

## Synthesis and characterization of metal and metal oxide sponges using Triton X-165 as sacrificial template

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Silver, gold and copper oxide sponges have been synthesized via thermal treatment using Triton X-165 as sacrificial template. Scanning electron microscopy, X-ray diffraction, Thermogravimetric analysis and Brunauer-Emmett-Teller adsorption isotherms techniques are used to characterize the monoliths. Additives like dextran, silica nanoparticles and 1,3,5 trimethylbenzene significantly affect the pore size of the monoliths from 50 nm to 50  $\mu\text{m}$ . The surface area of Au/Triton X-165 / dextran monolith has been determined to be 8.26  $\text{m}^2/\text{g}$ , which is greater than that of any pure metal.

**Keywords:** Composites, Oxides, Sponges, Porous metals

Porous metals have been used extensively in advanced catalysis, microelectronics, photonic crystals, sensors technology, fuel cell electrodes, bio-filtration, drug delivery and heat dissipation<sup>1-4</sup>. The fabrication of nanoporous materials makes use of the template sacrifice route, electrochemical reduction and dealloying processes<sup>5,6</sup>. Based on computer simulation Erlebacher *et al.*<sup>7</sup> have reported nanoporosity to be due to dealloying of Au – Ag alloy. Pores are formed by the aggregation of chemically driven noble atoms into two-dimensional clusters by phase separation.

Zhang and Cooper<sup>8</sup> have reported emulsion templating methods for synthesizing various nanoporous materials. Macropores with channel-like pores in Ca/alginate hydrogels have been reported by Khan *et al.*<sup>9</sup>, using ionotropic gelation followed by freeze drying methods. Triton-X series are versatile non-ionic surfactants recognized for their wetting, detergency, hard metal cleaning, non-toxicity and excellent emulsification properties. Different Triton-X surfactants with varying (ethyleneglycoether)<sub>x</sub> groups are available. A few porous sponges of Ag with Triton X-114 using different additives are also reported by Rao and coworkers<sup>10</sup>. Triton X-165, a member of Triton series with x = 16 (avg), is an

excellent emulsion stabilizer and dispersant used widely in paints and coatings.

Herein, we demonstrate the self-supporting macroporous monoliths of silver, gold and copper oxide using Triton X-165 as surfactant. The study has been extended to investigate the various additives such as dextran, silica nanoparticles, and swelling agent 1, 3, 5 trimethylbenzene (TMB) on the fabrication process.

### Experimental

Silver monoliths were prepared by dissolving 2.4 g  $\text{AgNO}_3$  (54.54 wt %, 7.06 M, BDH) in 2 ml of distilled water (45.45 wt %) and then adding to 2.4 g Triton X-165 (Fluka) at room temperature. The gel was stirred for 10 min to form a paste which gradually became dark in colour. The resulting gel was aged for 48 h at room temperature and then calcined at 600 °C for 2 h at a heating rate of 1 °C/min, followed by cooling at a rate of 1 °C/min to room temperature in a Carbolite EFL furnace.

Ag/Triton X-165/dextran ( $M_w = 2 \times 10^6$ , Fluka), Ag/Triton X-165/ludox (As-40, colloidal silica, 40 wt % suspension in water, Sigma, Aldrich) and Ag/Triton X-165/TMB (Fluka) monoliths were prepared using the above protocol by adding 2.5 g dextran ( $2.6 \times 10^{-4}$  M, 33.33 wt %) in 5 ml water (66.66 wt %), 0.21 g ludox ( $4.03 \times 10^2$  M, 40 wt %) or 3.02 g TMB (7.2 M, 86.5 wt %) separately to Ag/Triton X-165 gel. The dextran and TMB-containing gels were calcined at 600 °C with the above heating and cooling rates, whereas the Ag/Triton X-165/ludox gel was calcined at 800 °C for 1 h with heating and cooling rates of 2 °C/min. The calcined ludox monolith was treated with 30 % HF (Sigma, Aldrich) for 24 h, followed by repeated washing with water to remove silica from monolith.

Au/Triton X-165/dextran monoliths were prepared by dissolving 2 g  $\text{AuCl}_3$  (Aldrich 99.99 %) ( $21.97 \times 10^{-2}$  M, 6.25 wt %) in 30 ml water (93.75 wt %) and adding 5.17 g Triton X-165, followed by a paste of dextran prepared by dissolving 16 g dextran (0.0019 M, 78.94 wt %) in 4 ml water (21.05 wt %), and stirring for 15 min. The resulting yellow gel was aged for 20 days to allow polysaccharide-mediated reduction of the Au(III) complex to metallic gold. The resulting gel was calcined at 800 °C at a heating rate 5 °C/min for 2h, followed by cooling at the rate of 5 °C/min to room temperature.

In the case of CuO monoliths, 4 g copper(II) nitrate pentahemihydrate (3.22 M, 42.86 wt %, Riedel-deHaen) was dissolved in 4 ml water (57.14 wt %) and 2 g Triton X-165 and to this was added a paste of dextran prepared by dissolving 2 g (0.0006M, 50 wt %) in 2 ml water (50 wt %). The resulting mixture was stirred using a magnetic stirrer for 30 min at 50 °C to produce a blue-green gel that was aged for 4 days at room temperature. Then the gel was calcined at 600 °C for 2 h at heating and cooling rate of 5 °/min.

Scanning electron microscopic study was performed on a Jeol 5600 microscope. Except for the CuO monoliths which were coated with Pt and Pd, the other monoliths were coated with carbon and placed on aluminium stubs to get the SEM images.

Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D 8 diffractometer using Cu-K $\alpha$  radiation. Thermogravimetric analysis (TGA) profiles were obtained using a NETZSCH Simultaneous Thermal Analyser (STA 409 EP) using alumina reference crucible.

The Brunauer, Emmitt and Teller (BET) surface areas of monoliths prepared from Au/Triton

X-165/dextran gels were determined at -196 °C using a Quantachrome Autosorb-1C instrument. The corresponding micropore size distribution was determined from the BJH model using the desorption branch isotherm.

## Results and discussion

Figure 1a shows the SEM images of self supporting scaffold of Ag prepared using Triton X-165 with a disordered network of pores varied from 10  $\mu$ m to 50  $\mu$ m. Pore sizes were reduced to a values between 0.5 and 1  $\mu$ m when dextran was added to the Ag/Triton X-165 gel (Fig 1b), while in the case of Ag/Triton X-165/ludox (HF) treatment, there were significantly smaller pores in the range of 0.3-10  $\mu$ m (Fig. 1c). The treated monolith showed the absence of silica nanoparticles, which was confirmed by EDAX spectra (not shown here). Addition of TMB as a swelling agent to Ag/Triton X-165 gels produced slightly bigger pores with size varying from 1-10  $\mu$ m (Fig. 1d). TMB acts as a special swelling agent to enlarge the pore size because it is a nonpolar compound, which

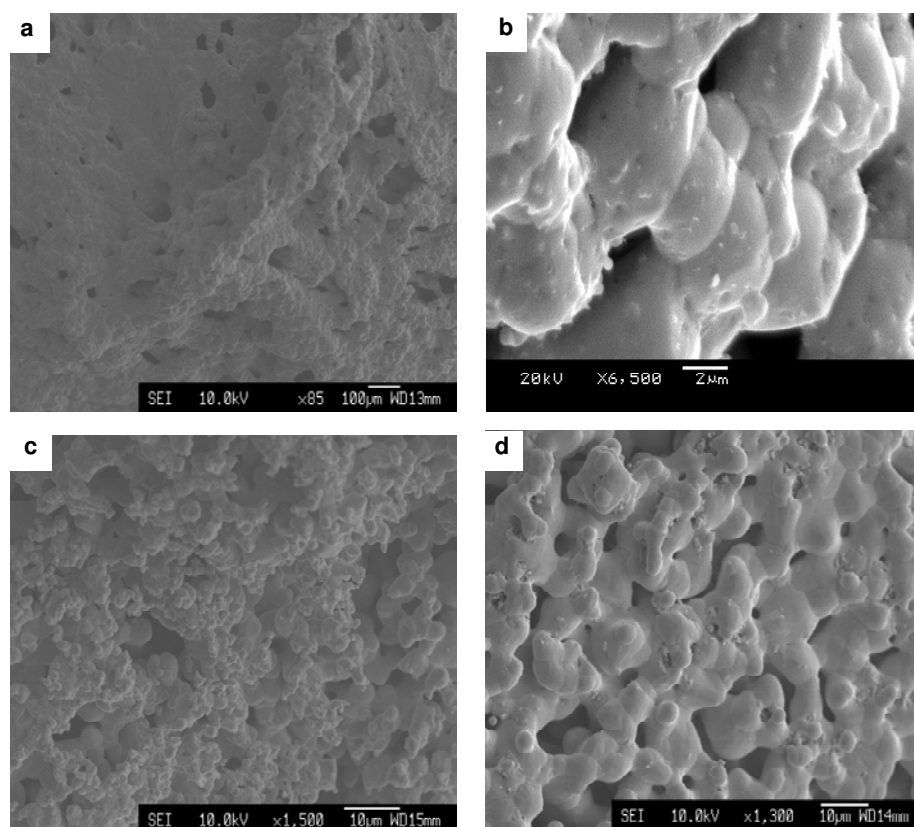


Fig. 1—SEM images of Ag macroporous sponges using Triton X-165 gel as sacrificial templates. [Monoliths prepared by calcination of (a) Ag/Triton X-165 gel, pore size 10-50  $\mu$ m, scale bar 100  $\mu$ m; (b) Ag/Triton X-165/dextran gel, pore size 0.5-1  $\mu$ m, monolith showed Ag nanoparticles varying from 50-200 nm, scale bar 2  $\mu$ m; (c) Ag/Triton X-165 /ludox gel after HF treatment, pore size 300 nm – 10  $\mu$ m, scale bar = 10  $\mu$ m; (d) Ag/Triton X-165/TMB gel, pore size 5 – 10  $\mu$ m, scale bar 10  $\mu$ m].

solubilises inside the surfactant assembly, thus increasing the volume of the resulting composite.

Similar experiments using Triton X-165 gels containing  $\text{AuCl}_3$  or copper(II) nitrate produced intact macroporous monoliths, which were yellow or black respectively. SEM studies indicated that the pore sizes varied from 1 – 5  $\mu\text{m}$  in the case of Au/Triton X-165/dextran monoliths (Fig. 2a). Significantly smaller pore sizes varying from 50 – 500 nm were observed in the case of CuO/Triton X-165/dextran monoliths (Fig. 2b).

XRD studies of the silver monoliths showed reflections pertaining to metallic silver with a face-centred cubic structure (Fig. 3a-d). In the case of CuO or Au monoliths, tenorite with base centred or face centred cubic unit cell structures were formed (Fig. 3 c&d).

Ag monoliths showed reflections at  $d$  spacings of 2.36, 2.04, 1.44, 1.23, 1.18, 1.02, 0.94, and 0.91  $\text{\AA}$  which correspond to (111), (200), (220), (311), (222) (400), (331) and (420) lattice planes of a face centred cubic unit cell (JCPDS No. 4.783). CuO monoliths showed reflections at 2.74, 2.51, 2.31, 1.95, 1.86,

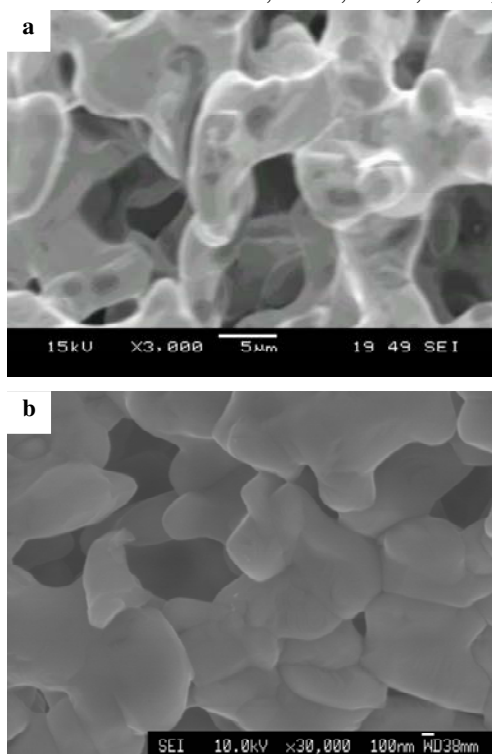


Fig. 2—SEM micrographs of Au and CuO monoliths using Triton X-165 as sacrificial template. [(a) Au/Triton X-165/dextran gel prepared by calcination of Au/Triton X-165/dextran, pore size 1–4  $\mu\text{m}$ , scale bar 5  $\mu\text{m}$ ; (b) CuO monolith prepared by calcination of CuO/Triton X-165/dextran gel, pore size 50 – 700 nm, scale bar 100 nm].

1.70, 1.57, 1.50, 1.41, 1.40, 1.30, 1.26, 1.19 and 1, 16  $\text{\AA}$  which correspond to (110), (002), (200), (-112), (-202), (020), (202), (-113), (022), (-311), (311), (004), (-204) and (312) of a base centred monoclinic unit cell (tenorite). Au monoliths showed reflections at 2.36, 2.04, 1.44, 1.23 and 1.17  $\text{\AA}$ , corresponding to (111), (200), (220), (311), and (222) lattice planes of a face centred cubic unit cell (original XRD pattern contains all the peaks). Peaks at 3.016, 2.50 and 2.31  $\text{\AA}$  were also observed indicating the presence of crystalline  $\text{AuCl}_3$ . This phase is the starting material, and could be formed by thermally induced reactions, ( $\text{AuCl}_3 = \text{AuCl} + \text{Cl}_2$ , and  $3\text{AuCl} = \text{AuCl}_3 + 2 \text{Au}$ ) during monolith preparation. In the case of Ag and Au profiles, broad bands from sample holder polymethyl methacrylate (PMMA) were observed at 2.20, 2.98 and 5.15  $\text{\AA}$  along with the monoliths. Small angle X-ray pattern of CuO composed of distinct diffraction lines appearing at low angle  $< 5.3^\circ$ .

Thermogravimetric analysis of Ag/Triton X-165 hydrogels with and without additives showed that about 3-5 % of mass was decomposed as a result of removal of moisture upto 175  $^\circ\text{C}$ . Then, about 15 – 18 % mass was removed between 170 – 220  $^\circ\text{C}$  due to the presence of excess Triton X-165 molecules. Thereafter, silver nitrate, Triton X-165, dextran and TMB (as the case may be) were removed with considerable mass loss varying from 35-50 %.  $\text{AgNO}_3$

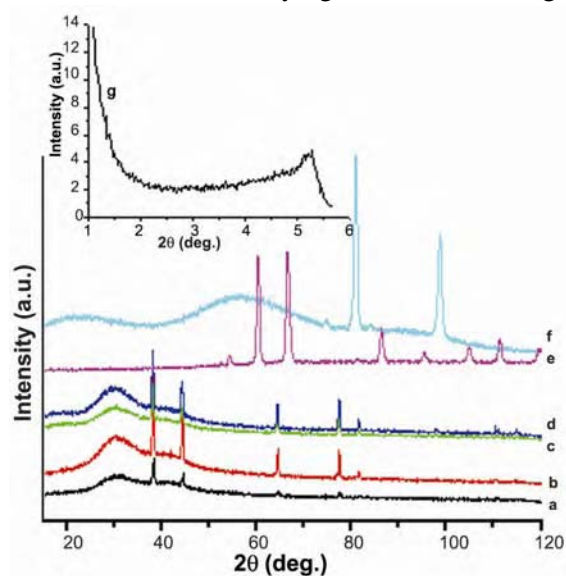


Fig. 3—X-ray diffraction patterns of silver, gold and copper oxide monolith with Triton X-165 as template. [(a) Ag/Triton X-165; (b) Ag/Triton X-165/dextran; (c) Ag/Triton X-165/ludox (after HF treatment); (d) Ag/Triton X-165/TMB; (e) CuO/Triton X-165/dextran monolith; (f) Au/Triton X-165/dextran monolith; (g) Inset: shows the small angle X-ray pattern of CuO composed of distinct diffraction lines appearing at low angle  $< 5.3^\circ$ .

decomposed to give Ag metal with release of considerable oxygen<sup>11</sup> that promotes the combustion of Triton X-165 and also dextran or TMB in the monoliths. Carbon was decomposed beyond 350 °C with about 5 % mass loss by using O<sub>2</sub> released due to thermolysis of AgNO<sub>3</sub>. In the case of Ag/Triton X-165/ludox monoliths, the major mass loss about 50 % was observed between 200 – 360 °C as a result of the decomposition of AgNO<sub>3</sub> and Triton X-165 from gels. Finally, 25 % Ag remained in the monolith.

In the case of Au/Triton X-165/dextran monoliths, about 7 % mass loss was observed initially up to 150 °C due to the removal of moisture and then excess Triton X-165 was decomposed in the temperature range between 150–200 °C with mass loss of 10 %. Triton X-165 from Au monolith along with dextran was removed at 200–375 °C. In this temperature range, AuCl<sub>3</sub> decomposed to give AuCl + Cl<sub>2</sub> and thereafter AuCl decomposed to give Au at 420 °C. Here, oxygen was not released during the decomposition of AuCl<sub>3</sub> and therefore, dextran and other additives followed by carbon decomposed at much higher temperatures. In the case of CuO monoliths, 3 % mass was removed due to the removal of moisture in the monolith, while excess Triton X-165 was decomposed at 120 – 150 °C with mass loss of 20 %. From 150 – 320 °C, copper nitrate decomposed to give CuO with release of NO<sub>2</sub> and O<sub>2</sub>. The O<sub>2</sub> also promotes the combustion of dextran and

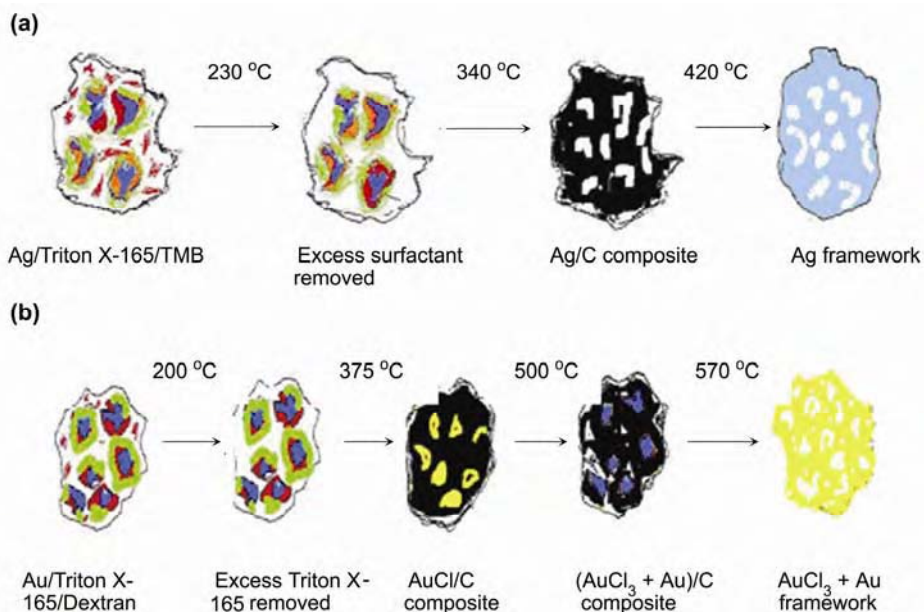
carbon at lower temperature with mass loss of 70 %. About 10 % of CuO of the original mass was retained in the scaffold.

The surface area Au/Triton X-165/dextran monolith was determined to be 8.26 m<sup>2</sup>/g, which is consistent with the pore size observed by SEM.

Scheme 1 shows the morphological transformations of Ag/Triton X-165/TMB and Au/Triton X-165/dextran monoliths during their formation. In the case of Au, the AuCl<sub>3</sub> first decomposed to AuCl at 170 °C which was later converted to AuCl<sub>3</sub> and Au at 420 °C.

The study shows that the porous monoliths of Ag, Au and CuO can easily be prepared by the thermal decomposition of Triton X-165 hydrogels containing appropriate reaction precursors. The size of the pores can be increased by adding appropriate swelling agents to get the appropriate pore size. This property is useful to encapsulate the drugs, cells and other nanoparticles in a porous matrix. Addition of silica nanoparticles to the gels reduces the pore size significantly suggesting that other types of nanoparticles may be used to design the sponge architecture. The size of the pores depends on the reaction temperature, nature of swelling agents, and composition of the hydrogels.

It is clear from the above study that porous monoliths of metals and metal oxides can readily be synthesized by a simple method using simple surfactants like Triton X-165 which is inexpensive,



Morphological changes of Ag and Au during calcination. [(a) Ag/Triton X-165/TMB monoliths: red, Triton X-165; green, TMB (Ag monoliths); black, carbon; blue, Ag ions; sky blue, Ag framework. (b) Au/Triton X-165/dextran monoliths: blue, Au ions; red or green, Triton X-165 or dextran; light yellow, AuCl; black, carbon; dark yellow, AuCl<sub>3</sub> + Au framework].

Scheme 1

and environmentally benign. The surface area determined in case of Au/Triton X-165/dextran is also greater than that of any pure metal<sup>10</sup>.

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