Preparation of Mesoporous Silica and Carbon Using Gelatin or Gelatin–Phenol–Formaldehyde Polymer Blend as Template

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Mesoporous silica and carbon with high surface area and large pore size were readily prepared in a dilute silica solution at pH ≈ 4.0–6.0 by using the biodegradable gelatin or gelatin–phenol–formaldehyde polymer blend as template.

Recently, the surfactant-templating method has been extensively performed to prepare various mesoporous silica with high surface area, tunable pore dimension, and desired morphology for the applications in catalysts, adsorbents, and nanocasting.[1–5] In the typical preparation, the cationic, anionic and neutral block-copolymer surfactants of amphiphilic property have widely used as the templates for the well-ordered mesostructures.[6–8] The pore volume and dimension are mainly dependent on the hydrophobic volume of the surfactants. While considering on the green chemistry, the hydrophobic parts of the surfactants degrade slowly under ambient condition.[9] With increasing concern on the environmental and aquatic toxicity from the amphiphilic surfactants, using biodegradable reagents to prepare the mesoporous materials is much attractive. According to silica chemistry,[10] gelatin of water-soluble natural protein, which possesses numerous amide groups (–CO–NH_2), can have a high affinity to strongly interact with silanol groups (Si–OH) on the silicate species via multiple hydrogen bonds. Herein, we used the gelatin as a template to prepare mesoporous silica. In addition, a gelatin–phenol–formaldehyde polymer blend can also be used as a novel template to conveniently prepare the mesoporous silica and carbon.

The typical preparation procedure for the gelatin-templating porous silica is as following: 1.0 g of gelatin was dissolved in 25.0 g of water to form a clear solution. Then, the gelatin solution was poured directly into a silicate stock solution at pH ≈ 4.0–6.0 under stirring, and light-yellow precipitate was generated. To prepare the silicate stock solution, a mixture of 4.0 g of sodium silicate (SiO_2: 27 wt %, Aldrich) and a 25.0 g of water was added into a 250 mL of 0.1 M aqueous H_2SO_4 solution, and then the pH value was adjusted to 4.0–6.0 at 40 °C. After stirring for 30 min, the gelatin–silica gel solution was transferred into an autoclave and hydrothermally treated at 100 °C for 1 day. Filtration, washing with water, drying, and calcination at 550 °C gave the mesoporous silica. In contrast, without adding the gelatin into the silicate solution, the silica condensation is quite slow. A glue-like silica gel was formed after 1–2 day or no precipitation was found.

Figures 1A–1C show the representative TEM images of the gelatin-templated silica samples prepared at different pH values. It is clear that these samples possess the disordered mesostructure, and the mesopore is estimated around few nanometers. In addition, the particle size is ranged from several ten to hundred nanometers, and the average particle size decreases as decreasing the pH value. Analyzing the N_2 adsorption–desorption isotherms of the calcined silica (Figure 1D), one can clearly observe that these mesoporous silica demonstrates type IV isotherms and has steep capillary condensation at P/P_0 around 0.65–0.90. The average pore size calculated by BJH method of the mesoporous silica prepared at pH 4.0, 5.0, and 6.0 are located at 7.6, 9.5, and about 15.6 nm, respectively. The BET surface areas are ranged from 385–280 $m^2\,g^{-1}$ and decrease with the increase of pH value.

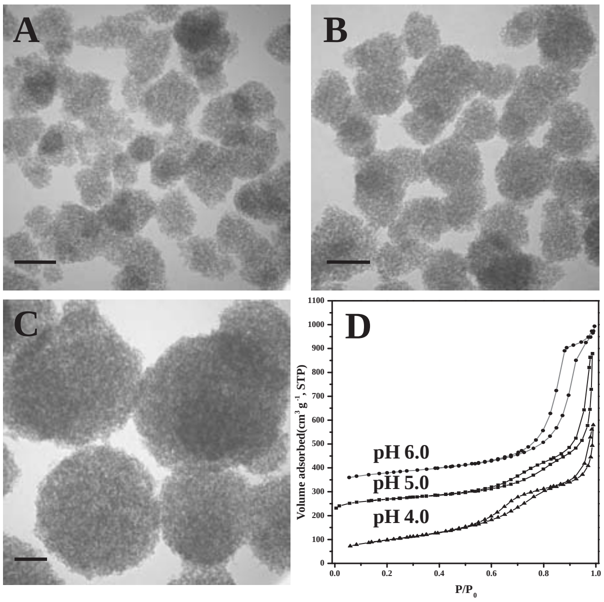

Figure 1. TEM images of the calcined mesoporous silica prepared at different pH values. (A). pH 4.0; (B). pH 5.0; (C). pH 6.0. (D). N_2 adsorption–desorption isotherms of the calcined mesoporous silica prepared at different pH values. Scale bar 100 nm.

According to TGA curves of the gelatin–silica composites prepared at different pH values (Supporting Information Figure S1),[15] 15–23 wt % organic content in the silica–gelatin composite indicates that the gelatin (pH ≈5.0) with lots of amide groups (–CO–NH_2) can bind with the silicate species through multiple hydrogen bonds at pH ≈ 4.0–6.0. The gelatin content decreases with the increase of the pH value. That should be ascribed to the negative-charge density on the silica species which increases as increasing the pH value in the range of 2.0 to 7.0.[10] The negatively charged silica species have slightly repulsion toward the partially negative charged –C=O groups in the gelatin and thus reduce the gelatin content in the silica–gelatin composite. Under high-magnification TEM observation (Supporting Information Figure S2),[15] we found the mesoporous silica nanoparticles consist of silica granules in few nanometer dimension. The mesopores are generated from the interconnection of these silica granules, which differs from the silica-wall nanochannels in the amphiphilic surfactant-templated silicas.[6] As increasing the pH value, the silica condensation rate increases, and hence the size of the granules increases. The larger granules construct the larger mesopores and particle size, but the resulting silica has lower surface area. Consequently, it is the first time to use the natural polymer gelatin as the template of mesoporous silica. In addition, the pore size and particle dimension can be tunable by changing the pH value of the reaction solution. Because of the interconnected 3-D mesostructure of the prepared silica, the mesoporous silica can be used as hard template to prepare mesoporous carbon with high surface area and porosity (Supporting Information Figure S3).[15]

Because the gelatin is one kind of natural polymers with numerous hydrogen-bonding sites, it thus can blend with other polymers via proper intermolecular interactions.[11,12] It is well known that the thermal-setting phenol–formaldehyde polymer (denoted as PF), a carbon source widely used in industry, has many –CH_2OH and phenol groups. Therefore, the gelatin and PF polymer can form a homogenous blend via multiple hydrogen-bonding interactions and used as another template. To prepare the PF–gelatin–silica composite, 1.0 g of gelatin and 1.0 g of phenol–formaldehyde polymer were dissolved in a solution of 20.0 g of ethanol and 25.0 g of water. Combining with the silicate stock solution at pH $\approx$ 5.0, a PF–gelatin–silica composite was generated. The TGA curve of the dried PF–gelatin–silica composite reveals that the organic content is around 50 wt % higher than that in the gelatin–silica ($\approx$15–20 wt %) (Supporting Information Figure S4).[15] The exceed fraction shloud be attributed to the embedded PF polymer. Because the PF–gelatin–silica composite contains the carbonizable PF polymer, the mesoporous carbon can be dierctly obtained by pyrolysis under N_2 atmosphere at 1000 °C and silica removal by 6.0 wt % HF solution. From the TGA curve of the resulted mesoporous carbon, it is clearly seen that the gelatin–PF blend-made carbon possesses highly thermally stable carbon framework (i.e., high decompose temperature), and the silica can be almost completely removed (Supporting Information Figure S5).[15] The TEM image of the resulted mesoporous carbon reveals the disordered mesostructure ($\approx$ few nanometers) (Figure 2A). In parallel, the mesoporous carbon sample exhibits a type-IV N_2 adsorption–desorption isotherm (Figure 2C, curve I). Analyzing the adsorption isotherm, the BET surface area is about 720 $m^2\,g^{-1}$, and pore size is around 13.7 nm. This method to prepare the mesoporous carbon can avoid some time- and energy-consuming processes (i.e., organic-template removal, carbon source impregnation) and included in the typical mesoporous silica-templating way.[13] In future, the effects of pH values, water content, and template/silica ratio on the mesostructure and textural properties of the gelatin–PF-templated carbon will be further explored. Alternatively, the mesoporous silica hollow spheres can be obtained from hydrothermal treatment at 100 °C and calcination of the PF–gelatin–silica composite (Figure 2B). The hollow-sphere silica possesses a tpye IV adsorption isotherm of a capillay condensation at $P/P_0 \approx 0.9$, BET surface area of 206 $m^2\,g^{-1}$ and pore size of 31.5 nm (Figure 2C, curve II). According to these results, the gelatin–PF polymer blend can be used as novel template to prepare the mesoporous carbon or silica in various forms.

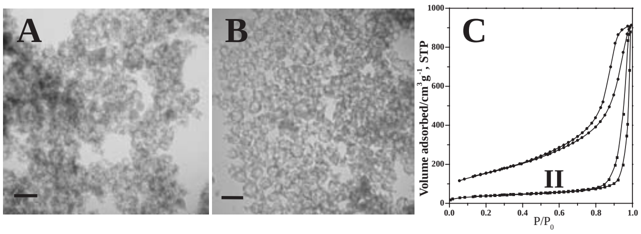

Figure 2. (A) TEM image of mesoporous carbon and silica prepared with PF–gelatin template at pH 5.0. (B) TEM image of the mesoporous silica. (C) N_2 adsorption–desorption isotherms of the mesoporous carbon and silica (Curve I: mesoporous carbon; curve II: mesoporous silica). Scale bar 100 nm.

In conclusion, we employed the enviroment-friendly gelatin and gelatin–PF polymer blend as new templates to prepare the mesoporous silicas and mesoporous carbons in nano- to submicron-meter scale with high surface area and large pore size in a high efficiency. With the fine textural poperties of the porous silica and carbon, expectional appliaction in catalyst, absorption for large molecules, hard-template for metal oxides and electrode materials can be further studied.[14]

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15 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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