

In Situ Modification of the Silica Backbone leading to Highly Porous Monolithic Hybrid Organic–Inorganic Materials via Ambient Pressure Drying

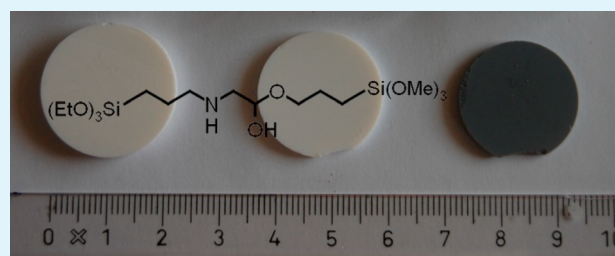
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ABSTRACT: We report the synthesis of monolithic porous hybrid organic–inorganic materials based on tetraethoxysilane (TEOS) and a bifunctional precursor synthesized from 3-aminopropyltriethoxysilane (APTES) and 3-glycidoxypropyltrimethoxysilane (GLYMO) via base catalysis. To compensate for the slower hydrolysis and condensation rate of the organically modified silane in basic media, it was prehydrolysed prior to adding it to the silane solution. This process leads to a lower shrinkage and stable monoliths with densities as low as 200 kg/m³. Analysis of the samples supports the assumption that the porous monolithic materials derived via ambient pressure drying of the gels consist of a network of homogeneous hybrid primary particles. These particles are larger than their inorganic counterparts in classical silica gels and therefore the capillary forces while drying the gels at ambient pressure are reduced. This leads to less shrinkage and thus lower densities of the materials derived via ambient pressure drying. An inorganic xerogel with the same low density can be achieved by a subsequent oxidation step that decomposes the organic moieties.

KEYWORDS: silica xerogel, hybrid, sol–gel, ambient pressure drying, monolith



INTRODUCTION

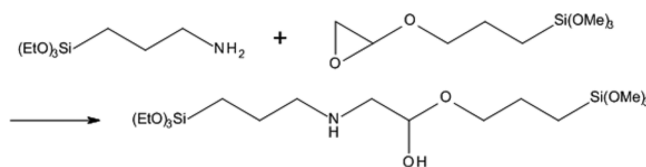
The most critical step upon the synthesis of monolithic silica xerogels, that is, gels dried at ambient conditions, is the drying procedure. Because of the surface tension of the pore liquid large capillary forces occur in the small pores of the fragile compliant gel structure leading to a large shrinkage upon drying.

There are a few options involving organic components to avoid the consequential high densities. One common way to improve the mechanical properties of silica gels to withstand the stress upon drying is the modification of the inorganic network with organic groups. The coating of the preformed inorganic network with organically modified silanes leads to a hydrophobization of the inner surface and prevents irreversible shrinkage.¹ If only organically modified silanes are used as precursors there are less alkoxide groups to build the network and the resulting gel is weakly cross-linked, which leads to mechanically flexible gels.² In another approach, the functional groups of such silanes (e.g., amines, olefins) are used as reacting sites for organic monomers, yielding polymer coatings.^{3–6} Here the organically modified silanes can be introduced in the sol–gel process as coprecursors⁶ or after the gelation,⁷ but because of lower reaction rates of most of the organically modified silanes the modification of the network leads to an organic coating of the particle forming network.¹ The hydrolysis and condensation reactions occur concurrent or after the reactions

of the unmodified silane and thus the inorganic network itself is not or only slightly changed.

In our study, we tried to compensate the lower reaction rate of the organofunctional silane in basic media by prehydrolysis of the coprecursor in order to modify the covalent silane network itself in the subsequent condensation/gelation of tetraethoxysilane (TEOS). For this purpose we used a new monomer, which was synthesized of two commonly used precursors, 3-aminopropyltriethoxysilane (APTES) and 3-glycidoxypropyltrimethoxysilane (GLYMO) (Scheme 1). The abbreviation for this precursor, whose IUPAC name is 14,14-diethoxy-3,3-dimethoxy-2,7,15-trioxa-10-aza-3,14-disilaheptadecan-8-ol, is AEGM and consists of the main functionalities of the reactants, that is, amino, ethoxy, glycidoxy, and methoxy.

Scheme 1. Synthesis of the Bifunctional Organically Modified Silicon Alkoxide Precursor AEGM



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Table 1. Physical Properties of Selected Hybrid Xerogels and a Silica Reference^a

sample	x_{RT}	ρ_{macro} (kg/m ³)	$\Delta l/l$ (%)	E (MPa)	S_{BET} (m ² /g)	S_{ext} (m ² /g)	d_{pore} (nm)	d_{particle} (nm)	$V_{\text{p,tot}}$ (cm ³ /g)	$V_{\text{p,sorp}}$ (cm ³ /g)	x_{macro}
pre05h	0.05	202	14	5.3	226	135	130	24.8	4.40	0.68	0.85
pre10h	0.10	212	10	13.1	357	237	69.5	14.1	4.16	1.29	0.69
pre20h	0.20	397	26	125	439	439	17.9	7.6	1.97	1.87	0.05
os10h	0.10	317	22	42.5	394	286	35.8	11.7	2.60	2.60	0.00
os20h	0.20	456	29	166	471	471	13.9	7.1	1.64	1.59	0.03
silica ref		814	48	350	524	489	6.3	5.6	0.77	0.39	0.49

^a x_{RT} is the molar ratio of organically modified Si per TEOS molecule. $\Delta l/l$ is the linear shrinkage upon ambient pressure drying, $V_{\text{p,sorp}}$ is the adsorbed nitrogen volume (STP) at a relative pressure $p/p_0 = 0.993$, and x_{macro} is the fraction of pores not detected by nitrogen sorption, given by $(V_{\text{p,tot}} - V_{\text{p,sorp}})/V_{\text{p,tot}}$.

We synthesized various xerogels with AEGM as coprecursor to tetraethoxysilane in basic environment and studied the influence of the amount and a prehydrolysis step of AEGM on the drying behavior at ambient pressure, as well as the microscopic and macroscopic properties of the resulting xerogels. In addition, the derived material can serve as an intermediate stage for a porous inorganic or carbon-modified inorganic material in a subsequent oxidation/carbonization step.

EXPERIMENTAL SECTION

Materials. Tetraethoxysilane (TEOS), 3-aminopropyltriethoxysilane (APTES), and 3-glycidioxypropyltrimethoxysilane (GLYMO) were used to synthesize the organic–inorganic hybrid materials. TEOS was purchased from Alfa Aesar, APTES, and GLYMO were purchased from Sigma Aldrich. Ethanol denat. was purchased from Nedalco Alcohol and the ammonia solution (0.1 M) was bought from Carl Roth. All chemicals were used as received without further purification.

Preparation of Monoliths. The bisilylated organically modified silicon alkoxide precursor AEGM was synthesized from APTES and GLYMO (see Scheme 1, ¹H NMR (500.13 MHz, C₆D₆, ppm) 1.13 (t), 1.29 (t), 1.30 (t), 2.57 (t), 3.27 (s), 3.52 (q), 3.54 (t), 3.91 (q), 7.27 (s)). For this purpose the mixture of the two reactants (molar ratio 1:1) was stirred in ethanol at 70 °C for 25 min in a temperature-controlled microwave oven and then cooled to room temperature. The success of this synthesis has been verified by ¹H and ¹³C nuclear magnetic resonance (NMR) studies. The prehydrolysis was initiated by adding 0.1 M aqueous ammonium hydroxide solution and stirring at 50 °C for 1 h. The dilution was chosen in a way that no formation of particles via condensation occurred. With dynamic light scattering (DLS) measurements no particles above the detection limit of 10 nm could be observed. For example, to synthesize a pre10 gel 0.62 g of APTES (2.8 mmol) and 0.66 g of GLYMO (2.8 mmol) in 3.59 g of ethanol (234 mmol) were mixed with 0.30 g ammonium hydroxide solution (0.03 mmol). After it was cooled to room temperature, a solution of TEOS (11.65 g, 56 mmol) in ethanol (3.59 g, 234 mmol) was poured into the mixture, then a solution of ethanol (3.59 g, 234 mmol), deionized water (1.87 g, 222 mmol), and ammonium hydroxide (0.1 M, 1.84 g, 0.18 mmol) as base catalyst was slowly added while stirring. The mixture was stirred for 2 min and then poured into polypropylene molds.

For the one-step samples (not prehydrolysed) the organically modified silane was mixed with the TEOS/ethanol solution after synthesis. As base catalyst the solution of the remaining ethanol, deionized water and ammonium hydroxide (0.1 M) was slowly added under constant stirring. The molar ratio applied upon synthesis of the single components of corresponding pre and os gels, respectively, for example, pre10 and os10, are identical.

The final molar ratio of ethanol/silicon was 3.8 and the molar ratio of water to silicon alkoxide was 0.9. Gelation took place within 30 to 50 min at 50 °C. The gels were aged in ethanol for 7 days and then dried at 50 °C at ambient pressure.

As a reference purely inorganic silica gels were produced by using the two-step method described by Scherer.⁸

After characterization of the hybrid materials, the uniform cylindrical xerogel samples with a diameter of approximately 20–25 mm were cut to discs with a height of ~2–3 mm each. These samples were heat treated for 1 h under ambient pressure in oxidizing (air) and inert (Ar) atmosphere, respectively. Because previous experiments had shown the unusual temperature stability of the organic moieties in the hybrid xerogels, the thermal treatment had to take place at higher temperatures as expected. To minimize sintering effects and simultaneously remove all organic moieties, the heat treatment in oxidizing atmosphere was carried out at 600 °C. To completely convert the organic components into carbon, this temperature turned out to be too low and therefore, a pyrolysis temperature of 850 °C was chosen.

Characterization. Particle size analysis was performed with a dynamic light scattering (DLS) instrument (Horiba LB-550) to detect potential formation of particles during prehydrolysis of the modified silicon alkoxides. The resulting xerogels (untreated and heat treated) were characterized by nitrogen sorption at 77 K (Micromeritics ASAP2000; software ASAP2020). This technique yields the external surface area S_{ext} , the micropore volume V_{mp} (t -plot, Broekhoff–de Boer thickness curve⁹) and the total specific surface area S_{BET} (BET evaluation¹⁰). It also gives the C parameter that allows qualitative evaluation of the surface chemistry. The average pore diameter was estimated by $d_{\text{pore}} = 4(V_{\text{p,tot}} - V_{\text{mp}}) \cdot S_{\text{ext}}^{-1}$ with the total specific pore volume $V_{\text{p,tot}} = \rho_{\text{macro}}^{-1} - \rho_{\text{solid}}^{-1}$. The size of the primary particles was calculated by $d_{\text{particle}} = 6(S_{\text{ext}} \rho_{\text{solid}})^{-1}$ (based on spherical particle geometry). Elastic properties of the gels were determined by ultrasonic velocity measurements¹¹ with the sound velocity v . The Young's modulus was calculated by $E = 0.9 \cdot (v^2 \cdot \rho_{\text{macro}})$ assuming a Poisson's ratio of 0.21. The oxidative removal of the organic fraction was monitored via thermogravimetric analysis and differential thermal analysis/differential scanning calorimetry (TGA-DTA/DSC) with a type 501 of Bähr thermal analysis GmbH. SEM measurements were carried out with a Zeiss Ultra Plus. The solid densities ρ_{solid} of the primary particles were measured with an AccuPyc II 1340 Helium pycnometer by Micromeritics.

RESULTS AND DISCUSSION

The physical properties of the synthesized xerogels compared to the reference xerogel made from TEOS only⁸ are compiled in Table 1. In the following sample notations the prefix “pre” stands for the prehydrolysed samples and “os” for the one-step samples. The subsequent number characterizes the molar ratio of organically modified Si per TEOS molecule (x_{RT} , see Table 1). The suffix distinguishes between hybrid xerogels (h) and samples heat treated in air (o2) or argon (ar). Figure 1 shows a hybrid and two heat treated xerogels (in air and argon, respectively) as well as the silica reference.

Hybrid Xerogels. Though drying silica gels and preserving the structure at ambient pressure is very difficult and often results in cracks or a complete collapse of the monolithic structure, the cylindrical hybrid xerogels made in this study with

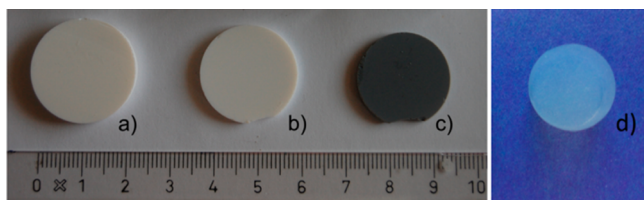


Figure 1. Discoidal xerogel samples synthesized with the bifunctional precursor AEGM: (a) hybrid xerogel, (b) heat treated in air and (c) in argon, and (d) silica xerogel as reference sample.

diameters and heights of about 20 mm, respectively, can be easily dried at 50 °C in 4 days at ambient pressure. The resulting materials are opaque and stable monoliths with densities as low as 200 kg/m³.

The tendencies in structural characteristics (densities, pores, surface areas, etc.) with increasing concentrations of AEGM are the same in the prehydrolysed and the one-step samples (Table 1). The particle size in a common silica xerogel is typically below 10 nm,¹² but the primary particles of the gels prepared here are up to five times larger than in the reference silica xerogel. For a given gel backbone structure and density, the size of the particles forming the backbone is directly correlated with the pore size. Furthermore, the capillary pressure in a cylindrical capillary is inversely proportional to the pore radius. Therefore, larger particles reduce the capillary force and consequently decrease the shrinkage upon drying, nearly preserving the original pore size of the wet gel. The influence of the increasing particle size on the pore size is shown in Table 1. Note that the values shown in Table 1 are mean values calculated from the solid density and the external surface area. A more precise distribution consisting of meso- and macropores cannot be derived from nitrogen sorption measurements, because only pores smaller than 50 nm are detectable. In SEM micrographs pores up to 300 nm are visible for the hybrid samples and the fraction of macropores (x_{macro} in Table 1) is inverse proportional to the concentration of the organically modified coprecursor. At $x_{\text{RT}} = 0.2$ nearly all pores are smaller than 50 nm and the whole pore volume can be detected with nitrogen sorption. Considering the series from $x_{\text{RT}} = 0.05$ to 0.2 the samples show hardly any microporosity (micropore surface area $S_{\text{micro}} = S_{\text{BET}} - S_{\text{ext}}$) the fraction of micropores decreasing with higher concentrations of AEGM.

The increasing shrinkage of the samples with the increasing molar fraction of coprecursor leads to higher densities. As expected for sol–gel derived porous solids, the correlation between the macroscopic density ρ and the Young's modulus E is given by $E \sim \rho^4$ (see Figure 2), but compared to supercritically dried aerogels based on TMOS¹³ the Young's modulus of the samples in this study is lower by a factor of about 2 at a given density.

The influence of AEGM on the gelation is on the one hand obvious because of its basic character: it therefore catalyzes the hydrolysis and condensation of TEOS. In addition, AEGM will, similar to a catalyst added to the initial solution, also affect the aging of the gel. The fact that not only the quantity but also the nature of the catalyst influences the gel properties¹⁴ becomes apparent when comparing hybrid and reference xerogels with the same pH value in the initial solution, however adjusted with ammonia. The latter samples show significant different properties and partly do not even form a homogeneous gel.

On the other hand, because of the basicity of AEGM, one would expect larger particles with increasing fraction of

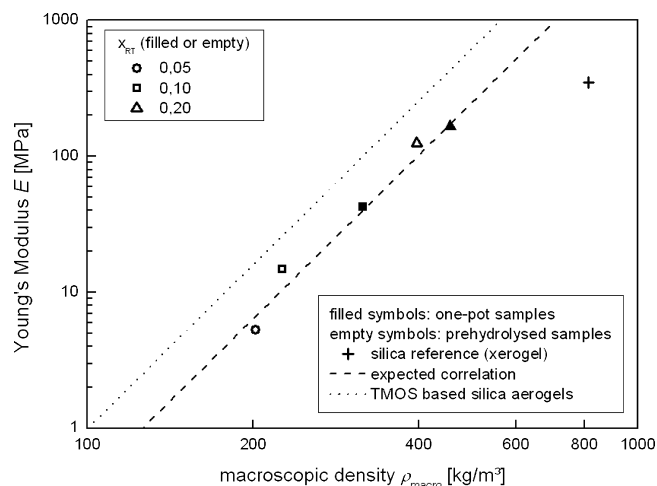


Figure 2. Young's modulus and macroscopic density of the hybrid xerogels prepared with different concentrations of AEGM, the value for the silica reference is shown for comparison. The dashed line shows the expected correlation $E \sim \rho^4$, the dotted line is a similar correlation for silica aerogels based on TMOS.¹³

coprecursor, but the exact opposite is observed. The results are therefore comparable to samples made of TEOS and the trialkoxysilanes $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$ (AMMO) and $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_3\text{NH}_2$ (AEAPS) by Hüsing et al.¹⁵ where a similar effect is noticed. The reason for this behavior is the building of a steric barrier and the stabilization of smaller particles by the large organic groups which overcompensates the catalytic role.

Another aspect is the impact of AEGM on the shrinkage of the samples. The higher local flexibility of the network introduced by this group results in a higher deformation and shrinkage of the gel. Similar effects were reported by Schubert et al. with GLYMO as a coprecursor to TMOS.¹⁶ This mechanism gives a hint to the small difference between the prehydrolysed and the one-step samples: the prehydrolysed AEGM reacts slightly faster than in the one-step gel and is better incorporated in the network, which is therefore more stable and shows less shrinkage. This is consistent with the observation of different shrinkage at nearly similar particle size. However, this hypothesis is hard to confirm, because different species of catalysts lead to different gel properties.

Heat Treatment. Figure 3 shows SEM images of a hybrid xerogel and a corresponding inorganic xerogel derived from the hybrid gel via heat treatment in inert atmosphere. Despite the fine network of the hybrid gel, small macropores are present. Moreover images taken with a backscattering detector that is sensitive to different chemical species do not reveal a formation

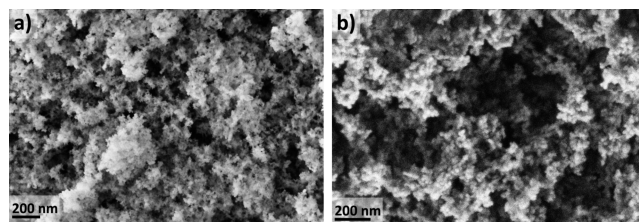


Figure 3. (a) Hybrid xerogel and (b) xerogel heated in Argon atmosphere (850 °C) for 1 h. Both samples were not sputtered to preserve the fine structure for analysis.

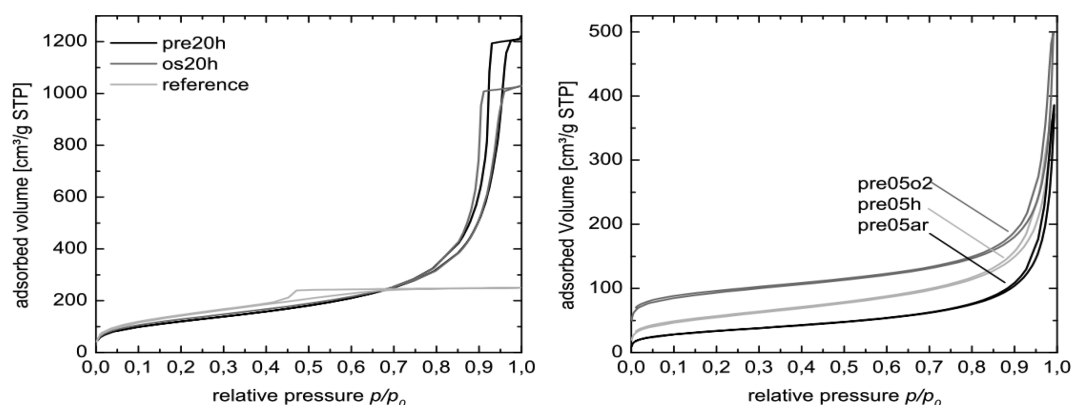


Figure 4. Nitrogen sorption isotherms of the pre20h, as well as the os20h, hybrid xerogel and the reference silica aerogel (left); the right plot shows the data for the pre05 hybrid xerogel (middle) and the corresponding heat treated xerogels in oxidizing (top, 600 °C) and inert atmosphere (bottom, 850 °C).

Table 2. Physical Properties of a Hybrid and the Corresponding Heat Treated Xerogels

sample	ρ_{macro} (kg/m ³)	ρ_{solid} (kg/m ³)	E (MPa)	S_{BET} (m ² /g)	C	S_{ext} (m ² /g)	d_{pore} (nm)	d_{particle} (nm)
pre05h	202	1.8	5.3	226	160	135	129	24.8
pre05o2	202	2.2	9.1	357	435	131	134	20.8
pre05ar	235	2.2	16.0	123	80.8	103	148	26.6

of organic clusters. Due to sintering processes the heat treated sample shows a much coarser network structure and large macropores. The same trends can be seen in the related nitrogen sorption isotherms (Figure 4). The properties determined from these measurements are listed in Table 2.

When exposed to temperatures above 400 °C classical silica xerogels usually show a decreasing micropore volume due to annealing accompanied by smoothing of the surface of the primary particles. The organically modified samples synthesized in this study show the same behavior when heated in argon atmosphere. Here the organic groups decompose and because of the inorganic remains no additional surface area or micropores are generated. The additional decrease of the specific surface area is due to sintering processes at the necks between the particles of the silica backbone structure. But the reverse effect is seen when the hybrid samples are heated in oxidizing atmosphere. Here the specific surface area and micropore volume increase.

As determined by Helium pycnometry measurements the density of the primary particles increases with the heat treatment, which is explained by the removal of the organic phase and a more dense packing of the silica. The solid density after the heat treatment matches the density of amorphous silica (2200 kg/m³).

An organic coating of an inorganic network is expected to be removed at temperatures above 400 °C in oxidizing atmosphere within a few hours, but the samples described here show a different behavior. The mass loss is slowed down and even after 6 days at 450 °C some mass loss is still observed. Together with the increasing microporosity this leads to the conclusion that the organic moieties are at least partly incorporated in the primary particles and evenly distributed within the inorganic network.

CONCLUSION

We have shown the successful preparation of monolithic, porous, low density inorganic–organic hybrid materials via sol–gel process with subsequent ambient pressure drying.

From the hybrid xerogels purely inorganic materials can be obtained by calcination. The change in the network structure by means of an organically modified silane leads to larger pores and thus reduced capillary forces in the drying step. Therefore less shrinkage occurs and higher porosities are achieved than for typical silica xerogels. Analysis of the samples suggests that the organic groups are evenly distributed within the backbone of the hybrid gel and can be removed via an oxidation step without a network collapse. The resulting inorganic monolithic materials are mechanically stable and show good resistance to abrasion.

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

- Hüsing, N.; Schubert, U. *Angew. Chem.* **1998**, *110* (1/2), 22–47.
- Rao, A. V.; Bhagat, S. D.; Hirashima, H.; Pajonk, G. M. *J. Colloid Interface Sci.* **2006**, *300* (1), 279–285.
- Leventis, N. *Acc. Chem. Res.* **2007**, *40* (9), 874–884.
- Ilhan, U. F.; Fabrizio, E. F.; McCorkle, L. S.; Scheiman, D. A.; Dass, A.; Palczar, A.; Meador, M. A. B.; Johnston, J. C.; Leventis, N. *J. Mater. Chem.* **2006**, *16* (29), 3046–3054.
- Zhang, G. H.; Dass, A.; Rawashdeh, A. M.; Thomas, J.; Council, J. A.; Sotiriou-Leventis, C.; Fabrizio, E. F.; Ilhan, F.; Vassilaras, P.;

Scheiman, D. A.; McCorkle, L. S.; Palczer, A.; Johnston, J. C.; Meador, M. A. B.; Leventis, N. *J. Non-Cryst. Solids* **2004**, *350*, 152–164.

(6) Meador, M. A. B.; Fabrizio, E. F.; Ilhan, F.; Dass, A.; Zhang, G. H.; Vassilaras, P.; Johnston, J. C.; Leventis, N. *Chem. Mater.* **2005**, *17* (5), 1085–1098.

(7) Rao, A. V.; Latthe, S. S.; Nadargi, D. Y.; Hirashima, H.; Ganesan, V. *J. Colloid Interface Sci.* **2009**, *332*, 484–490.

(8) Scherer, G. W. *J. Non-Cryst. Solids* **1995**, *186*, 309–315.

(9) de Boer, J. H.; Linsen, B. G.; Broekhoff, J. C. P.; Osinga, T. J. *J. Catal.* **1968**, *11* (1), 46–53.

(10) Brunauer, S.; Emmett, P.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309–319.

(11) Reichenauer, G.; Pfrang, T.; Hofmann, M. *Colloids Surf., A* **2007**, *300*, 211–215.

(12) Wang, P.; Emmerling, A.; Tappert, W.; Spormann, O.; Fricke, J.; Haubold, H.-G. *J. Appl. Crystallogr.* **1991**, *24* (5), 777–780.

(13) Groß, J.; Fricke, J. *J. Non-Cryst. Solids* **1992**, *145*, 217–222.

(14) Schmitt, W. J. Masters thesis, University of Wisconsin, Madison, WI, 1982.

(15) Hüsing, N.; Schubert, U.; Mezei, R.; Fratzl, P.; Riegel, B.; Kiefer, W.; Kohler, D.; Mader, W. *Chem. Mater.* **1999**, *11* (2), 451–457.

(16) Hüsing, N.; Schubert, U.; Misof, K.; Fratzl, P. *Chem. Mater.* **1998**, *10* (10), 3024–3032.