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Porous Silver Monolith Formation Using a Hydrogel Template

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We report the formation of a porous silver monolith via a novel one-pot, low-temperature reaction. This is achieved using silica hydrogel as an inorganic sacrificial template to control the resultant pore structure of the metal.

Porous metallic materials have attracted considerable attention because of the large variety of applications they find in catalysis, electrochemistry, and sensing.[2,3] Various methods of preparation have been used to produce these materials where thermal reduction of the metal ions on porous insoluble supports has been used extensively.[2–7] Recently, there have been significant advances in forming porous metals with monolithic structures.[8–11] Primarily, this work focused on the use of organic templates (such as cellulose or dextran) which are mixed with concentrated metal salt solutions.[9,10] The organic template can be removed by annealing the metal template monolith, resulting in a self-supporting macroporous framework of a noble or coinage metal. There are several advantages of metals with 3D porosity such as increased catalytic capabilities due to enhanced transport of reactants and ease of catalyst recovery.

Here, we describe a new approach for the synthesis of porous silver monoliths using a soft sacrificial silica hydrogel template. Cylindrical porous silver monoliths of approximately 1.0 cm diameter were prepared by using a silica template, formed from hydrolysis and condensation of tetramethoxysilane (TMOS).[12–14] The synthesis consists of a one-pot reaction in which the concentrated aqueous metal salt solution was mixed with a preformed silica sol.[1] During the subsequent gelation and aging, the hydrogel progressively darkened indicating the partial in situ reduction of the Ag(I) ions. The Ag/SiO_2–hydrogels were processed further to form either an Ag/SiO_2–xerogel or a porous silver monolith. The Ag/SiO_2–hydrogel was washed with ethanol and dried via slow evaporation to form an Ag/SiO_2–xerogel monolith. During drying the monolith underwent considerable shrinkage, which is consistent with previous published data.[15,16]

In this study, the porous silver monolith was successfully achieved because of high metal to silica molar ratio (0.56:1) used, which is significantly higher than metal loading previously reported.[17,18] The high metal concentration allows for alternative processing of the Ag/SiO_2–hydrogel to remove the silica template, and simultaneously completes the reduction of any residual Ag(I) to Ag. The Ag/SiO_2–hydrogel was washed five times with concentrated sodium borohydride, after each washing the excess solution was removed prior to the addition of fresh reducing agent. The addition of the reducing agent resulted in a rapid evolution of H_2 gas which was accompanied by a considerable darkening in color of the monolith, indicating the further reduction of the metal ions contained within the Ag/SiO_2–hydrogel. The concentrated sodium borohydride simultaneously acts as an etching agent for the removal of the silica template. The etching results from the in situ formation of hydroxide ions resulting from the decomposition of the $NaBH_4$ in the presence of water. This reaction is facilitated by the presence of the nanocrystalline silver which is a catalyst for this reaction. Upon complete reduction of the metal and removal of the silica template the resultant monolith was washed with water to remove residual soluble species and allowed to dry under ambient conditions to result in the formation of a dark grey porous silver monolith. During drying, there was no noticeable shrinkage of the metal monolith compared to the initial Ag/SiO_2–hydrogel, indicating that the resultant monolith is formed from a continuous self-supported metal network. The method is not only simplistic and inexpensive but can also be conducted at room temperature. One of the major advantages of using silica hydrogels as a soft sacrificial template is that reaction conditions can be readily modified to control surface area, density, and porosity of the template.

The bright field TEM image of the Ag/SiO_2-xerogel on an ultrathin carbon grid is shown in Figure 1a. The image clearly shows that there are discrete silver nanoparticles (40–120 nm) embedded in the SiO_2 matrix forming the Ag/SiO_2–xerogel. Figure 1b shows the bright field TEM image of the porous silver monolith. The porous structure is clearly seen to be composed of interconnected silver filaments with widths of approximately 40–100 nm with enclosed pores; additional inspection of the sample showed no visible evidence of the SiO_2 matrix. The continuous pore structure of the monolith is also evident in the SEM image shown in Figure 1c. The size of the metal filaments is consistent with that observed via TEM analysis.

The powder X-ray diffraction analysis of the porous silver monolith showed sharp reflection peaks at θ (Å) $= 19.08$ (2.36), 22.16 (2.04), 32.22 (1.44), 38.67 (1.23), 40.76 (1.18), and 48.96° (1.02) which correspond to d spacings of (111), (200), (220), (311), (222), and (400), respectively. The metallic porous silver was associated with the face-centred cubic cell structure of silver.

The surface areas, pore volumes, and average pore diame-

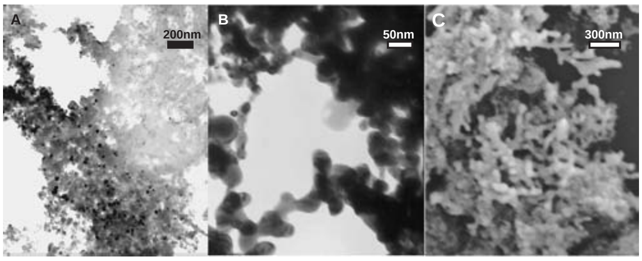

Figure 1. **A**. TEM image of silver nanoparticles embedded inside a porous silica xerogel. **B**. TEM image of a porous silver monolith prepared by the sodium borohydride reduction of the metal and etching of the silica template. **C**. SEM image of porous silver monolith showing silver fibers and continuous pores.

Table 1. Physical properties of the silver containing monoliths

	Surface area/m^2 g^{-1}	Pore volume /cc g^{-1}	Pore radius /Å
Ag/SiO$_2$–xerogel	29.36 ± 6.72	0.05 ± 0.01	29.45 ± 5.21
Ag monolith	17.83 ± 4.54	0.09 ± 0.02	76.37 ± 6.57

ters for both the Ag/SiO$_2$–xerogel and the porous silver monolith were measured using nitrogen adsorption/desorption techniques, see Table 1.[19] The Ag/SiO$_2$–xerogel exhibited a surface area of 29.36 m^2/g, with relatively a narrow pore size distribution and an average pore diameter of 29.45 Å. Brunauer–Emmett–Teller (BET) analysis of the porous Ag monolith indicated that the surface area was 17.83 m^2/g, and the Barrett–Joyner–Halenda (BJH) analysis showed a significant increase in pore volume with an average radius of 76.37 Å. This increase in pore size and decrease in surface area are consistent with the removal of the hydrogel template. The surface area of the porous Ag monolith is far higher than those reported using the dextran template which is likely due to the highly porous nature of the silica template.[9]

In conclusion, we have demonstrated the ability of a silica hydrogel to template the formation of a high surface area porous silver monolith, via a two stage one-pot, low-temperature reaction. The unique ability to control the morphology of silica hydrogels makes them novel, versatile templates for the formation stable porous metal monoliths with controlled density and surface area. Future work will optimize the reaction conditions, such as template to metal ratio and gelation conditions to further control the porosity, surface area, and density of the porous metal monolith.

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References and Notes

1 In a typical synthesis, tetramethoxysilane (10 mL, 0.0678 mol) was dissolved in distilled water (4 mL, 0.22 mol) and absolute ethanol (49 mL, 0.84 mol), followed by addition of AgNO$_3$ (3 mL, 12.6 M). The reaction mixture was stirred for 30 min. *tert*-Butylammonium hydroxide (0.59 mL, 0.0022 mol) was then added with vigorous stirring for 5 min to form an opaque sol. This was transferred to vials of 1 cm diameter, and the solutions were allowed to gel for 24 h. Gel formation typically occurred within 30 min to form an AgSiO$_2$–hydrogel. AgSiO$_2$–xerogel: The AgSiO$_2$–hydrogels were soaked in absolute ethanol for 2 days to exchange the water and reaction by-products from the pore of the material. The wet gels were then dried via slow evaporation over a 4 week period, affording the AgSiO$_2$–xerogel as a dark brown monolith. Porous silver monolith: The AgSiO$_2$–hydrogels were washed in concentrated NaBH$_4$ (5 × 5 mL), followed by water (5 × 5 mL), to remove reaction by-products. The wet gels were then dried under ambient conditions, affording the dark-grey porous Ag monolith.

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19 Supporting Information available: XRD pattern of porous silver monolith and adsorption/desorption isotherms for AgSiO$_2$–xerogel and porous Ag monolith.