Supporting Information for

The Pore Network and the Adsorption Characteristics of Mesoporous Silica Aerogel: Adsorption Kinetics on a Timescale of Seconds

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Nitrogen porometry of the dry aerogel:

Quantachrome NovaWin - Data Acquisition and Reduction
for NOVA instruments

version 11.0

Quantachrome INSTRUMENTS
Optimizing particle performance

Analysis
Operator: AerogelLab **Date:**2015/03/20
Sample ID: KE-10 **Filename:**

Report
Operator: AerogelLab **Date:**4/9/2015
C:\QCdata\Physisorb\KE-10.qps

Isotherm

Relative Pressure	Volume @ STP [cc/g]	Relative Pressure	Volume @ STP [cc/g]	Relative Pressure	Volume @ STP [cc/g]
4.59500e-03	117.3788	7.78239e-01	570.2218	7.24804e-01	644.1934
6.20900e-03	125.1163	7.95381e-01	587.7940	6.99596e-01	607.8998
1.06310e-02	140.3717	8.20460e-01	614.0372	6.82569e-01	584.5793
1.68750e-02	154.7747	8.36550e-01	635.7924	6.63094e-01	565.9544
6.41740e-02	205.5995	8.55154e-01	664.3955	6.43445e-01	544.7244
9.55050e-02	225.9026	8.75292e-01	698.3475	6.21781e-01	527.6891
1.40361e-01	248.1658	8.96115e-01	741.5098	6.04912e-01	512.7755
1.78347e-01	264.7490	9.16339e-01	797.5208	5.81454e-01	496.0251
2.15245e-01	280.2587	9.36384e-01	888.0622	5.60459e-01	479.5198
2.56026e-01	295.6425	9.54980e-01	1047.3297	5.42287e-01	468.7991
2.97108e-01	311.1668	9.75976e-01	1970.4994	5.19030e-01	452.6769
3.38220e-01	326.1445	9.80549e-01	3836.8341	5.04568e-01	443.5763
3.79252e-01	341.9842	9.85087e-01	4209.1974	4.61965e-01	419.5782
4.18275e-01	357.1890	9.91000e-01	4781.6923	4.23101e-01	396.7614
4.59300e-01	375.3219	9.88436e-01	4780.6416	3.82637e-01	376.0169
4.97409e-01	389.9705	9.88040e-01	4773.6272	3.41562e-01	353.9203
5.18209e-01	399.5852	9.84035e-01	4674.8408	3.01559e-01	332.7234
5.35200e-01	409.2308	9.64949e-01	4096.8807	2.59440e-01	311.9851
5.56411e-01	420.0262	9.44421e-01	3521.4295	2.19063e-01	290.5330
5.75577e-01	429.9238	9.24881e-01	3135.5462	1.80270e-01	270.0771
5.96284e-01	439.6438	9.04325e-01	2839.4637	1.43502e-01	249.0135
6.16134e-01	452.0632	8.84555e-01	2526.9761	1.03802e-01	223.9096
6.39369e-01	464.7054	8.63985e-01	2176.2634	5.64460e-02	187.4070
6.60126e-01	478.3503	8.44329e-01	1644.0337	2.31630e-02	147.9990
6.76865e-01	490.7141	8.24141e-01	1197.0243	1.85460e-02	139.7889
6.95454e-01	502.9364	8.03794e-01	956.3965	1.27990e-02	127.1067
7.17163e-01	519.4899	7.83115e-01	825.4082	9.61500e-03	118.0342
7.38864e-01	533.8366	7.64295e-01	746.3590		
7.59772e-01	550.7087	7.43235e-01	683.2997		

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Analysis		**Report**	
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Sample ID: KE-10	**Filename:**	C:\QCdata\Physisorb\KE-10.qps	

DFT method Pore Size Distribution

Pore width [nm]	Cumulative Pore Volume [cc/g]	Cumulative Surface Area [m¸/g]	dV(d) [cc/nm/g]	dS(d) [m¸/nm/g]
1.3790	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
1.4320	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
1.4980	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
1.5640	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
1.6310	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
1.6970	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
1.7800	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
1.8680	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
1.9480	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
2.0270	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
2.1070	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
2.1860	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
2.2660	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
2.3450	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
2.4250	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
2.5040	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
2.5830	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
2.7030	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
2.8220	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
2.9410	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
3.0600	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
3.1790	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
3.2980	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
3.4180	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
3.5370	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
3.6560	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
3.7750	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
3.9340	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
4.0930	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
4.2520	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
4.4110	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
4.5700	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
4.7280	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
4.8870	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
5.0860	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
5.2850	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
5.4830	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
5.6820	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
5.8800	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
6.0790	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
6.3170	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
6.5560	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
6.7940	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
7.0320	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
7.3100	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
7.5880	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
7.8670	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
8.1450	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
8.4620	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
8.7800	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
9.0980	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
9.4160	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
9.7730	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
10.1310	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
10.4880	4.9846e-03	1.9011e+00	1.3962e-02	5.3251e+00
10.8850	4.1399e-02	1.5282e+01	9.1723e-02	3.3706e+01
11.2830	1.0154e-01	3.6605e+01	1.5112e-01	5.3573e+01
11.6800	1.7862e-01	6.3002e+01	1.9416e-01	6.6493e+01

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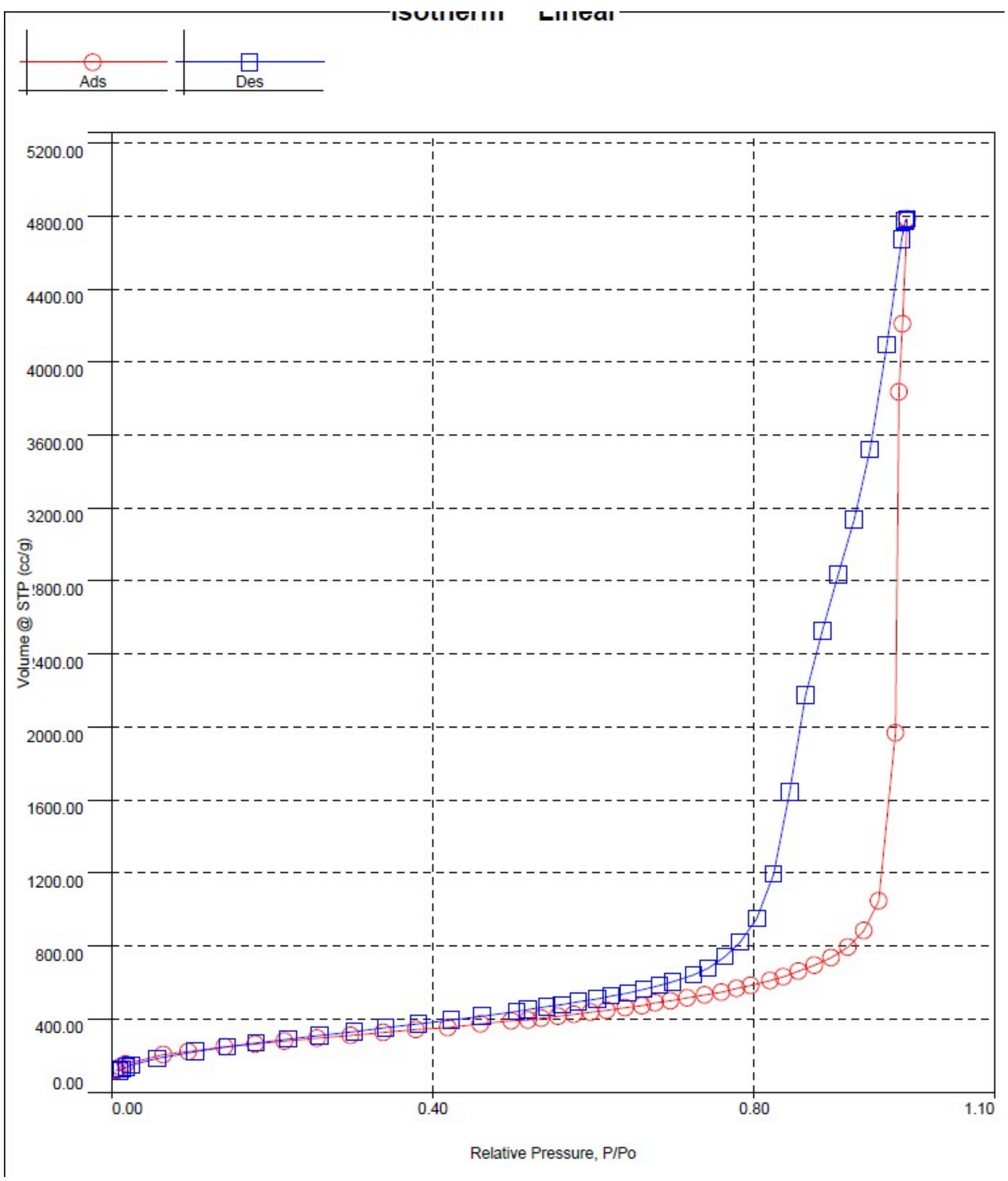
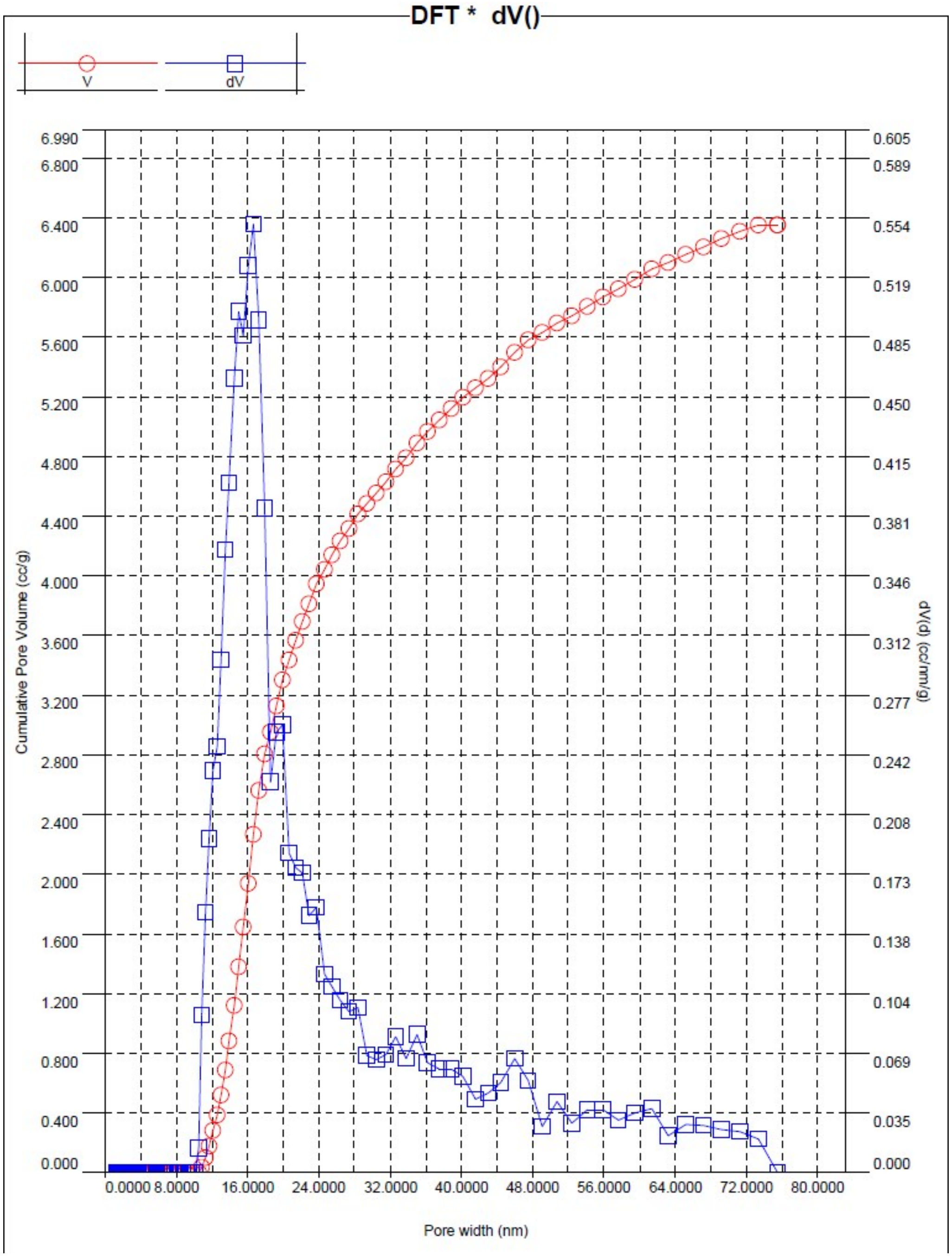
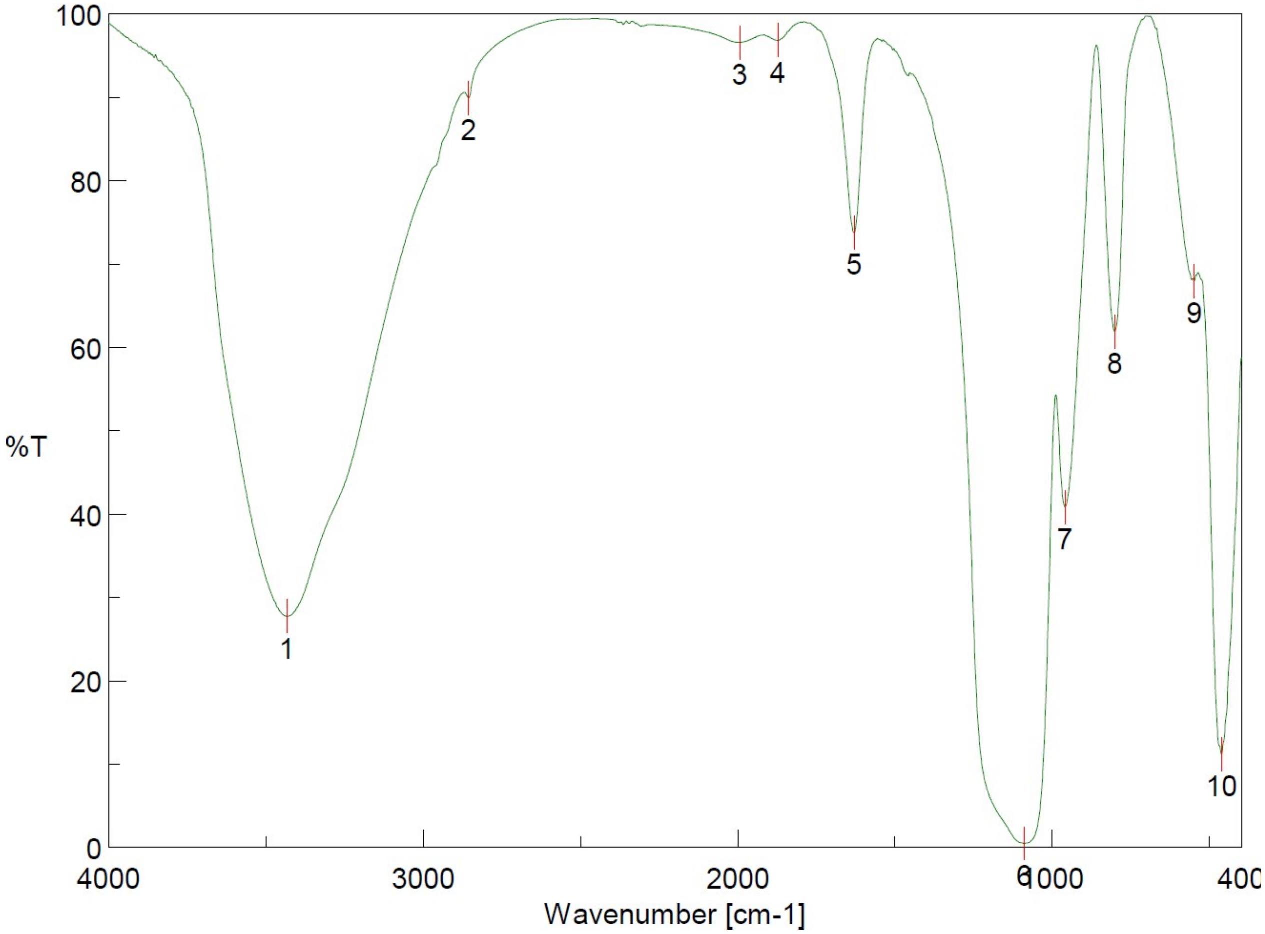
DFT method Pore Size Distribution continued

Pore width [nm]	Cumulative Pore Volume [cc/g]	Cumulative Surface Area [m./g]	dV(d) [cc/nm/g]	dS(d) [m./nm/g]
12.1170	2.8065e-01	9.6683e+01	2.3347e-01	7.7073e+01
12.5540	3.8858e-01	1.3107e+02	2.4697e-01	7.8691e+01
12.9910	5.1864e-01	1.7112e+02	2.9763e-01	9.1641e+01
13.4670	6.9061e-01	2.2220e+02	3.6128e-01	1.0731e+02
13.9440	8.8158e-01	2.7698e+02	4.0035e-01	1.1485e+02
14.4600	1.1194e+00	3.4278e+02	4.6097e-01	1.2752e+02
14.9770	1.3778e+00	4.1177e+02	4.9970e-01	1.3346e+02
15.5330	1.6478e+00	4.8131e+02	4.8562e-01	1.2506e+02
16.0890	1.9404e+00	5.5406e+02	5.2633e-01	1.3086e+02
16.6850	2.2682e+00	6.3264e+02	5.4995e-01	1.3184e+02
17.2810	2.5629e+00	7.0086e+02	4.9450e-01	1.1446e+02
17.9160	2.8079e+00	7.5556e+02	3.8583e-01	8.6142e+01
18.5520	2.9521e+00	7.8664e+02	2.2663e-01	4.8865e+01
19.2270	3.1246e+00	8.2253e+02	2.5563e-01	5.3181e+01
19.9020	3.2999e+00	8.5777e+02	2.5969e-01	5.2194e+01
20.6170	3.4323e+00	8.8345e+02	1.8519e-01	3.5930e+01
21.3720	3.5658e+00	9.0844e+02	1.7680e-01	3.3090e+01
22.1270	3.6971e+00	9.3216e+02	1.7385e-01	3.1427e+01
22.9210	3.8156e+00	9.5285e+02	1.4930e-01	2.6055e+01
23.7550	3.9438e+00	9.7444e+02	1.5371e-01	2.5883e+01
24.6290	4.0444e+00	9.9078e+02	1.1512e-01	1.8697e+01
25.5030	4.1390e+00	1.0056e+03	1.0826e-01	1.6980e+01
26.4170	4.2305e+00	1.0195e+03	1.0005e-01	1.5149e+01
27.3700	4.3193e+00	1.0325e+03	9.3257e-02	1.3629e+01
28.3630	4.4144e+00	1.0459e+03	9.5769e-02	1.3506e+01
29.3960	4.4849e+00	1.0555e+03	6.8214e-02	9.2822e+00
30.4680	4.5555e+00	1.0647e+03	6.5840e-02	8.6438e+00
31.5410	4.6294e+00	1.0741e+03	6.8913e-02	8.7395e+00
32.6530	4.7172e+00	1.0848e+03	7.8883e-02	9.6632e+00
33.8050	4.7934e+00	1.0939e+03	6.6182e-02	7.8309e+00
34.9970	4.8891e+00	1.1048e+03	8.0258e-02	9.1732e+00
36.2280	4.9675e+00	1.1135e+03	6.3751e-02	7.0388e+00
37.4990	5.0438e+00	1.1216e+03	5.9966e-02	6.3965e+00
38.8100	5.1226e+00	1.1297e+03	6.0104e-02	6.1947e+00
40.1600	5.1983e+00	1.1373e+03	5.6144e-02	5.5920e+00
41.5510	5.2574e+00	1.1429e+03	4.2453e-02	4.0869e+00
42.9810	5.3235e+00	1.1491e+03	4.6199e-02	4.2995e+00
44.4500	5.4004e+00	1.1560e+03	5.2395e-02	4.7149e+00
45.9600	5.5008e+00	1.1648e+03	6.6483e-02	5.7862e+00
47.5090	5.5839e+00	1.1718e+03	5.3616e-02	4.5142e+00
49.0980	5.6271e+00	1.1753e+03	2.7204e-02	2.2163e+00
50.7270	5.6948e+00	1.1806e+03	4.1562e-02	3.2773e+00
52.3950	5.7430e+00	1.1843e+03	2.8884e-02	2.2050e+00
54.1030	5.8056e+00	1.1889e+03	3.6682e-02	2.7121e+00
55.8510	5.8696e+00	1.1935e+03	3.6598e-02	2.6212e+00
57.6380	5.9240e+00	1.1973e+03	3.0430e-02	2.1117e+00
59.4650	5.9878e+00	1.2016e+03	3.4949e-02	2.3509e+00
61.3320	6.0570e+00	1.2061e+03	3.7031e-02	2.4151e+00
63.2390	6.0979e+00	1.2087e+03	2.1450e-02	1.3568e+00
65.1850	6.1523e+00	1.2120e+03	2.7950e-02	1.7151e+00
67.1710	6.2065e+00	1.2152e+03	2.7326e-02	1.6273e+00
69.1970	6.2578e+00	1.2182e+03	2.5277e-02	1.4612e+00
71.2630	6.3072e+00	1.2210e+03	2.3947e-02	1.3441e+00
73.3680	6.3480e+00	1.2232e+03	1.9380e-02	1.0566e+00
75.5130	6.3480e+00	1.2232e+03	0.0000e+00	0.0000e+00


Isotherm Linear
Ads
Des
5200.00
4800.00
4400.00
4000.00
3600.00
3200.00
2800.00
2400.00
2000.00
1600.00
1200.00
800.00
400.00
0.00
Volume @ STP (cc/g)
0.00
0.40
0.80
1.10
Relative Pressure, P/Po


DFT * dV()
V
dV
Cumulative Pore Volume (cc/g)
dV(d) (cc/nm/g)
Pore width (nm)
6.990
6.800
6.400
6.000
5.600
5.200
4.800
4.400
4.000
3.600
3.200
2.800
2.400
2.000
1.600
1.200
0.800
0.400
0.000
0.605
0.589
0.554
0.519
0.485
0.450
0.415
0.381
0.346
0.312
0.277
0.242
0.208
0.173
0.138
0.104
0.069
0.035
0.000
0.0000
8.0000
16.0000
24.0000
32.0000
40.0000
48.0000
56.0000
64.0000
72.0000
80.0000

Infrared spectroscopy:



1: 3434 cm^{-1}: (adsorbed water)

2: 2856 cm^{-1}

3: 1994 cm^{-1}

4: 1873 cm^{-1}

5: 1631 cm^{-1}: (adsorbed water)

6: 1090 cm^{-1}: Si–O–Si asymmetric stretching

7: 960 cm^{-1}: Si–OH stretching

8: 802 cm^{-1}: Si–O–Si symmetric stretching

9: 550 cm^{-1}

10: 463 cm^{-1}: Si–O–Si bending

Figure S1. Transmission IR spectrum of the calcined silica aerogel.

Microscopy of the aerogel suspension:

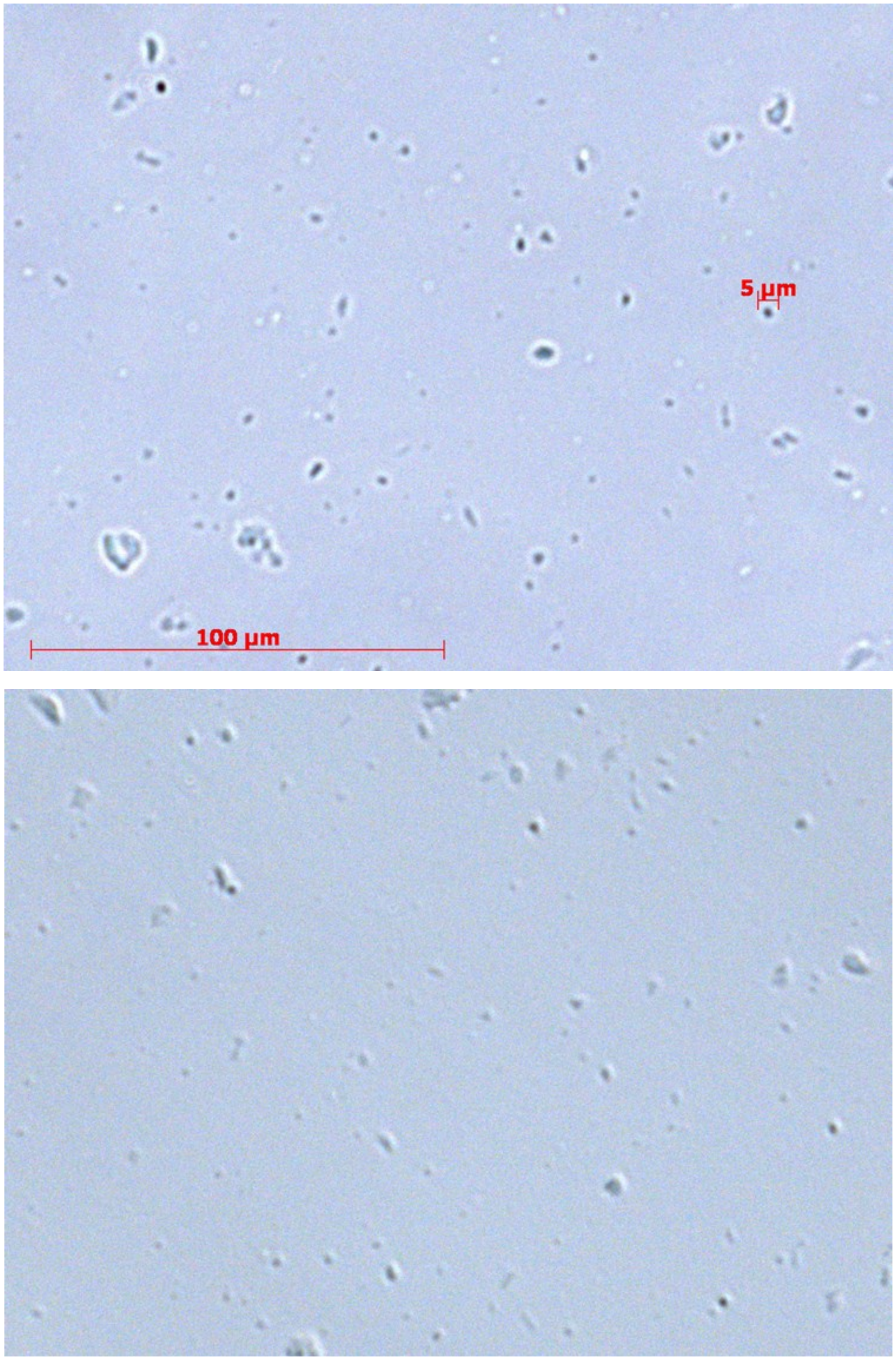


Figure S2A. Micrograph of a fresh aerogel suspension. Small, homogeneous particles (5 – 10 µM) dominate.

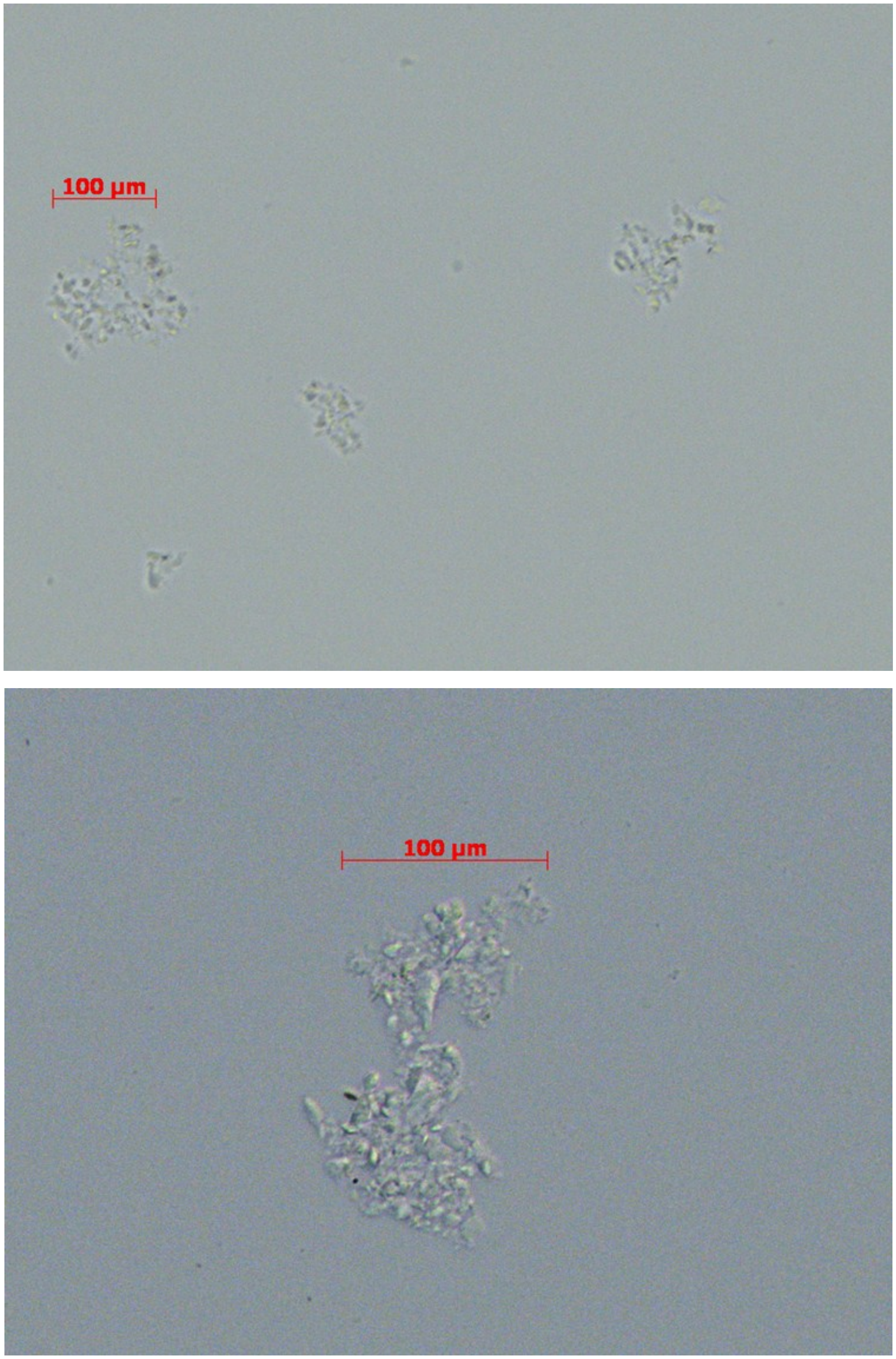


Figure S2B. Micrograph of a 2 h aerogel suspension. Small aerogel particles spontaneously aggregate to larger (20 – 100 µM) blocks.

Self-diffusion of water in the aerogel suspension:

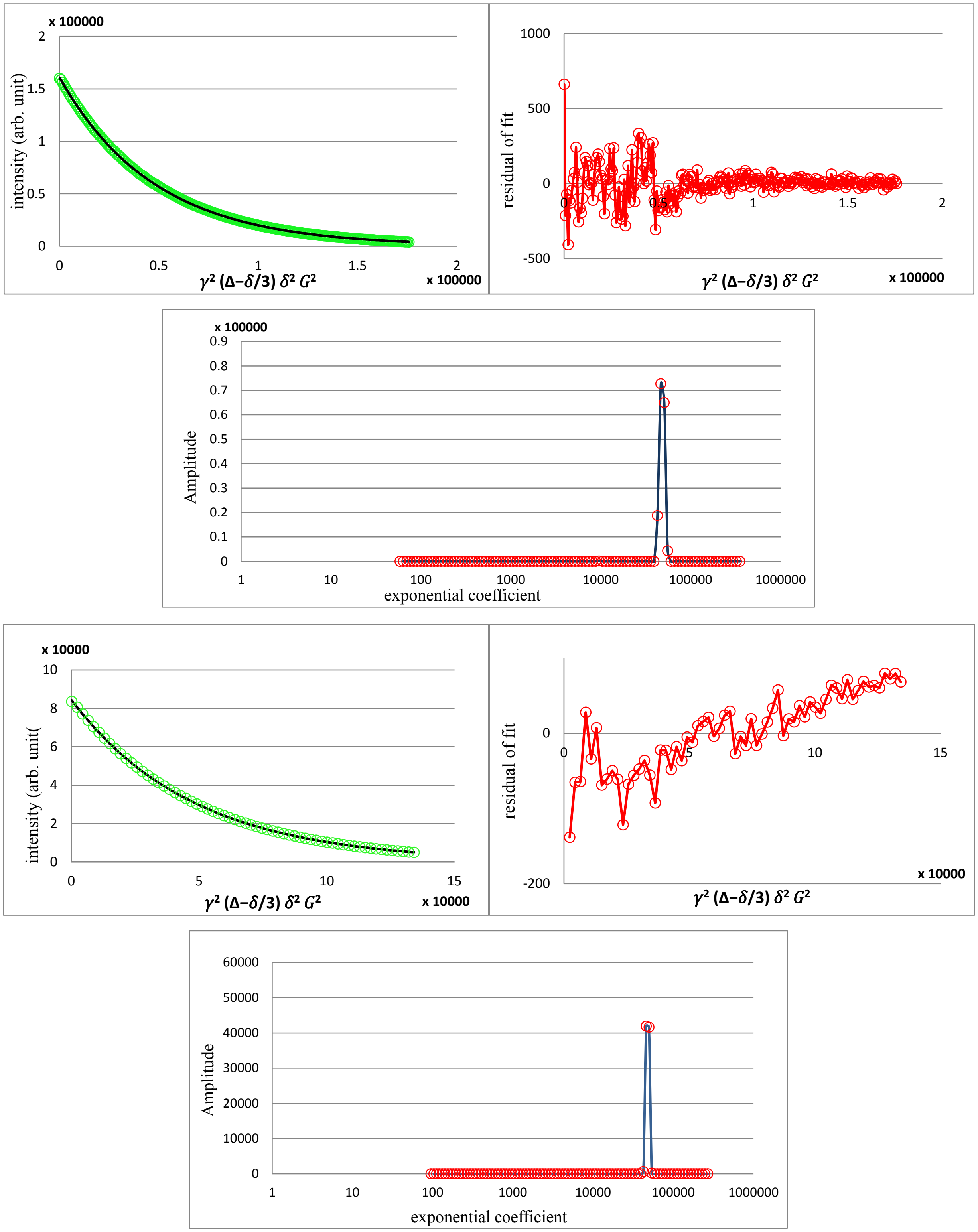


Figure S3. NMR diffusiometry: self-diffusion of water in suspended aerogel. Experimental curves (upper left corner), and inverse Laplace transformation and single exponential fitting of these curves. Up: Δ = 16 ms, δ = 4.0 ms. Down: Δ = 150 ms, δ = 1.6 ms.

The validity of Beer's law in the aerogel suspension:

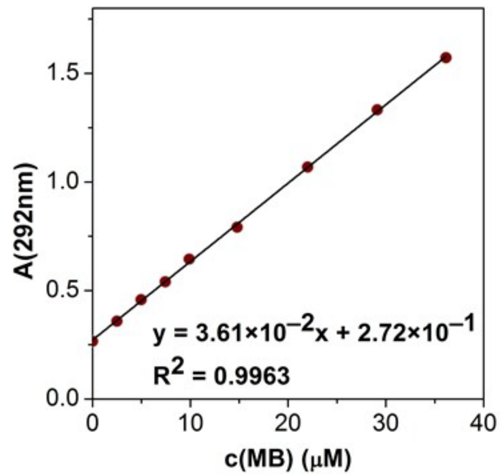


Figure S4. Absorbance versus concentration plot of methylene blue (MB) added to an aerogel suspension. The intercept is due to the light scattering of the suspension. c(gel) = 338 μg/mL; $c(NaH_2PO_4+Na_2HPO_4)$ = 50 mM; pH = 6.91; 25 °C; 1000 rpm stirring.

The Langmuir isotherm:

The following equations describe the adsorption equilibrium and account for the mass balances in the Langmuir model:

$$\mathbf{MB} + \mathbf{S} \rightleftharpoons \mathbf{SMB} \tag{4}$$

$$K_{ads} = \frac{\theta_{SMB}}{[MB]\theta_S} \qquad c_{MB} = [MB] + c_{gel} s\,\theta_{SMB} \qquad 1 = \theta_S + \theta_{SMB} \tag{5}$$

where MB is hydrated methylene blue, S represents an unoccupied adsorption site and SMB is the adsorbed dye occupying a site. K_{ads} is the equilibrium constant of monolayer adsorption. The total concentration of MB is c_{MB}. The total concentration of the aerogel is c_{gel} in g/L units. The number of adsorption sites on the aerogel particles is s in mol/g units. Thus, s represents the adsorptive capacity of the aerogel. θ_S and θ_{SMB} represent the surface coverage of free and occupied sites, respectively. Square brackets denote equilibrium concentrations. ([MB] is the concentration of hydrated MB in the adsorption equilibrium.) The adsorbed amount of MB can be easily expressed from eq. 5:

$$[MB]_{ads} = c_{gel} s \theta_{SMB}$$

and

$$[MB] = c_{MB} - c_{gel} s \theta_{SMB}$$

Inserting this expression to K_{ads} in eq. 5 yields:

$$K_{ads} = \frac{\theta_{SMB}}{(c_{MB} - c_{gel} s \theta_{SMB})(1 - \theta_{SMB})}$$

By solving the above second order mathematical equation to give θ_{SMB}, the absorbed amount of MB can be expressed as the function of c_{MB} and c_{gel}:

$$[MB]_{ads} = c_{gel} s \theta_{SMB} = \frac{1}{2}\left\{\left(c_{gel} s + c_{MB} + \frac{1}{K_{ads}}\right) - \sqrt{\left(c_{gel} s + c_{MB} + \frac{1}{K_{ads}}\right)^2 - 4 c_{MB} c_{gel} s}\right\}$$

In the case, if $c_{MB} >> [MB]_{ads}$:

$$K_{ads} = \frac{\theta_{SMB}}{c_{MB}(1 - \theta_{SMB})}$$

and

$$[MB]_{ads} = c_{gel} s \theta_{SMB} = \frac{K_{ads} c_{MB} c_{gel} s}{1 + K_{ads} c_{MB}}$$

The absorbance of the solution decreases because some dissolved MB is removed by the aerogel. Using Lambert-Beer's law:

$$\Delta A = \varepsilon l [MB]_{ads} = \varepsilon l c_{gel} s \theta_{SMB}$$

The absorbance change due to the depletion of dissolved MB is ΔA. The molar absorbance of MB at 292 nm is ε and the optical path length of the cuvette is l:

$$\Delta A = \varepsilon l c_{gel} s \theta_{SMB} = \frac{\varepsilon l}{2}\left\{\left(c_{gel} s + c_{MB} + \frac{1}{K_{ads}}\right) - \sqrt{\left(c_{gel} s + c_{MB} + \frac{1}{K_{ads}}\right)^2 - 4c_{M}} \quad (6)$$

Kinetics of the adsorption of MB on aerogel particles:

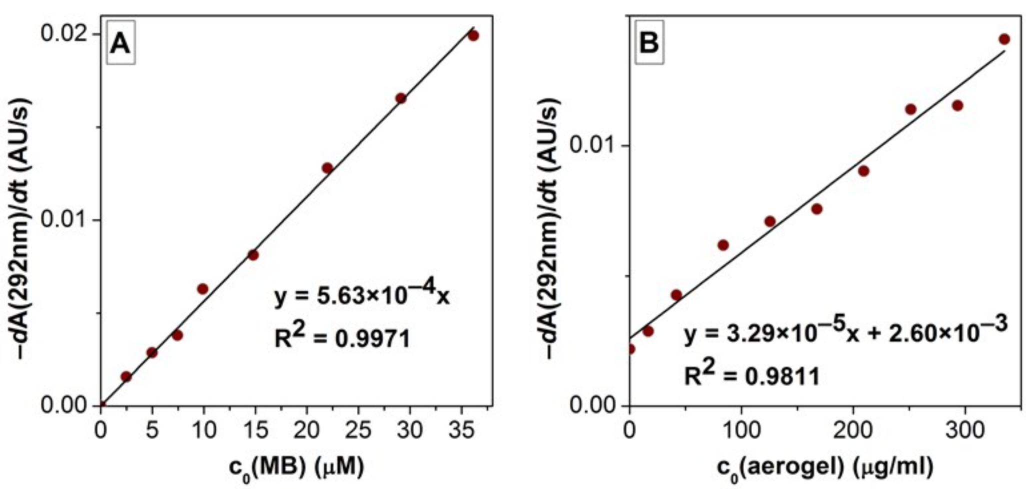


Figure S5. Dependence of the initial rate of adsorption on the initial concentration of MB (A) and on the initial concentration of the aerogel in suspension (B). Dots are experimental data points. Continuous lines are the results of linear data fitting. $c(NaH_2PO_4+Na_2HPO_4)$ = 50 mM; pH = 6.93 (A), 6.91 (B); 25 °C; 1000 rpm stirring.

Aggregation of aerogel particles following the adsorption of MB:

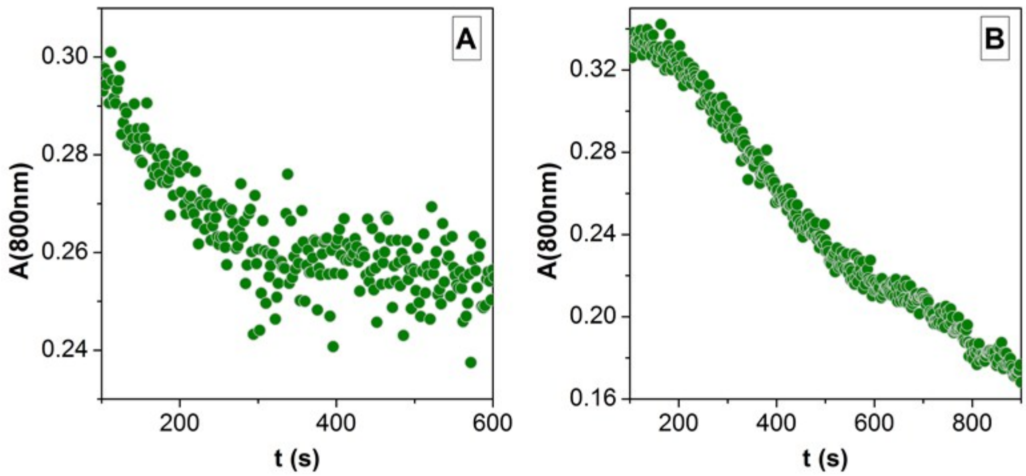


Figure S6. The aggregation of aerogel particles following the adsorption of MB. The absorbance decreases because the light scattering of the particles decreases. Methylene blue does not absorb at 800 nm. A: Aged aerogel suspension: *c*(gel) = 340 µg/mL; *c*(MB) = 22.0 µM. B: Fresh aerogel suspension: *c*(gel) = 341 µg/mL; c(MB) = 45.3 µM. *c*(NaH_2PO_4+Na_2HPO_4) = 50 mM; pH = 6.93 (A), 6.96 (B); 25 °C; 1000 rpm stirring.