Synthesis of Microporous Silica Templated by Gelatin

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Gelatin, a low cost biopolymer was successfully used as a porogen to form microporous silica in the presence of formic acid as a cosolvent.

In the past decade the use of templating methods to form porous silica structures has been an area of active research.[1] Numerous templates including surfactants,[2] and polymers[3] either in dilute solutions[4] or concentrated liquid crystal phases[5] have been successfully employed as materials with which the inorganic precursor interacts to form initially an organic/inorganic nanostructured composite. On removal of the organic matter micro- and/or mesoporous silica in powder,[4] film,[6] or monolithic[7] form result. Although variation in the type of surfactant, its chain length and headgroup, the polymer block lengths, the monomer constituents and their respective charge has been widely studied for their effect on the resulting silica pore structure, little work has appeared in the literature using biomolecular or biopolymer templates for the specific formation of porous silica materials.

The biopolymer gelatin has been used in conjunction with silica for the formation of porous materials, but not as the porogen. For example porous gelatin–silica hybrids have been documented for application in bone tissue engineering.[8] Another method involved gelatin/AOT organogels and microemulsions that resulted in the formation of silica–gelatin nanocomposites.[9] The use of easily obtained, cheap templating materials has prompted this research into the use of readily available biopolymers as porogens during silica monolith formation.

Gelatin is a high molecular weight polypeptide that is derived from collagen and is widely used in the food and pharmaceutical industries. It is highly abundant and inexpensive, making it a favorable candidate for templating. In this report gelatin from calf skin was used as a porogen to form amorphous microporous silica. The amount of gelatin present in the initial reaction mixture was varied to observe its templating effect on the final material. To enhance the gelatin solubility a number of cosolvents were employed: Formic acid was found to successfully increase the amount of gelatin solubilized without inducing porosity itself, and an increase in surface area of the final silica material was obtained with increasing gelatin content.

In a typical experiment, the appropriate amount of gelatin (Aldrich, from calf skin, ≈225 bloom, 74% protein), see Table 1, was added to a mixture consisting of 1.70-g water and 1.50-g formic acid (Aldrich, 88%). The reaction mixture was then stirred at room temperature. After the gelatin was completely dissolved, 4.0 g of tetramethyl orthosilicate (TMOS, Aldrich, 98%) was added under vigorous stirring. Within 10 min the solution had gelled to form a brown monolithic solid. The sample was then heated at 60 °C for 24 h in an open vial, during which time hydrolysis/condensation reactions continued. The resulting solid (monolithic or broken into smaller clumps) was then calcined at 500 °C (ramp rate 5 K min^{-1}) under N_2 for 3 h, followed by 9 h under O_2 to obtain a white, porous silica.

Gelatin present at a sufficient quantity in the reaction mixture brings about microporosity in the final silica material. However, it has a limited solubility (about 5% at room temperature) and hence cosolvents were added to the reaction mixture to enhance solubility of the gelatin. The cosolvents studied were acetic acid (Aldrich, 99.7%), dimethyl sulfoxide (DMSO, Merck, 99.5%), ethylene glycol (Aldrich, 99.8%), formamide (Aldrich, 98%), formic acid (Aldrich, 88%), and glycerol (Aldrich, 99%).

The addition of acetic acid to the reaction mixture resulted in nonhomogeneous solutions, while with DMSO, ethylene glycol as well as glycerol, the dissolved gelatin concentration does not significantly increase. The cosolvent formamide did result in increased solubility of the gelatin but there was not a correlation between the gelatin concentration and the final surface area of the silica material, hence these cosolvents were not further studied. Formic acid was found to work successfully in increasing the gelatin solubility and did not induce porosity in the silica material.

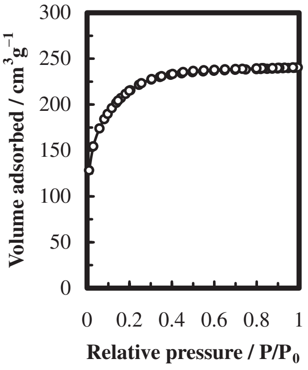

Figure 1. N_2 adsorption and desorption isotherm of the silica formed in the presence of 1.31 g of gelatin (Gel. 4) after being calcined at 500 °C in N_2 followed by O_2. The isotherm was collected on a Micromeritics Tristar Analyzer after the sample was degassed at 150 °C for 12 h.

The N_2 adsorption and desorption isotherm of the calcined silica sample, Gel. 4, where 1.31 g of gelatin and the cosolvent formic acid were used during preparation, is shown in Figure 1. A typical type I isotherm, with an initial increase at low relative pressure followed by a plateau, indicates the presence of micropores in the silica material. The BET surface area and the specific pore volume were calculated from Figure 1 to be 761 m^{2}g^{-1} and 0.37 cm^{3}g^{-1}, respectively. The BET surface area was found to be negligibly small (zero, or close to zero) if the sample was dried but not calcined, i.e., if the gelatin had not been removed

Table 1. BET surface area and specific pore volume of porous silica materials obtained after calcinations of samples containing different amounts of gelatin.

Sample	Gelatin/g	Surface area /m^{2}g^{-1}	Pore volume /cm^{3}g^{-1}
Gel. 0	0.00	0.15	—
Gel. 1	0.40	332	0.16
Gel. 2	0.70	549	0.26
Gel. 3	1.00	654	0.32
Gel. 4	1.31	761	0.37
Gel. 5	1.51	686	0.34

from the sample.

The effect of gelatin concentration on the formation of porous silica was investigated using formic acid as a cosolvent and the results are shown in Table 1. N_2 sorption measurements showed type I isotherms independent of the amount of gelatin used during the synthesis, indicating the formation of microporous silica in all cases, regardless of the quantity of gelatin under the experimental conditions used. The BET surface area and the specific pore volume of the porous silica increased from 332 to 761 m^{2}g^{-1} and 0.16 to 0.37 cm^{3}g^{-1} while increasing the amount of gelatin from 0.40 to 1.51 g. This result clearly illustrates that the pores in the porous silica are templated by the gelatin molecules.

The morphology of the microporous silica was analyzed by high-resolution transmission electron microscopy (HRTEM). It shows that highly packed and randomly ordered pores are formed throughout the particles (Figure 2). The pore size was estimated to be around 4 Å. XRD analyses show only a broad halo of amorphous silica at 2θ of ca. 23° (not shown), and no diffraction corresponding to long-range ordering suggesting the formation of disordered pore structure. The disordered array of the micropores in this case is a feature of gelatin, which is different from that of the frequently used templates, such as surfactant or polymer where the self-assembly of the template leads to the formation of a well-ordered, generally mesoporous, pore structures in the final material. In the case of aqueous gelatin solutions, it is known that the dissolved gelatin molecules are in a conformationally disordered sol state.[10] The hydrolyzed or partly hydrolyzed Si precursors are bound to the gelatin molecule via hydrogen bonding and covalent bonding with the amino acid hydroxyproline,[9] which leads to gelling of the solution. The removal of the gelatin from the silica during calcination indicates that the pores are continuous. Significant variation between the samples Gel.1 and Gel.4 could not be observed during TEM analysis although the template concentrate and the BET surface area are quite different. Such fine pore structure made differentiation difficult during the microscopy analysis.

Formic acid was found to be necessary in producing the porous silica. Only a small amount of gelatin (≈5%) can be dissolved in water at room temperature when formic acid was not added. This low gelatin concentration was not sufficient to act as a template, resulting in nonporous samples after calcination. With the addition of formic acid, however, the solubility of gelatin is greatly improved, and thus produces the porous materials. Investigating changes in the formic acid concentration (from 0.3 to 1.5 g) had no effect on the resulting porous materials, i.e. the same BET surface areas as well as pore volumes were obtained. This result, together with the fact that nonporous silica was obtained when there was not any gelatin present in the reaction mixture, confirmed that formic acid only assisted by solubilizing the gelatin without itself acting as a template during the formation of the porous material.

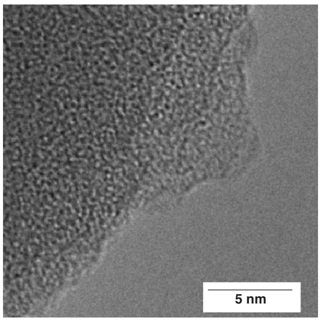

Figure 2. Transmission electron micrographs of the calcined samples with 0.4-g gelatin being added. The images were obtained with a Philips CM200FEG equipped with a Gatan Imaging Filter GIF100.

In conclusion, gelatin, a low-cost biopolymer was successfully used as a porogen for the formation of microporous silica materials. The resulting BET surface areas and pore volumes were found to be proportional to the gelatin concentration. A study of the effect of a number of cosolvents on the porosity of the final material found that formic acid improved the solubility of gelatin in water and was therefore a necessary additive. This method has the advantages of short reaction times and easy preparation of large batches.

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