pore size distribution that is consistent throughout the bulk of the material. The peak of this plot near 47 Å represents the size of pores that contribute most to the pore volume. Fig. 2 shows the N<sub>2</sub> adsorption isotherm plot with a Z-shaped hysteresis loop. This hysteresis loop is common in mesoporous materials including inorganic oxides and glasses.<sup>22</sup> The specific surface area of **5** is 232 m<sup>2</sup> g<sup>-1</sup>, and the total pore volume is 0.24 cm<sup>3</sup> g<sup>-1</sup> for all pores of the monolith less than 174 Å.

### SEM imaging of the sol-gel surface

SEM images of monolith **5**, taken at 45 000× and 130 000× magnification (Fig. 3) show that the surface is not smooth. The network of spherical particles packed together is representative of a base-catalyzed process in which colloidal silica clusters are initially formed and then linked through gelation.<sup>23</sup>



**Fig. 2** N<sub>2</sub> gas adsorption-desorption isotherm for **5**; adsorption (●) desorption (▼).



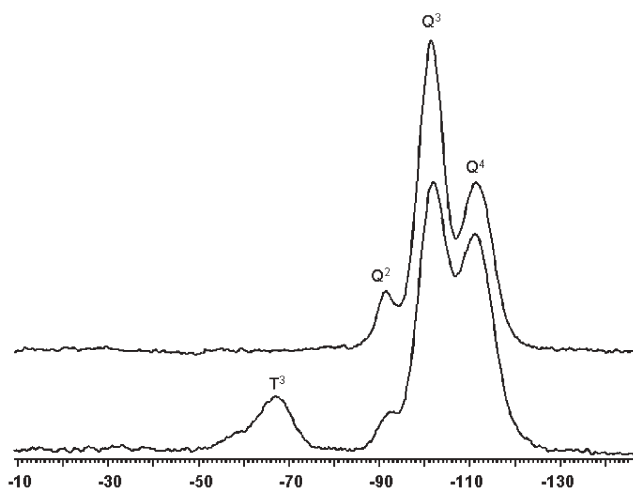
**Fig. 3** SEM images of monoamine imprinted-grafted monolith **5** at 45 000× (upper) and 130 000× (lower) magnification.

### <sup>29</sup>Si MAS solid-state NMR spectroscopic characterization

<sup>29</sup>Si solid-state NMR spectroscopy has been used extensively to elucidate the molecular environment in silicate materials.<sup>24</sup> <sup>29</sup>Si solid-state NMR spectra of the sol-gel solids show signals representative of various substructures of the T<sup>n</sup> and Q<sup>n</sup> silane moieties. Spectra displaying Q<sup>n</sup> (*n* ≤ 4) peaks indicate that the condensation of the silicon alkoxide precursor is incomplete.<sup>24e</sup> As the degree of condensation increases, the T<sup>n</sup> and Q<sup>n</sup> peaks are shifted to higher field in the NMR spectrum. Characteristic NMR signals of unmodified silica gel are silanediol groups (Q<sup>2</sup>), silanol groups (Q<sup>3</sup>), and siloxane groups (Q<sup>4</sup>), which appear at -92, -101, and -110 ppm, respectively.<sup>24a</sup> Q<sup>n</sup> peaks, which are representative of the silica support, are the only peaks expected for the blank sol-gel monolith **2** in the current studies. T<sup>n</sup> peaks are representative of silicon atoms in the sol-gel matrix directly bonded to an organic species. As *n* increases in the T<sup>n</sup> species, the number of organic species bonded to a silicon atom decreases. Since the APS ligand has only one organic group attached directly to the silicon atom, only T<sup>3</sup>, Q<sup>2</sup>, Q<sup>3</sup>, and Q<sup>4</sup> peaks are expected in the NMR spectrum of APS-grafted **5**. The <sup>29</sup>Si NMR spectra of blank **2** and APS-grafted **5** are shown in Fig. 4. As expected, the blank **2** shows only Q<sup>2</sup>, Q<sup>3</sup>, and Q<sup>4</sup> peaks in the NMR spectrum which are representative of a siloxane matrix with no organic groups directly bound to silicon. The APS grafted **5** shows only a T<sup>3</sup> peak in addition to the expected Q peaks, which indicate that the APS ligand is in fact, bound to the sol-gel monolith as proposed.

### Conclusions

Preparation of a transparent, crack-free silica sol-gel monolith is a challenging process. The techniques reported herein provide a convenient method to make in bulk transparent,



**Fig. 4**  $^{29}\text{Si}$  MAS solid-state NMR spectra of blank **2** (top) and APS imprint-grafted **5** (bottom).

crack-free, mesoporous monoliths from off-the-shelf chemicals. These sol-gel monoliths are highly reproducible. Monoliths prepared at different times each displayed similar physical properties such as pore size distribution and optical quality. The use of the monoliths in metal ion sensing has been the subject of a separate study.<sup>21</sup>

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## References

- (a) U. Schubert, N. Hüsing and A. Lorentz, *Chem. Mater.*, 1995, **11**, 2010; (b) J. H. Clark and D. K. Macquarrie, *Chem. Soc. Rev.*, 1996, **25**, 303; (c) J. Blum, D. Avnir and H. Schumann, *Chemtech*, 1999, **29**, 2, 32; (d) A. Corma, *Chem. Rev.*, 1997, **97**, 2373; (e) T. Maschmeyer, R. D. Oldroyd, G. Sankar, J. M. Thomas, I. J. Shannon, J. A. Klepetko, A. F. Masters, J. K. Beattie and C. R. A. Catlow, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1639; (f) A. Ghattas, R. Abu-Reziq, D. Avnir and J. Blum, *Green Chem.*, 2003, **5**, 40.
- (a) X. Feng, G. E. Fryxell, L.-Q. Wang, A. Y. Kim, J. Liu and K. M. Kemner, *Science*, 1997, **276**, 923; (b) L. Mercier and T. J. Pinnavaia, *Adv. Mater.*, 1997, **9**, 500; (c) J. S. Bradshaw and R. M. Izatt, *Acc. Chem. Res.*, 1997, **30**, 338; (d) M. G. Hankins, T. Hayashita, S. P. Kasprzyk and R. A. Bartsch, *Anal. Chem.*, 1996, **68**, 2811; (e) M. H. Lim, C. F. Blanford and A. Stein, *Chem. Mater.*, 1998, **10**, 467; (f) J. Seneviratne and J. A. Cox, *Talanta*, 2000, **52**, 801; (g) J. Brown, R. Richer and L. Mercier, *Microporous Mesoporous Mater.*, 2000, **37**, 41; (h) H.-J. Im, C. E. Barnes, S. Dai and Z. L. Xue, *Microporous Mesoporous Mater.*, 2004, **70**, 57.

- There have been many reports of new sensors based on organically modified silica gels. See, e.g., (a) D. Avnir, *Acc. Chem. Res.*, 1995, **28**, 328; (b) B. C. Dave, B. Dunn, J. S. Valentine and J. I. Zink, *Anal. Chem.*, 1994, **66**, 1120A; (c) O. Lev, M. Tsionsky, L. Rabinovich, V. Glezer, S. Sampath, I. Pankratov and J. Gun, *Anal. Chem.*, 1995, **67**, 22A; (d) E. Bescher and J. D. Mackenzie, *Mater. Sci. Eng. C*, 1998, **6**, 145; (e) L. C. Klein, *Annu. Rev. Mater. Sci.*, 1993, **23**, 437; (f) C. M. Ingersoll and F. V. Bright, *Chemtech*, 1997, **27**, 1, 26; (g) O. Lev, *Anal. Chem.*, 1992, **20**, 543; (h) Y. Tang, E. C. Tehan, Z. Tao and F. V. Bright, *Anal. Chem.*, 2003, **75**, 2407; (i) U. Narang, P. N. Prasad, F. V. Bright, K. Ramanathan, N. Kumar, M. B. D. Deepak, M. N. Kamalasanan and S. Chandra, *Anal. Chem.*, 1994, **66**, 3139.
- (a) O. Lev, Z. Wu, S. Bharathi, V. Glezer, A. Modestov, J. Gun, L. Rabinovich and S. Sampath, *Chem. Mater.*, 1997, **9**, 2354; (b) R. W. Murray, *Molecular Design of Electrodes Surfaces*, in *Techniques of Chemistry*, Wiley, New York, 1992, vol. 22; (c) M. M. Collinson and A. R. Howells, *Anal. Chem.*, 2000, **72**, 702A.
- (a) F. Gelman, J. Blum and D. Avnir, *J. Am. Chem. Soc.*, 2002, **124**, 14460; (b) R. Abu-Reziq, D. Avnir and J. Blum, *Angew. Chem., Int. Ed.*, 2002, **41**, 4132; (c) K. Hamza, R. Abu-Reziq, D. Avnir and J. Blum, *Org. Lett.*, 2004, **6**, 925.
- (a) C. J. Brinker and G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press, San Diego, 1990; (b) L. L. Hench and J. K. West, *Chem. Rev.*, 1990, **90**, 33; (c) preparation of microporous silica sol-gel monoliths without organic functional groups has been reported (ref. 6(a),(b)).
- M. Buelow, D. Shen, A. Brandt and B. Unger, *Eur. Pat. Appl.*, 2002, 308513; *Chem. Abs.* No. 136:327721.
- (a) G. S. Attard, J. C. Glyde and C. G. Göltner, *Nature*, 1995, **378**, 366; (b) C. G. Göltner, Su. Henke, M. C. Weissenberger and M. Antonietti, *Angew. Chem., Int. Ed.*, 1998, **37**, 613; (c) N. Hüsing, C. Raab, V. Torma, A. Roig and H. Peterlik, *Chem. Mater.*, 2003, **15**, 2690.
- (a) N. Hüsing, U. Schubert, K. Misof and P. Fratzl, *Chem. Mater.*, 1998, **10**, 3024; (b) N. Hüsing, U. Schubert, R. Mezei, P. Fratzl, B. Riegel, W. Kiefer, D. Kohler and W. Mader, *Chem. Mater.*, 1999, **11**, 451.
- (a) R. Gvishi, U. Narang, G. Ruland, D. N. Kumar and P. N. Prasad, *Appl. Organomet. Chem.*, 1997, **11**, 107; (b) J. Phalippou, in *Chemical Processing of Ceramics, Materials Engineering*, vol. 8, ed. B. I. Lee and E. J. A. Pope, Marcel Dekker, New York, 1994, p. 265.
- Monolithic silica columns have been developed for chromatographic separations. These columns are usually not optically transparent. See recent reviews: (a) N. Tanaka, H. Kobayashi, K. Nakanishi, H. Minakuchi and N. Ishizuka, *Anal. Chem.*, 2001, **73**, 420A; (b) A.-M. Siouffi, *J. Chromatogr. A*, 2003, **1000**, 801.
- For organic-inorganic hybrid solids, see, e.g., ref. 1(a) and J. D. Mackenzie and E. P. Bescher, *J. Sol-Gel Sci. Technol.*, 1998, **13**, 371.
- E. J. A. Pope, M. Asami and J. D. Mackenzie, *J. Mater. Res.*, 1989, **4**, 1018.
- J. A. Ruffner, P. G. Clem, B. A. Tuttle, C. J. Brinker, C. S. Sriram and J. A. Bullington, *Thin Solid Films*, 1998, **332**, 356.
- C. W. Clavier, Masters Thesis, The University of Tennessee, Knoxville, 2001.
- D. Dollimore, P. Spooner and A. Turner, *Surf. Technol.*, 1976, **4**, 121.
- (a) L. R. Allain, K. Sorasaene and Z.-L. Xue, *Anal. Chem.*, 1997, **69**, 3076; (b) L. R. Allain and Z.-L. Xue, *Anal. Chem.*, 2000, **72**, 1078; (c) L. R. Allain and Z.-L. Xue, *Anal. Chim. Acta*, 2001, **433**, 97; (d) L. R. Allain, T. A. Canada and Z.-L. Xue, *Anal. Chem.*, 2001, **73**, 4592; (e) T. A. Canada, L. R. Allain, D. B. Beach and Z.-L. Xue, *Anal. Chem.*, 2002, **74**, 2535; (f) T. A. Canada and Z.-L. Xue, *Anal. Chem.*, 2002, **74**, 6073; (g) T. L. Yost, B. C. Fagan, L. R. Allain, C. E. Barnes, S. Dai, M. J. Sepaniak and Z.-L. Xue, *Anal. Chem.*, 2000, **72**, 5516.
- H.-J. Im, Y.-H. Yang, L. R. Allain, C. E. Barnes, S. Dai and Z.-L. Xue, *Environ. Sci. Technol.*, 2000, **34**, 2209.
- J. E. Huheey, E. A. Keiter and R. L. Keiter, *Inorganic Chemistry*, 4th edn., HarperCollins, New York, 1993, pp. 522–531.
- (a) G. Wulff, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1812; (b) K. J. Shea, *Trends Polym. Sci.*, 1994, **2**, 166; (c) S. Dai, M. C. Burleigh, Y. Shin, C. C. Morrow, C. E. Barnes and

- 
- Z. Xue, *Angew. Chem., Int. Ed.*, 1999, **38**, 1235; (d) S. Dai, Y. S. Shin, Y. H. Ju, M. C. Burleigh, J. S. Lin, C. E. Barnes and Z.-L. Xue, *Adv. Mater.*, 1999, **11**, 1226; (e) S. Dai, M. C. Burleigh, Y. H. Ju, H. J. Gao, J. S. Lin, S. J. Pennycook, C. E. Barnes and Z.-L. Xue, *J. Am. Chem. Soc.*, 2000, **122**, 992; (f) M. C. Burleigh, S. Dai, E. W. Hagaman and J. S. Lin, *Chem. Mater.*, 2001, **13**, 2537.
- 21 The current mesoporous monolith has been used as an optical metal ion sensor that is based on diffusion into the monolith followed by an immobilizing reaction by the grafted amine ligands. See D. L. Rodman, H. Pan, C. W. Clavier, X. Feng and Z.-L. Xue, *Anal. Chem.*, 2005, **77**, in press.
- 22 (a) M. Kruk and M. Jaroniec, *Chem. Mater.*, 2000, **12**, 222; (b) M. Kruk and M. Jaroniec, *Chem. Mater.*, 2001, **13**, 3169.
- 23 A. M. Buckley and M. Greenblatt, *J. Chem. Educ.*, 1994, **71**, 599.
- 24 (a) G. Engelhardt and D. Michel, *High-Resolution Solid-State NMR of Silicates and Zeolites*, John Wiley and Sons, New York, 1987; (b) C. A. Fyfe, *Solid State NMR for Chemists*, CFC Press, Ontario, 1983; (c) M. Magi, E. Lippmaa, A. Samoson, G. Engelhardt and A. R. Grimmer, *J. Phys. Chem.*, 1984, **88**, 1518; (d) J. M. Maher and N. J. Cooper, *J. Am. Chem. Soc.*, 1980, **102**, 7606; (e) B. Grolach, S. S. Hellriegel, H. Yiksel, K. Albert, E. Plies and M. Hanack, *J. Mater. Chem.*, 2001, **11**, 3317.