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Effect of sol–gel synthesis conditions on physical properties of silica hydrogels

Ekaterina S. Dolinina, Anton S. Kraev and Elena V. Parfenyuk

Density measurement

The silica hydrogel densities were determined by the hydrostatic weighing method using DEMCOM DA balance (Italy). A sample of semisolid hydrogel was weighted in air (w_1), then immersed in n-hexane and weighted again (w_2). The density of hydrogel (ρ_{HG}) was calculated as

$$\rho_{HG} = \frac{W_1}{W_1 - W_2}(\rho_{hex} - \rho_{air}) + \rho_{air} \quad (1),$$

where ρ_{hex} and ρ_{air} are the densities of hexane and air. The density values of hexane and wet air at 20^0C are 0.6594 g/cm^3 [1] and 0.0012 g/cm^3 (Density of air. https://en.wikipedia.org/wiki/Density_of_air), respectively.

The densities of liquid hydrogels were determined using known density calibration weights according the formula:

$$\rho_{HG} = \alpha \frac{P}{V} + \rho_{air},$$

where P is the displaced fluid weight, α is correction factor (0.99985) taking into account buoyancy force acting in air on the calibration weight, V is the volume of the calibration weight.

Porosity evaluation

The porosity (P) of materials can be calculated as

$$P = \frac{V_p}{V} \quad (2),$$

V_p is the pore volume, V is the total volume of sample.

Silica hydrogel is two-phase material composed of a three-dimensional network formed from silica particles bound together, the pores of which are filled with liquid.

Therefore, void volume (pore volume) in hydrogel is equivalent to volume of liquid in the material.

The porosity of the synthesized silica hydrogels was evaluated as follows. A sample of hydrogel was weighed in air (w_1). To determine the volume of the sample by the hydrostatic weighing method, it was weighted in hexane (w_2), and the volume was calculated as

$$V = \frac{W_1 - W_2}{\rho_{hex}} \quad (3)$$

Then the sample was dried in the oven at 600^0C for a day, and the obtained silica powder was weighed (w_3). The porosity was calculated using the following formula (4):

$$P = \frac{W_1 - W_3}{V\rho} \quad (4),$$

where (w_1 - w_3) is the weigh of liquid in the sample, ρ is the density of liquid. The liquids in the synthesized silica hydrogels have complex composition (buffer solution with additions of NaCl). The liquids were collected after shrinking of the hydrogels during aging and their densities were measured.

Particle size measurements

The particles size and size distribution of the silica hydrogel particles in phosphate buffer solution (pH 7.4) was determined using a Zetasizer Nano ZS (Malvern Instrument, UK). Before the measurements, the sample hydrogel was placed into the solution and sonicated for 5 min. As an example, the particle size distributions for HG (0.25M, b/s), HG (0.25M, s/b), HG (1.0M, b/s), HG (1.0M, s/b) are presented in Figure S1.

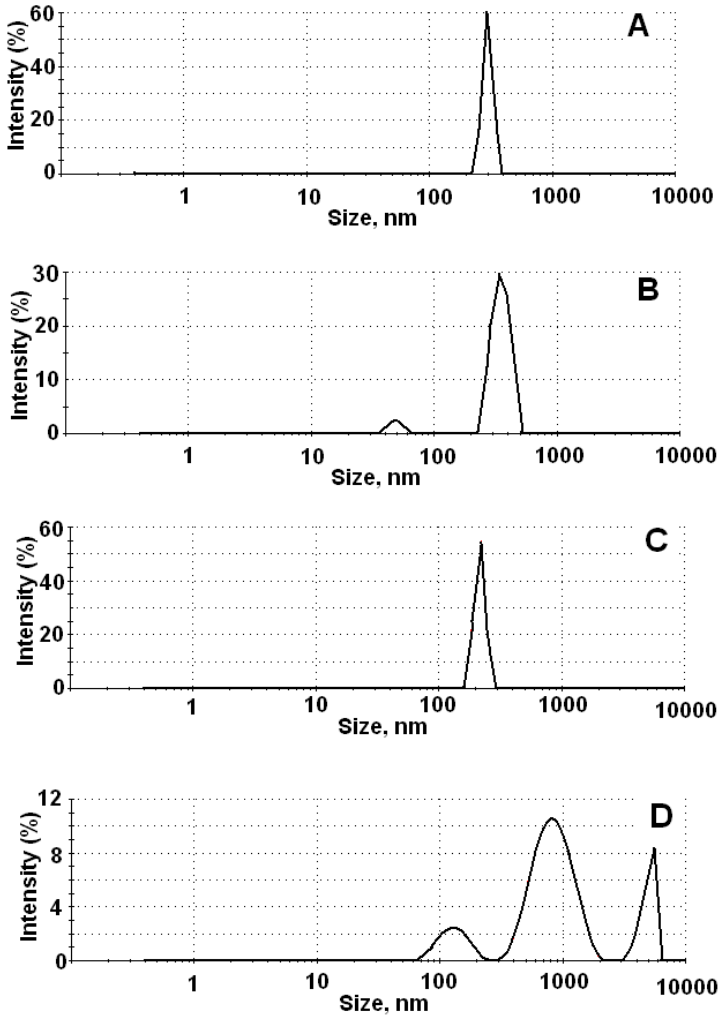

Figure S1 Particle size distribution for HG (0.25M, b/s) (A), HG (0.25M, s/b) (B), HG (1.0M, b/s) (C), HG (1.0M, s/b) (D).

Mechanical tests of silica hydrogels

Uniaxial compression and tension measurements were conducted at room temperature (22°C) using a test machine with a 10 N sensor[2]. Samples of height (H=5 mm) and diameter (D=20 mm) were used. Before the tests, an initial compressive contact of 0.05 N was applied to ensure a complete contact between the gel and the plates. The tests were performed at a constant cross-head speed of 0.021 $mm \cdot s^{-1}$. The compressive strain (ε_c) and the tensile strain (ε_t) were determined as $\varepsilon_c = 1 - \lambda$ and $\varepsilon_t = \lambda - 1$, respectively, where $\lambda = l/l_0$ (l_0 and l are the heights of sample before and after deformation). The compression stress (σ_c) and the tensile stress (σ_t) were calculated as $\sigma_c = F_c / A_0$ and $\sigma_t = F_t/A_0$, respectively, where F_c and F_t are the load forces at compression and tension, A_0 is the surface area. The Young's modules (compressive modulus and tensile modulus) were calculated from the slope of initial linear part of the stress-strain curves.

The visual features of the synthesized silica hydrogels

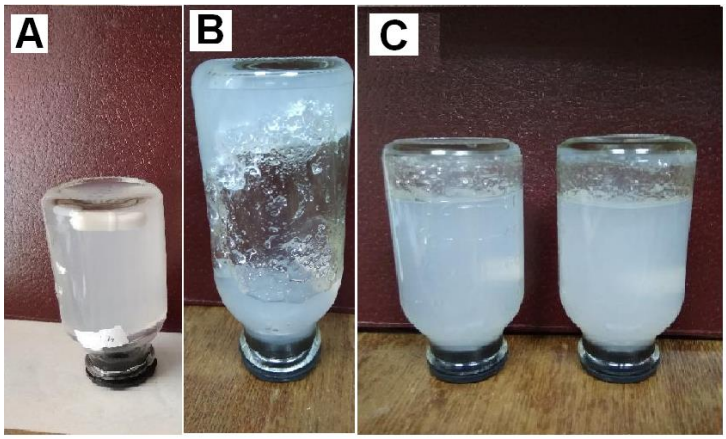

Figure S2 Representation of silica hydrogels prepared using different concentration of catalyst and at different mixing order: A- HG (b/s, 0.25 M); B-HG (s/b, 0.25 M); C- HG (b/s, 0.5 M) and HG(s/b, 0.5 M).

Table S1 Phenomenological observations for synthesized hydrogels.

Hydrogel sample	Visual observations
HG(b/s,0.25M) pH 6.87	Uniform elastic gel. Release very small amount of liquid phase upon breaking of surface. Don't flow down when turned over.
HG(s/b,0.25M) pH 6.75	Uniform gel. Release a small amount of liquid phase upon breaking of surface. Flow down partially when turned over after breaking of surface. After stirring or shaking, the released liquid includes into gel structure, the hydrogel becomes uniform again.
HG(b/s,0.50M) pH 6.75	Uniform semi-liquid gels. Flow down when turned over. Release liquid after breaking of surface. After stirring or shaking, the released liquid includes into gel structure, the hydrogel becomes uniform again.
HG(s/b,0.50M) pH 6.77	
HG(b/s,1.0M) pH 6.79	Uniform, more liquid than HGs (0.50M). Flow down when turned over.After storage for 6 weeks, they are divided into a denser hydrogel phase at the bottom and less dense phase above it. After shaking, uniform hydrogels are obtained.
HG(s/b,1.0M) pH 6.77	

References

S1. J. Zhou, R. Zhu, H. Xu and Y. Tian, *J. Chem. Thermodyn*., 2010, **42**, 1429.

S2. O.I. Davydova, A.S. Kraev, A.A. Redozubov, T.A. Trusova and A.V. Agafonov, *Russ. J. Phys. Chem.*, 2016, **90**, 1269.