

# Supplementary Information

## Effect of aging on silica aerogel properties

*Subramaniam Iswar<sup>a,b</sup>, Wim J. Malfait<sup>a\*</sup>, Sandor Balog<sup>b</sup>, Frank Winnefeld<sup>c</sup>, Marco Lattuada<sup>b</sup> and Matthias M. Koebel<sup>a\*</sup>*

*<sup>a</sup>Laboratory for Building Energy Materials and Components, Swiss Federal Laboratories for Materials Science and Technology, Empa, Überlandstrasse 129, 8600 Dübendorf, Switzerland*

*<sup>b</sup>Adolphe Merkle Institute, University of Fribourg, 1700 Fribourg, Switzerland*

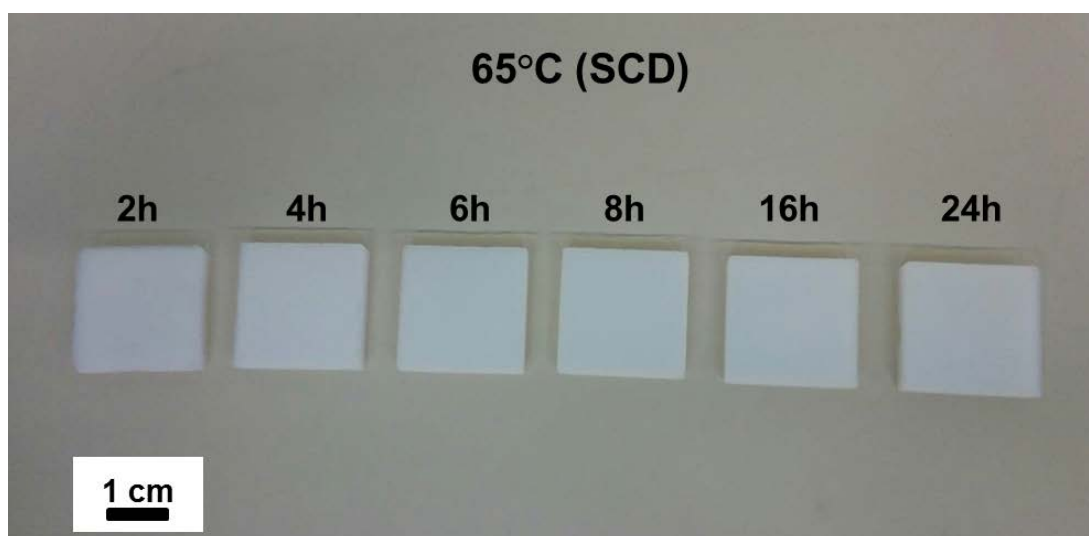
*<sup>c</sup>Laboratory for Concrete and Construction Chemistry, Swiss Federal Laboratories for Materials Science and Technology, Empa, Überlandstrasse 129, 8600 Dübendorf, Switzerland*

*\*Corresponding authors: [wim.malfait@empa.ch](mailto:wim.malfait@empa.ch), [matthias.koebel@empa.ch](mailto:matthias.koebel@empa.ch)*

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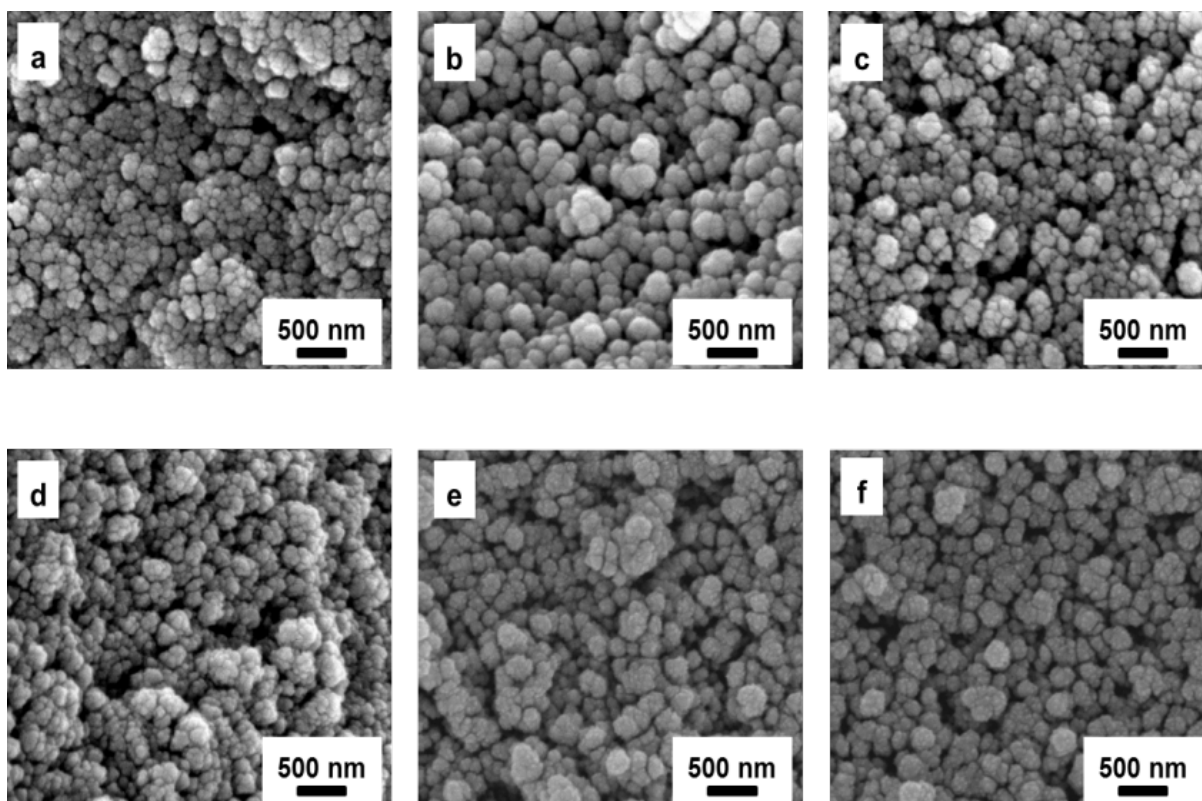
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## Sample appearance



**Figure S1.** Supercritically dried (SCD) silica aerogels aged at 65°C for 6 aging times.

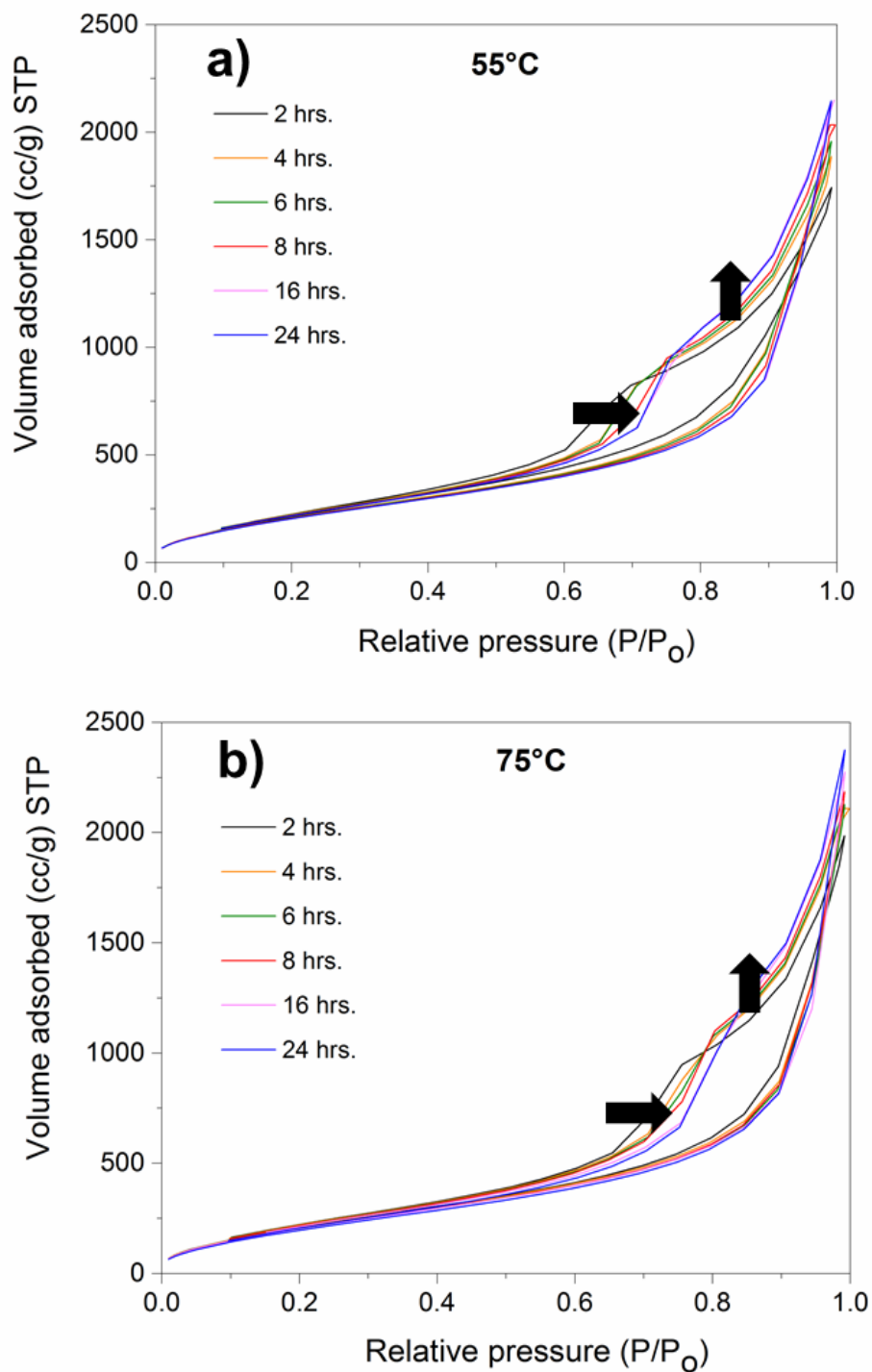
## SEM images



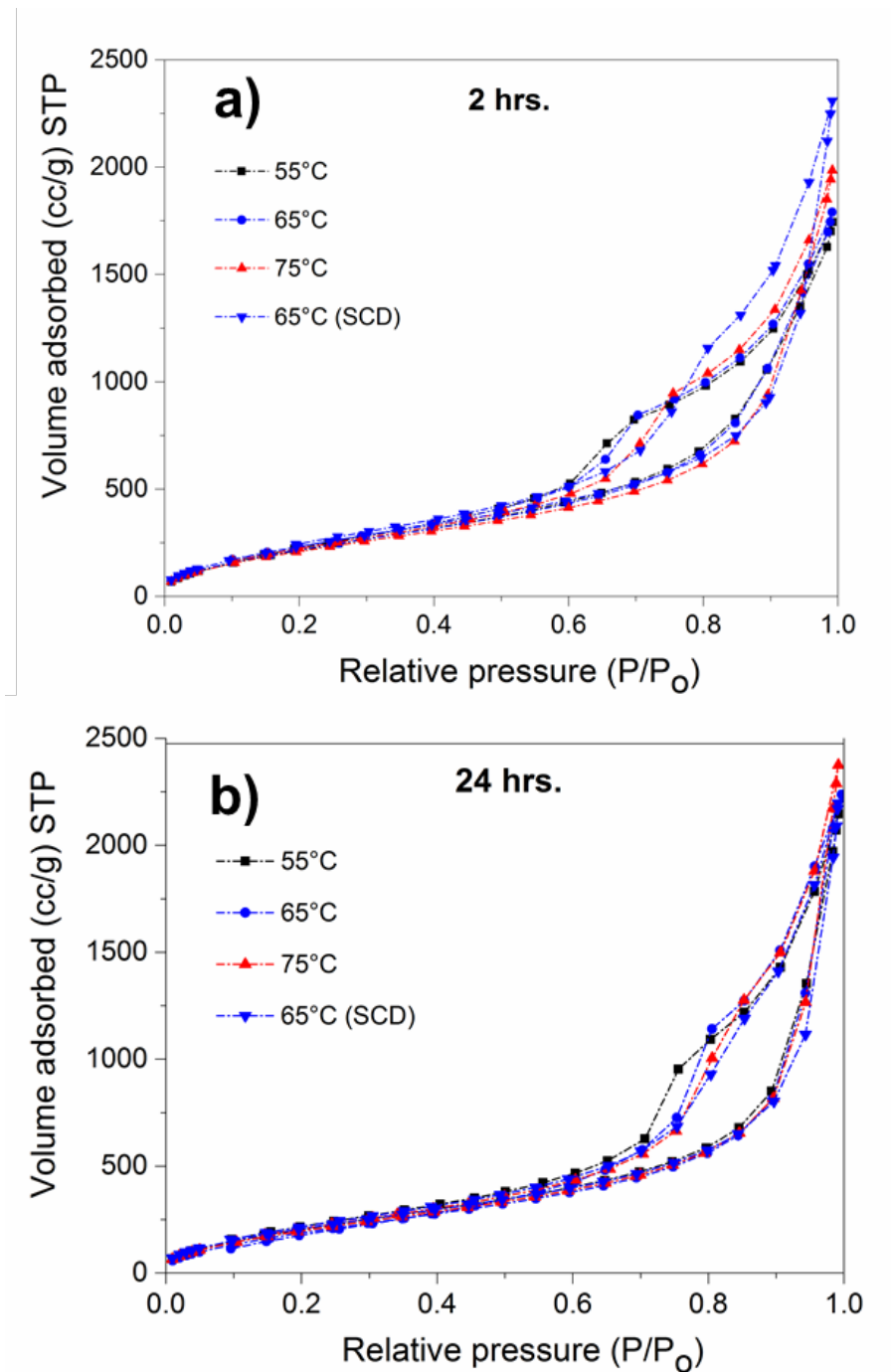
**Figure S2.** SEM images of ambient dried silica aerogels aged at 65°C for 6 aging times

(a) 2 hrs. (b) 4 hrs. (c) 6 hrs. (d) 8 hrs. (e) 16 hrs. (f) 24 hrs.

## Nitrogen sorption isotherms

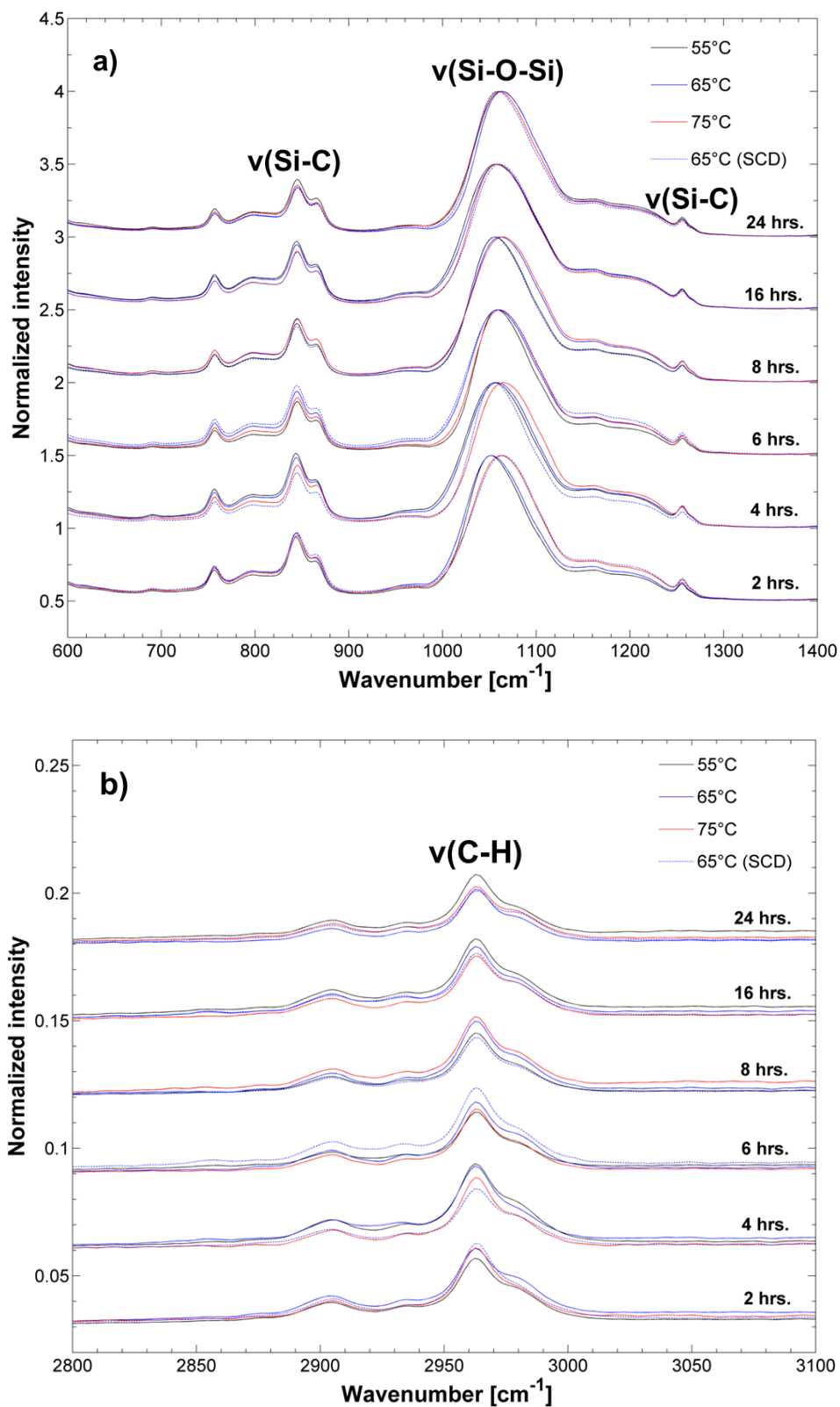


**Figure S3.** Influence of aging time on the nitrogen sorption isotherms of silica aerogel aged at (a) 55°C and (b) 75°C. The arrows indicate the increase in aging time.



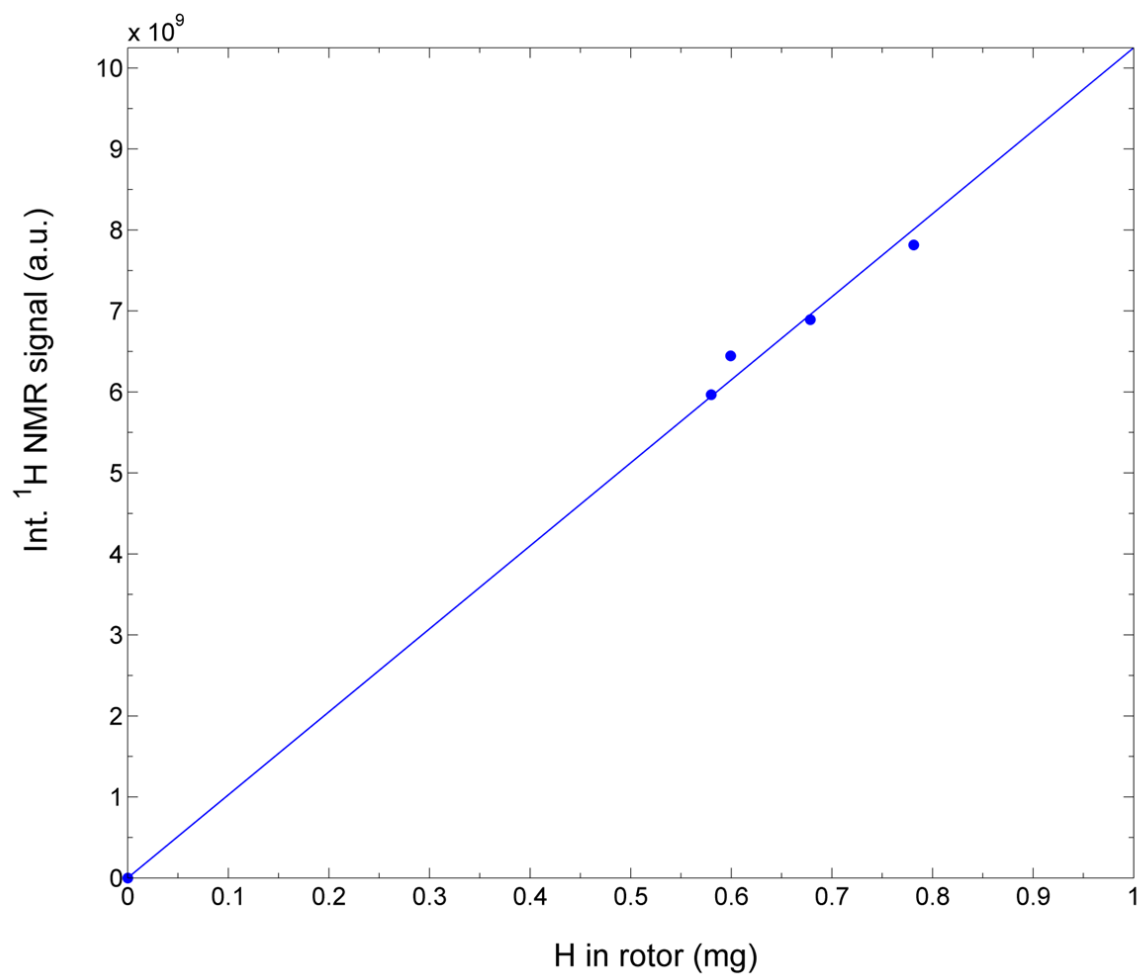
**Figure S4.** Influence of aging temperature on the nitrogen sorption isotherms of silica aerogel aged for (a) 2 hours and (b) 24 hours.

## ATR-FTIR spectra

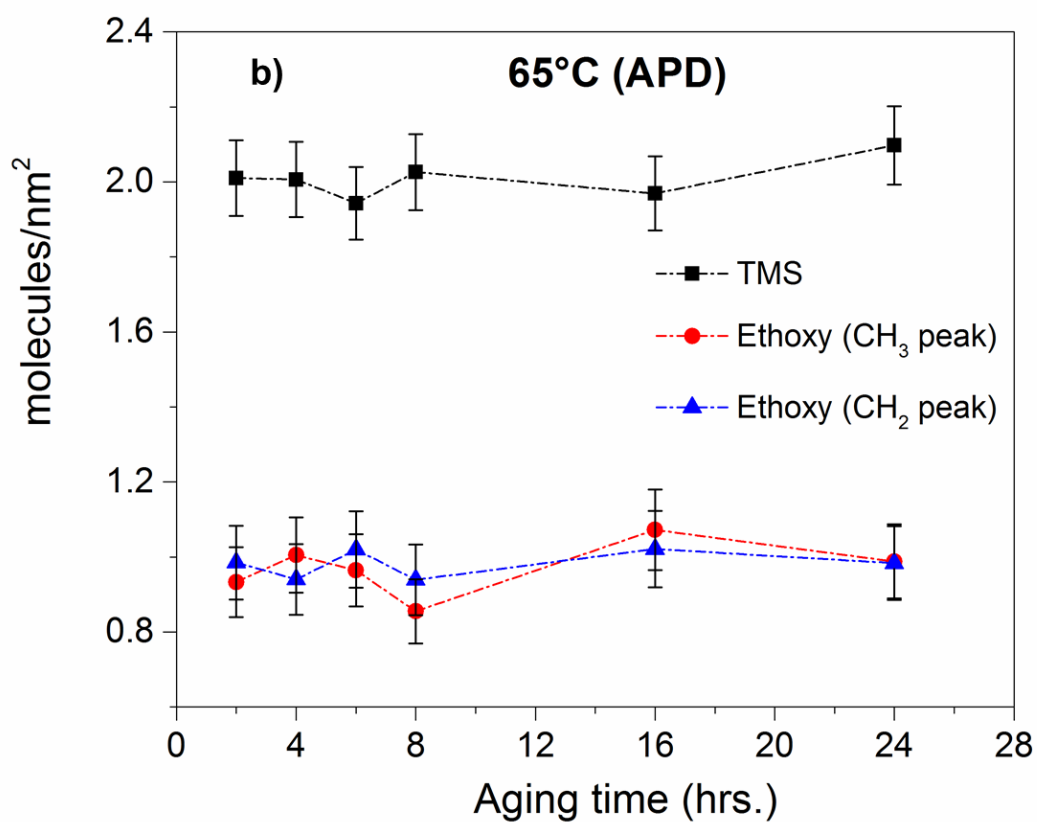
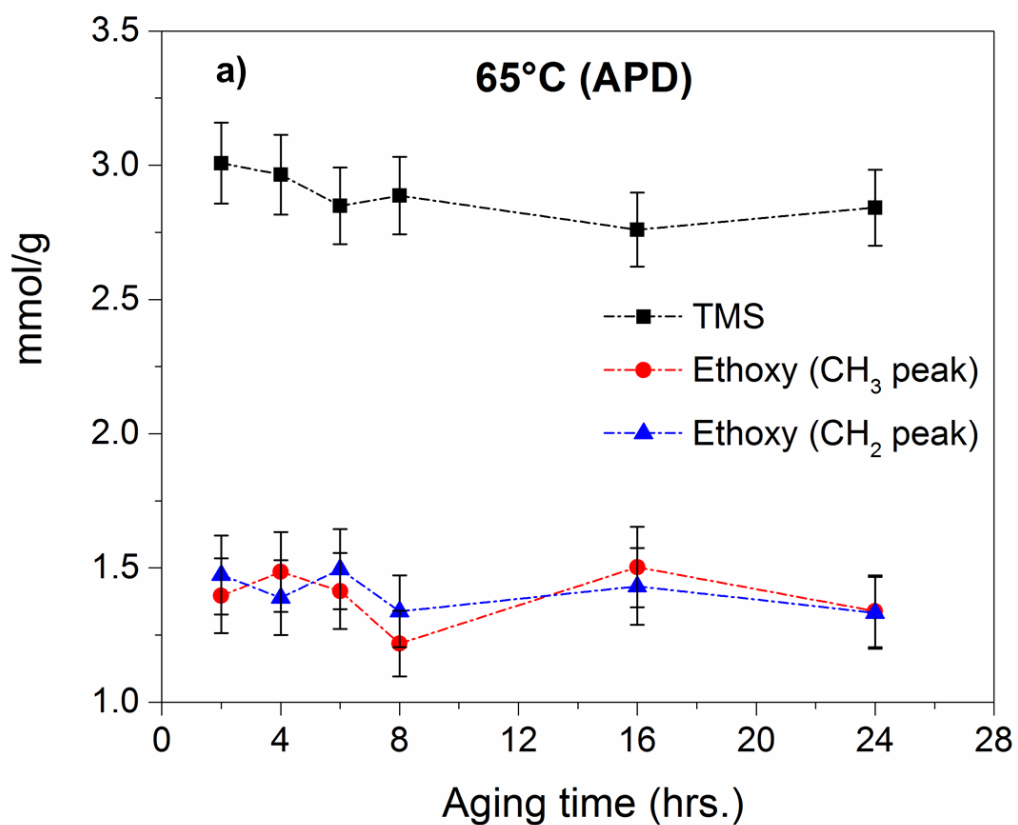


**Figure S5.** ATR-FTIR spectra of ambient dried silica aerogels aged at 65°C at 6 aging times (a) Si-C; Si-O-Si region and (b) C-H region.

## NMR data



**Figure S6.** Calibration curve for quantitative solid-state <sup>1</sup>H MAS NMR.

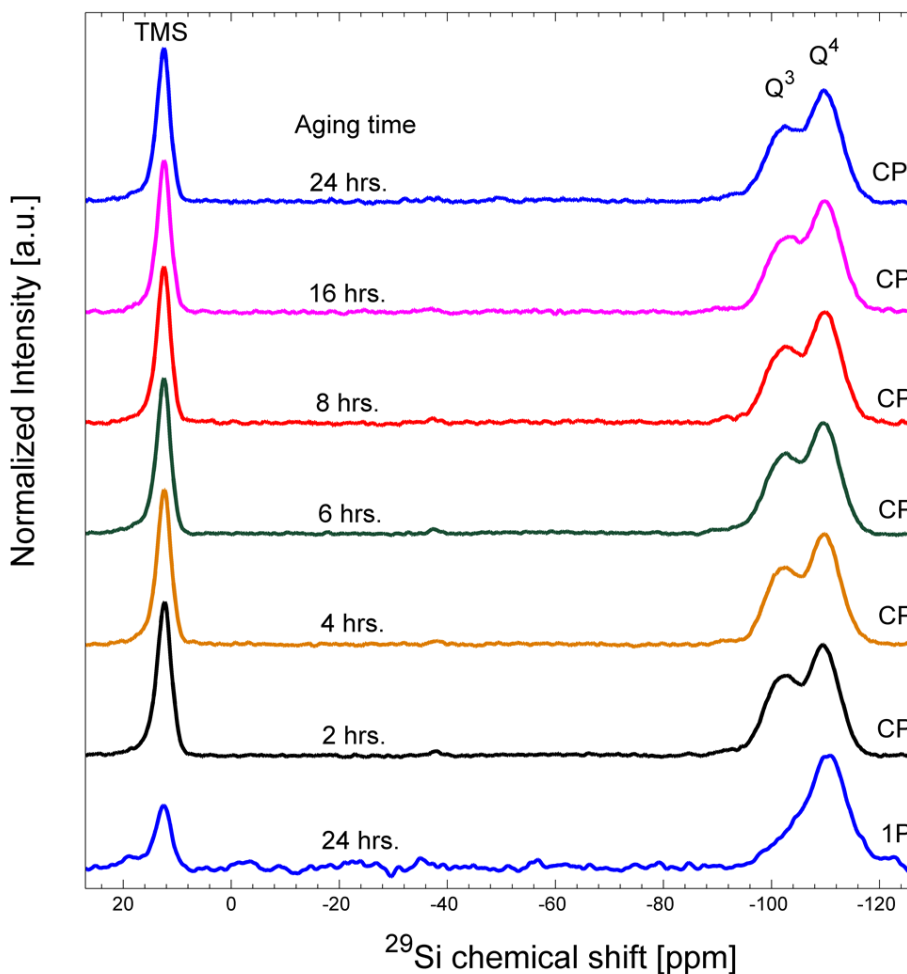


**Figure S7.** Surface modification of ambient dried silica aerogels aged at 65°C as a function of aging time expressed as (a) mmol/g, and (b) molecules/ $\text{nm}^2$ .



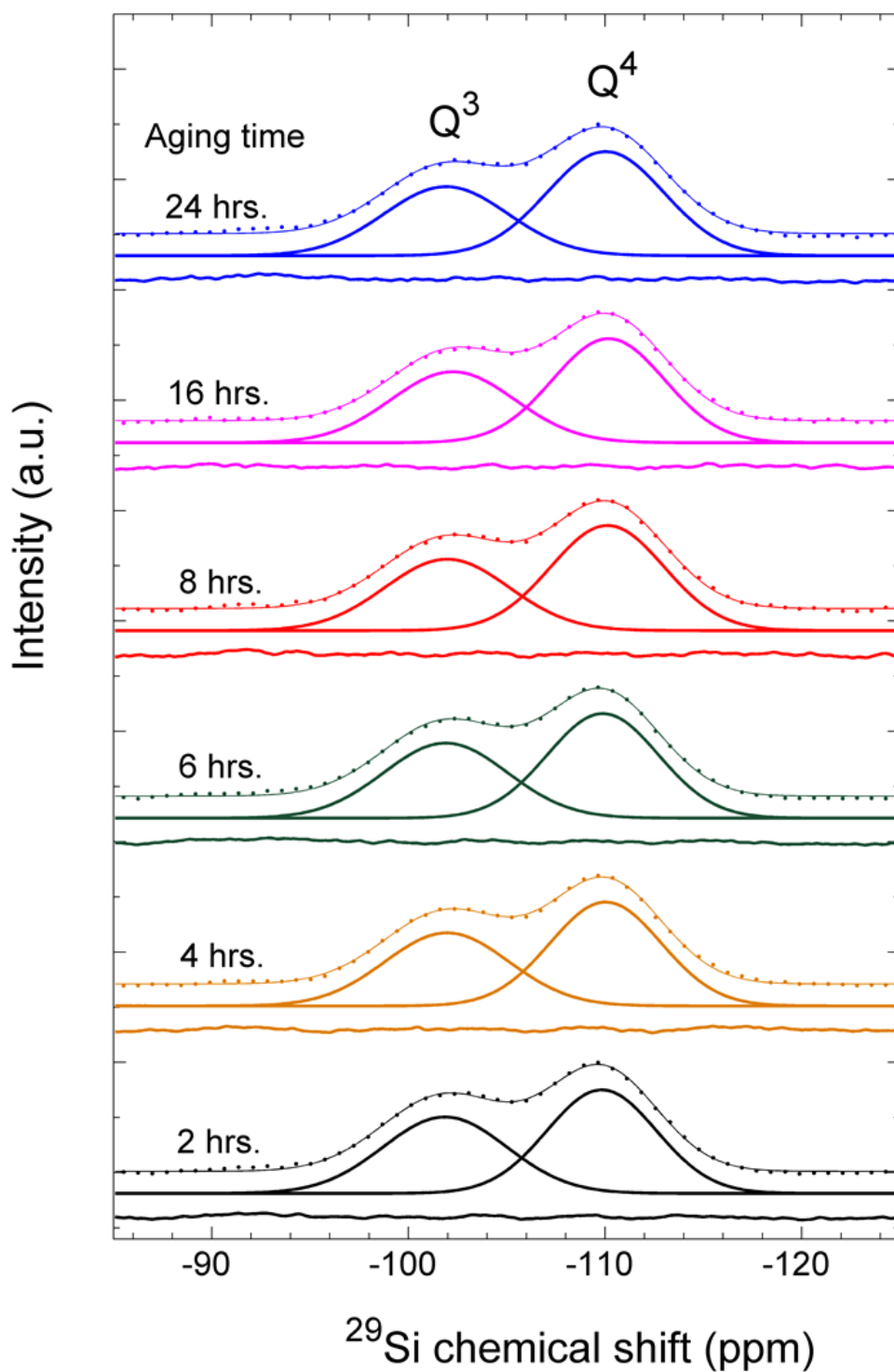
**Table S1.** Surface modification of ambient dried silica aerogels aged at 65°C as a function of aging time.

Aging time (hrs.)	S <sub>BET</sub> (m <sup>2</sup> /g)	Concentration (mmol/g)			Surface coverage (molecules/nm <sup>2</sup> )		
		TMS	Ethoxy CH <sub>3</sub> peak	Ethoxy CH <sub>2</sub> peak	TMS	Ethoxy CH <sub>3</sub> peak	Ethoxy CH <sub>2</sub> peak
2	901	3.01 ± 0.15	1.40 ± 0.14	1.47 ± 0.14	2.01 ± 0.1	0.93 ± 0.1	0.99 ± 0.1
4	890	2.96 ± 0.15	1.49 ± 0.15	1.39 ± 0.14	2.01 ± 0.1	1.01 ± 0.1	0.94 ± 0.1
6	883	2.85 ± 0.14	1.41 ± 0.14	1.50 ± 0.15	1.94 ± 0.1	0.96 ± 0.1	1.02 ± 0.1
8	858	2.89 ± 0.14	1.22 ± 0.12	1.34 ± 0.13	2.03 ± 0.1	0.86 ± 0.1	0.94 ± 0.1
16	844	2.76 ± 0.14	1.50 ± 0.15	1.43 ± 0.14	1.97 ± 0.1	1.07 ± 0.1	1.02 ± 0.1
24	816	2.84 ± 0.14	1.34 ± 0.13	1.33 ± 0.13	2.10 ± 0.1	0.99 ± 0.1	0.98 ± 0.1



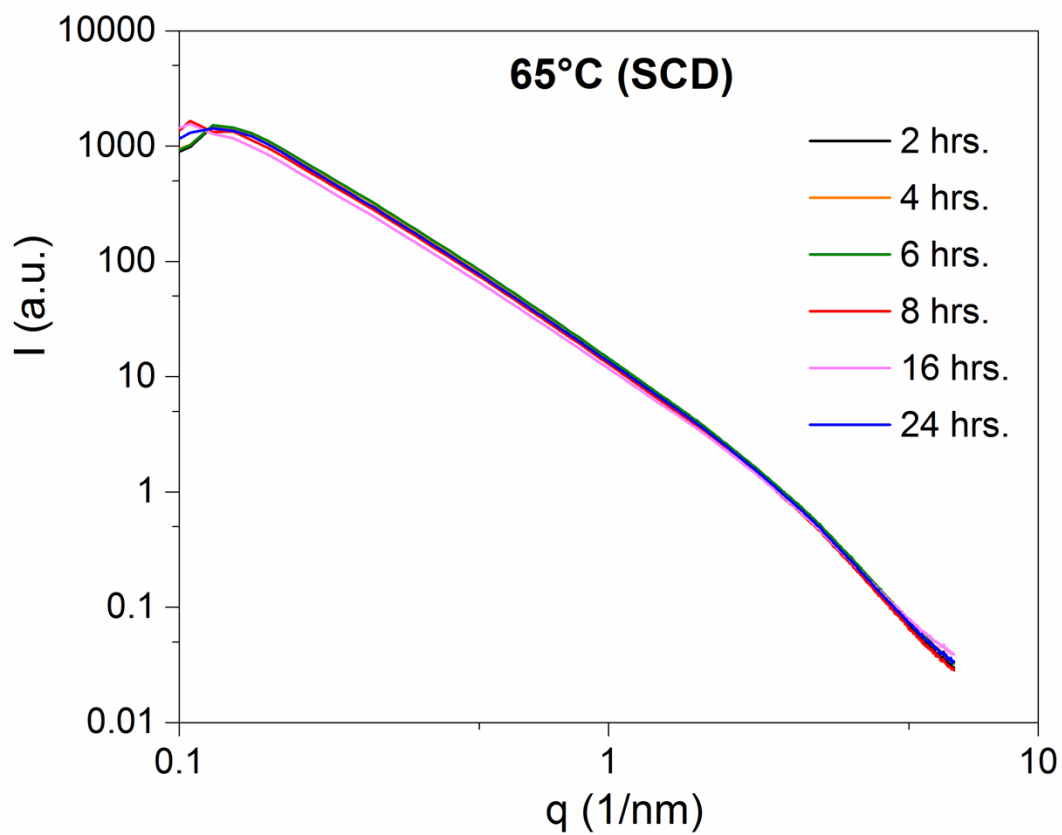
**Figure S8.**  $^1\text{H}$ - $^{29}\text{Si}$  cross polarization (CP) MAS NMR spectra of ambient dried silica aerogels aged at  $65^\circ\text{C}$  for 6 aging times and the quantitative  $^1\text{H}$ - $^{29}\text{Si}$  single pulse (1P) MAS NMR spectrum of ambient dried silica aerogel aged at  $65^\circ\text{C}$  for 24 hours.

Note that cross polarization from  $^1\text{H}$  enhances the relative signal intensity for the TMS and  $\text{Q}^3$  relative to  $\text{Q}^4$  as the former are in closer proximity to hydrogen from the TMS, ethoxy or silanol groups and as a result, the  $^1\text{H}$ - $^{29}\text{Si}$  CP spectra selectively amplify the TMS and  $\text{Q}^3$  signal compared to its abundance. Nevertheless, the observed trends in the  $\text{Q}^3/\text{Q}^4$  peak area ratios between different samples are indicative of real variations in the  $\text{Q}^3$  content as all spectra were collected with the same CP conditions.

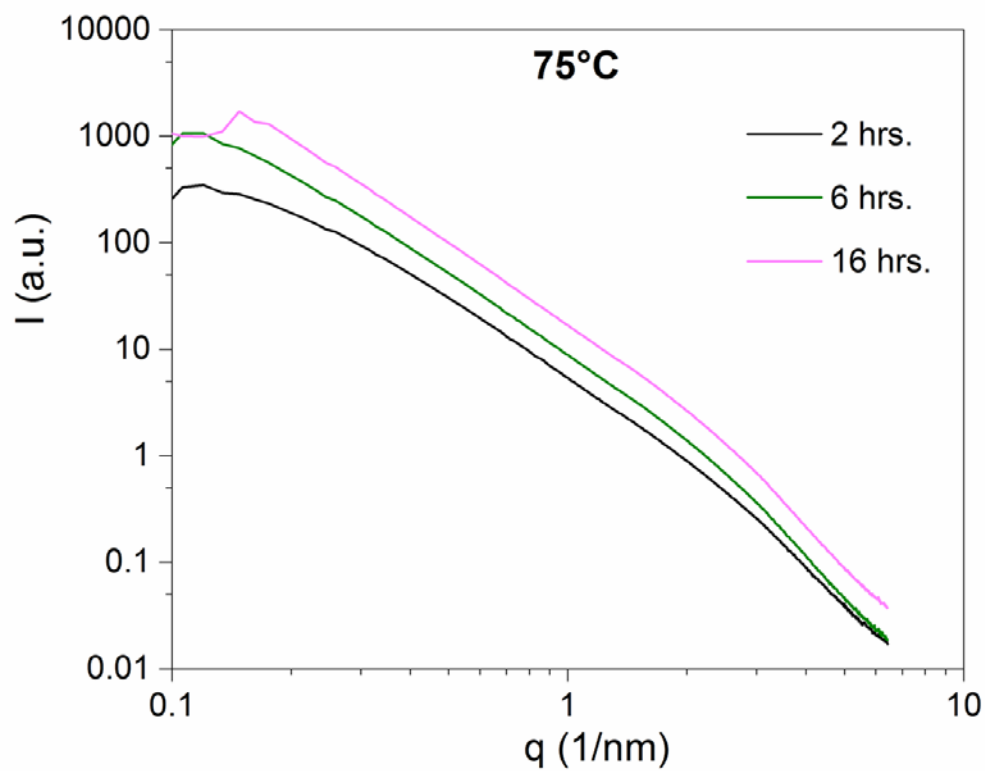
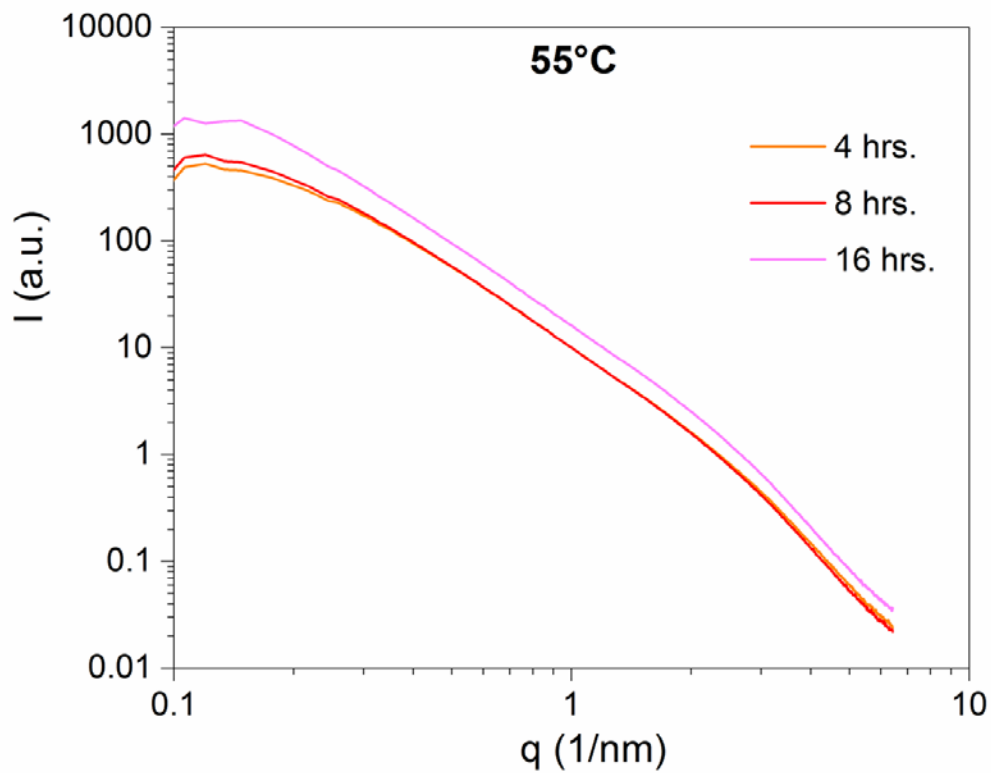


**Figure S9.** Gaussian fits to the  $\text{Q}^3$  and  $\text{Q}^4$  region of the  $^1\text{H}$ - $^{29}\text{Si}$  cross polarization (CP) MAS NMR spectra of ambient dried silica aerogels aged at  $65^\circ\text{C}$  for 6 aging times. The dots denote the experimental data; the lines correspond to the fitting envelope, fitted components and fit residual.

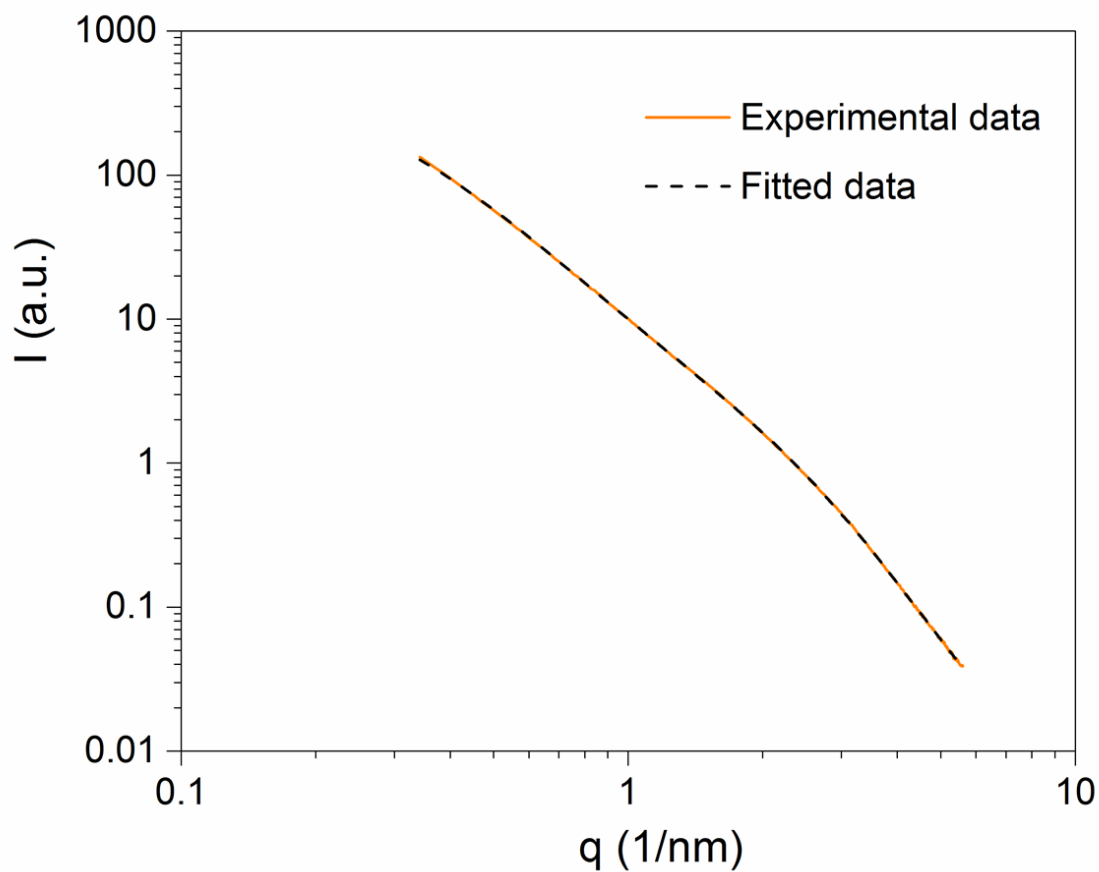
## SAXS spectra



**Figure S10.** SAXS spectra as a function of the momentum transfer vector  $q$  of supercritically dried (SCD) silica aerogels aged at 65°C for 6 aging times, indicated in the legends.



**Figure S11.** SAXS spectra as a function of the momentum transfer vector  $q$  of ambient dried silica aerogels aged at (a) 55°C and (b) 75°C, measured at aging times indicated in the legends.



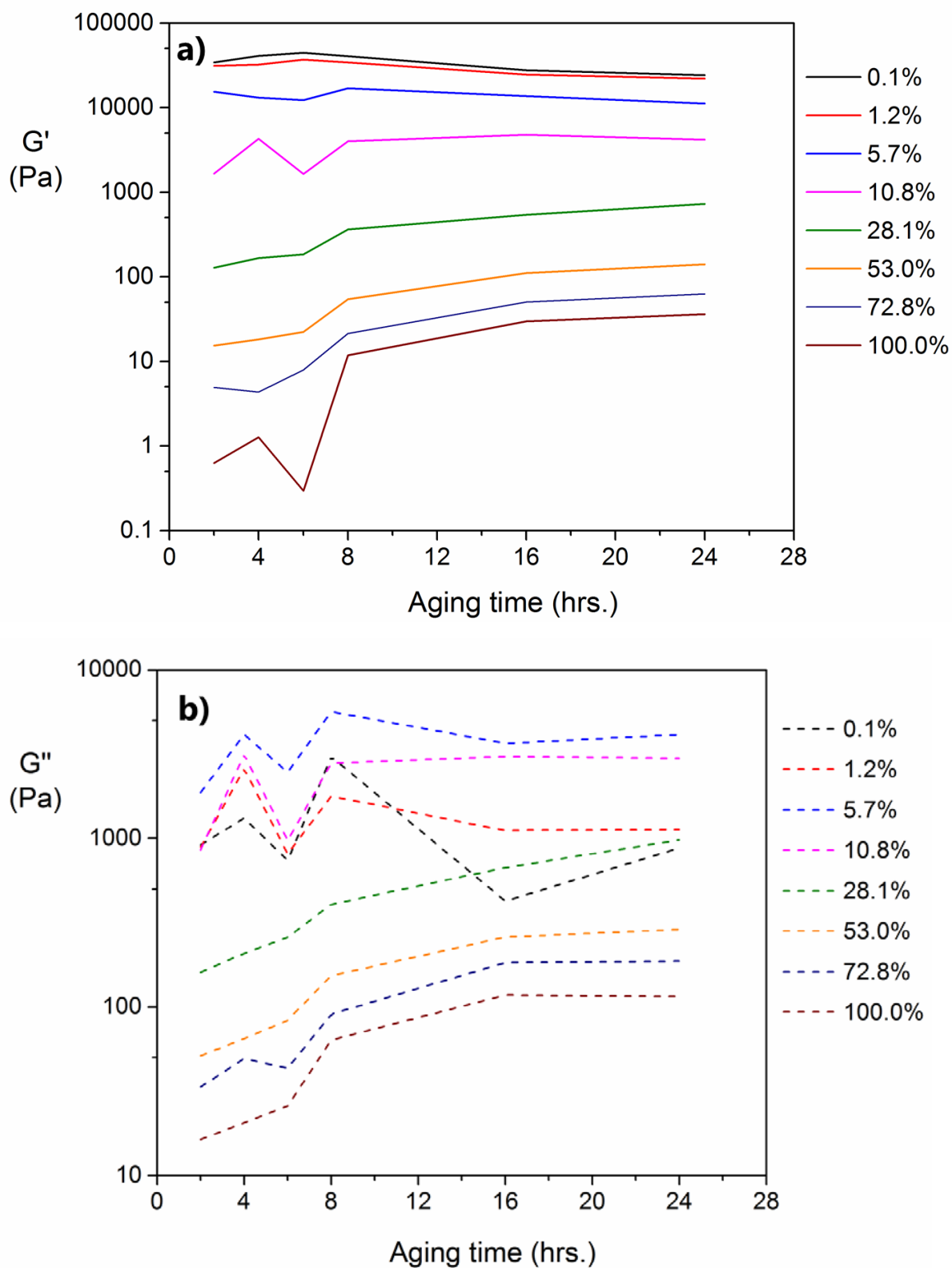
**Figure S12.** SAXS spectra as a function of the momentum transfer vector  $q$  of ambient dried silica aerogel aged at  $55^{\circ}\text{C}$  for 4 hrs. The solid line denotes the experimental data; the dashed line corresponds to the fit of the scattered intensity experimental data by using the model (Main text, Equation 3-4).

## Elemental analysis

**Table S2.** Elemental analysis of ambient dried silica aerogels for different aging times and temperatures.

<b>Aging time (hrs.)</b>	<b>Carbon (%)</b>	<b>Hydrogen (%)</b>
<b>Aging temperature - 55°C (APD)</b>		
2	15.39 ± 1.0	3.94 ± 0.5
4	14.56 ± 1.0	3.65 ± 0.5
6	14.55 ± 1.0	3.69 ± 0.5
8	14.03 ± 1.0	3.65 ± 0.5
16	13.85 ± 1.0	3.39 ± 0.5
24	14.05 ± 1.0	3.59 ± 0.5
<b>Aging temperature - 65°C (APD)</b>		
2	14.87 ± 1.0	3.37 ± 0.5
4	15.13 ± 1.0	3.34 ± 0.5
6	14.20 ± 1.0	3.50 ± 0.5
8	14.01 ± 1.0	3.39 ± 0.5
16	14.02 ± 1.0	3.37 ± 0.5
24	13.54 ± 1.0	3.20 ± 0.5
<b>Aging temperature - 75°C (APD)</b>		
2	14.10 ± 1.0	3.68 ± 0.5
4	14.26 ± 1.0	3.64 ± 0.5
6	14.10 ± 1.0	3.55 ± 0.5
8	14.10 ± 1.0	3.60 ± 0.5
16	13.86 ± 1.0	3.37 ± 0.5
24	13.56 ± 1.0	3.24 ± 0.5

## Rheology data



**Figure S13. (a) Storage modulus ( $G'$ ) and (b) Loss modulus ( $G''$ ) of silica alcogels aged at 65°C at different deformation strains for 6 aging times.**