Soft templating of metallic and metal oxide porous sponges using sacrificial dextran-based composites

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Abstract

High surface area macroporous sponges of silver, gold, copper oxide, and silver/copper oxide or silver/titania composites were prepared by heating metal salt-containing pastes of the polysaccharide, dextran (M_r 70,000), to temperatures between 500 and 900°C. Magnetic sponges were similarly prepared by replacing the metal salt precursor by preformed iron oxide (magnetite) nanoparticles. In each case, expansion of the dextran matrix during thermal degradation gave rise to a foam-like intermediate and associated patterning of a self-supported framework of interconnecting metal/metal oxide rods or filaments that were between 1 and 20 μm in thickness depending on the calcination temperature. The use of dextran as a sacrificial template for the fabrication of metallic sponges for applications in catalysis, separations science and magnetism should have significant benefits over existing technologies as the method is facile, inexpensive, environmentally benign, and amenable to
scale-up and processing.

Keywords: dextran, porous silver, gold, maghemite, metal sponge.

Metals such as silver and gold are important materials for a wide range of important applications in catalysis and electrochemistry (1). Properties such as high surface area and macroscopic architecture (thin films, monoliths etc) are key factors in determining the technological use of these metals as they impact significantly on the physical and chemical aspects of materials functionality. Of particular interest is the fabrication of metal or metal oxide materials with open framework macrostructures that have a combination of high surface area and bulk accessibility. Existing alumina impregnated supports have been used extensively in electronics (2), heat dissipation (3), and bio-filtration (4), although the level of metal loading is limited compared with porous materials prepared from pure catalysts. In this paper we demonstrate that self-supporting silver catalysts with surface areas of *ca.* 0.5 m^2g^{-1} can be routinely prepared using a facile method involving dextran as a framework generating agent. Previous investigations have used soft sacrificial templates such as starch gels and

sponges in association with zeolite nanoparticles to produce porous materials with structural hierarchy (5), but no studies have investigated the formation of metallic sponge-like architectures by this bio-inspired approach. Dextran is a polysaccharide composed of D-glucose with a predominance of alpha-1,6-linkages and differs from polysaccharides such as starch and cellulose in that it is highly soluble in water at room temperature. Thus, problems associated with the low metal loading of insoluble supports are circumvented because the high solubility facilitates homogeneous mixing of concentrated aqueous solutions of metal salts such as $AgNO_3$ with the organic template in the liquid phase prior to deposition of a solid or semi-solid precursor. Moreover, the metal-ion loaded dextran gel is readily shaped and patterned through the use of appropriate molds to produce sponge-like materials with a range of macroscopic morphologies. In addition, the presence of reductive aldehyde groups associated with dextran can be exploited for the *in situ* facile reduction of metal ions, such as Ag(I) and Au(III), and nucleation of monodisperse metallic clusters. Finally, because the method is not dependent on highly stringent conditions, it can be readily extended to the fabrication of sponge-like frameworks of gold, copper oxide, and silver/copper oxide or silver/ titania composites, indicating that a wide range of applications should be possible.

Silver sponges in the form of macroscopic wires, 1 cm^3 cubes or cylindrical monoliths 10 cm in diameter were prepared (Fig.1) (6). Dextran (M_r = 70,000) was dissolved in a concentrated solution of silver nitrate to form a viscous liquid that was poured into a mould prior to solidification, which occurred within 30 minutes at room temperature to form a thick paste containing *ca.* 40 wt% of $AgNO_3$ ($AgNO_3$/dextran = 1 : 1.07 by weight). The paste progressively darkened over this period due to reduction of a proportion of the Ag(I) ions by aldehyde groups present in the polysaccharide. TEM and SEM observations showed the presence of dispersed particles of silver, 50-100nm in size (data not shown). Subsequent heating of the composite to temperatures between 520 and 900°C removed the organic template by thermal degradation and produced an intact silver-white monolith that roughly took the shape of the mould. Alternatively, macroscopic fibres were drawn from the dextran-reagent mixture prior to solidification and then heated. In both cases, SEM and energy dispersive X-ray analysis studies revealed that the calcined materials consisted of an interconnected framework of silver filaments, approximately 4µm in width and composed of rows and rings of fused micron-sized particles that enclosed pores, 1 to 20 µm in size. X-ray diffraction data corresponded to metallic silver.

BET measurements using N_2 desorption indicated that the surface area of the silver sponge materials prepared at 600°C was 0.5 m^2 g^{-1}, and that the surface area progressively decreased as the heating temperature used to prepare the samples was increased. Although the mechanical strength increased significantly at higher heating temperatures, the sponges were sufficiently ductile to allow samples to be cut and shaped as required.

Thermal gravimetric analysis (TGA) showed a marked weight loss for the Ag(I)-loaded dextran composites at 167°C associated with melting and

decomposition of the dextran matrix. In the absence of $AgNO_3$, pure dextran softened at 160 °C to become a viscous liquid at around 170°C that darkened to a fluid at 180°C, followed by decomposition at 200°C to produce a carbon foam. The presence of $AgNO_3$ lowers the dextran decomposition temperature due to the release of oxygen during the thermal transformation of the inorganic salt to silver nitrite followed by reduction to silver metal, which occurred at 160°C. Increasing the temperature above 170°C resulted in minimal additional weight loss (final weight loss, 65%), indicating that near complete conversion of the dextran matrix to carbon dioxide and water was coupled with the decomposition of the inorganic salt.

In situ formation of the dextran foam was critical for the synthesis of intact silver sponges. Foam formation appeared to be associated with trapping of steam and carbon dioxide bubbles in the viscous polysaccharide such that growth and sintering of the silver particles occurred preferentially along the wall structure of the expanded dextran matrix. In this regard, the viscosity of the dextran was of key importance in the templating of high fidelity inorganic replicas. Modifications in the composition of the silver sponges could be readily achieved without affecting the framework architecture. For example, addition of a catalytic promoter to the silver sponge material was accomplished by mixing copper nitrate with the silver nitrate solution prior to mixing with dextran and heating to 800°C for 30 minutes. This resulted in a silver sponge with pores of 2-50 μm and an interconnecting metallic framework that contained discrete copper oxide (CuO)

crystallites, 1-2 μm in diameter. Interestingly, doubling the copper nitrate content resulted in a higher number of copper oxide crystallites rather than an increase in the particle size. In addition, the copper oxide particles could be dissolved with aqueous HCl to form voids in the silver framework, or reduced by treatment with hydrazine solution for several hours, to form orange sponges containing localized disks of copper metal along with copper (I) and (II) oxides.

Changes in the composition and potential functionality of the wall structure were also achieved by addition of preformed nanoparticles to the silver nitrate solution followed by mixing with dextran and heat treatment at 600°C. For example, addition of small quantities of a titania colloidal photocatalyst (anatase particle size, 100nm, 0.15 wt%) resulted in a sponge-like silver/TiO_2 framework of reduced width (1-2μm) (data not shown). Incorporation of the titania nanoparticles disrupted the bonding between the dextran polymer chains and reduced the viscosity of the matrix to give highly expanded metallic foams that were structurally unstable for titania contents exceeding 0.45 wt%.

The above methods were extended to the soft templating of gold sponges and metal oxides with open framework structures. Metallic gold sponges with macropores, 2 to 100 μm in size, were prepared by dissolving dextran in aqueous solutions of gold(III) chloride and heating the air-dried pastes. Thermal decomposition of the Au-dextran matrix occurred at a much higher temperature than with silver nitrate due to the absence of released oxygen from salt decomposition. Heating to 800°C was required

to remove residual carbon and produce intact orange/ brown gold monoliths. The sponges consisted of continuous open frameworks of metallic gold strands that were composed of fused crystallites, 1-2 μm in width.

Similarly, intact sponges of catalytic oxides of copper or iron were prepared either from solution-based precursors or preformed nanoparticles. For example, thermal degradation and reduction of dextran-copper nitrate pastes produced copper oxide sponges. Magnetic iron oxide sponges were fabricated by addition of a colloidal suspension of magnetite (Fe_3O_4) nanoparticles to aqueous solutions of dextran followed by air drying and heating. The intact brown monoliths responded strongly to an applied magnetic field and consisted of a loose framework of curved strands of fused particles, *ca.* 5 μm in size, with pores between 2 and 80 μm across. XRD diffraction showed *d* spacings corresponding to maghemite (γFe_2O_3; JCPDS card 39-1346) indicating that oxidation of magnetite occurred during thermal processing.

In conclusion, our results illustrate the potential application of dextran as a framework-generating agent to produce robust macroporous sponges without the requirement of extraneous support materials. The method exploits several general properties of dextran (high water solubility, viscosity etc), and should be applicable to a wide range of metallic and metal oxide catalytic materials for use in diverse applications.
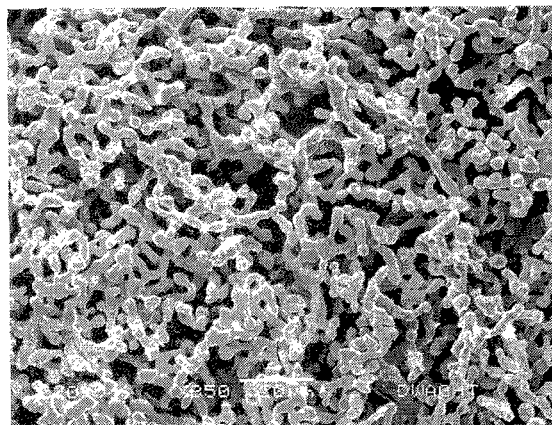

Fig. 1. SEM micrograph of silver sponge obtained from heating dextran/ silver nitrate mixture.

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