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Template synthesis of porous gold microspheres

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Received 17th April 2003, Accepted 22nd May 2003
First published as an Advance Article on the web 30th May 2003

Macroporous gold spheres with a diameter of ~9 μm have been formed by a facile method, employing porous organic bead templates and preformed gold nanoparticles.

The ability to synthesize porous materials possessing tailored properties, such as porosity, mechanical stability or a predetermined specific surface area, is a topic of intense research activity in modern materials science. One approach for the preparation of such materials with controlled characteristics is template synthesis. Organic structures have been utilized for the formation of inorganic porous materials using this method, where the organic substance is removed by either calcination or dissolution in certain solvents. The employment of template synthesis techniques has been demonstrated for the preparation of a range of inorganic materials, especially single and mixed metal oxides.[1,2] Comparatively, these examples far outnumber demonstrations of the use of template synthesis for the production of porous metal structures. Porous metals have potential application in the areas of advanced catalysis, electronics, optics, separations and sensors. Metals have been templated using polycarbonate membranes,[3] colloidal crystals,[4] lyotropic liquid crystalline phases of surfactants,[5] and echinoid skeletal structures[6] for the formation of films, membranes or powders of porous metal with controlled pore sizes and structures.

The templating of individual entities such as spheriodal architectures has not received much attention due to difficulty in maintaining, and hence obtaining, separate spherical particles (that is, preventing agglomeration occurring during the procedure). Two recent approaches to fabricate porous metal colloids are the sonication of a toluene solution containing a dispersion of gold nanoparticle-filled aqueous droplets, to form discrete 0.5 μm spheres.[7] The other approach uses nickel hydroxide-doped poly(vinyl alcohol) films, which are thermally decomposed to form nickel nanoparticle agglomerates.[8] The advantages of the templating approach using preformed nanoparticles for the formation of porous spheres are that the process is facile, it is applicable to a range of nanoparticle materials, plus there is an ability to (i) vary the sphere diameter while maintaining monodispersity and (ii) control the pore size, both of these properties being dependent on the initial template.

In this paper, the template synthesis of porous gold spheres of about 9 μm diameter is described. Polystyrene cross-linked with divinyl benzene beads (Source 15ETH beads, hydroxyl functionality, average diameter of dry beads is 11.5 μm) purchased from Amersham Biosciences (Uppsala, Sweden), were employed as the organic template material. These beads have only recently been used for the formation of porous silica and titania spheres using a sol–gel procedure.[9] Here, the templating approach applied was that of preformed nanoparticle impregnation utilizing two different gold sols prepared as follows: The first was synthesised according to Turkevich *et al.*,[10] where tetrachloroauric acid was reduced with trisodium citrate dihydrate in an aqueous solution at 100 °C. The colloidal sol obtained by this method (hereafter referred to as citrate gold) had a concentration of 0.1 g L^{-1} and an average gold particle size of 7 ± 2 nm. The second sol was prepared using a phase transfer method,[11] which resulted in a more concentrated gold sol (2 g L^{-1}). The obtained gold sol (referred to as DMAP gold, as 4-dimethyl-aminopyridine, DMAP, used during phase transfer) had an average particle size of 6 ± 2 nm.[12]

To prepare the porous gold spheres the dried organic template was soaked in the corresponding gold sol for 4 days at room temperature. Excess gold material was removed by rinsing before the composite gold/polymer beads were dried at 60 °C for 1 h and then calcined at 280 °C (ramp rate of 3 °C min^{-1}) under an oxygen atmosphere until removal of the organic material (75 h). Thermogravimetric analysis of the resulting metal spheres (Netzsch TG 209 apparatus) confirmed removal of the template.

Fig. 1 shows scanning electron microscopy (SEM, Gemini Leo 1550) images of the initial template beads (Fig. 1a) and the resulting gold spheres (Fig. 1b–d). A comparison of the initial polystyrene beads with the gold spheres prepared from the citrate gold sol (Fig. 1b) indicates the absence of the inherent porous structure in the latter. The surface of the final gold material obtained using the citrate sol is dense, quite irregular in topology, with only the occasional macropore. Transmission electron microscopy (TEM, Zeiss EM 912 Omega) analysis of non-calcined polymer beads impregnated with citrate gold (not shown) confirms the uniform distribution of gold particles throughout the bead volume, however, during calcination and removal of the template material, collapse of the initial porous scaffold occurs forming gold spheres with a diameter one order of magnitude less than that of the organic beads. Thus the use of

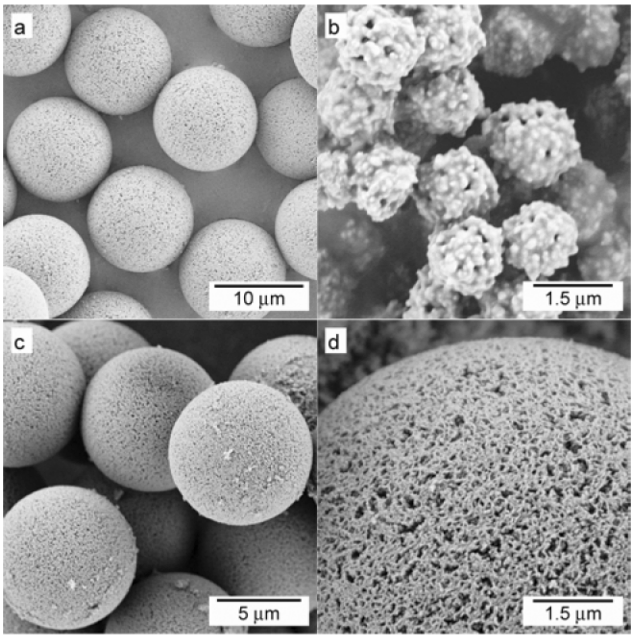

Fig. 1 SEM images of (a) the initial polystyrene beads; (b) the gold spheres prepared from the citrate gold sol; (c) the porous gold spheres prepared from the DMAP gold sol; and (d) the porous surface of a gold sphere prepared by using the DMAP gold sol.

DOI: 10.1039/b304259f

citrate gold sol during the templating process did not lead to successful templating, as the template morphology was lost during removal of the organic bead.

In contrast, the use of the concentrated DMAP gold sol resulted in porous, non-aggregated gold spheres (Fig. 1c and d), structurally similar to the initial template. During calcination of the DMAP gold sample, an approximate 25% reduction of sphere diameter was observed, compared with the initial template. This shrinkage is similar to that observed during template synthesis of metal oxide structures from either metallorganic precursor or preformed nanoparticles using polymer gel templates.[2] Velev *et al.*[13] observed negligible shrinkage using a colloidal crystal of polystyrene beads and preformed gold nanoparticles, whereas a colloidal crystal of PMMA and precipitation of metal acetate precursors using oxalic acid resulted in shrinkage between 19 and 58% depending on the metal and the calcination conditions.[4] The degree of shrinkage is dependent on the overall coverage and stability of the inorganic material, and also changes if the inorganic nanoparticle size is modified during the heating procedure.

The proposed mechanism for the formation of the templated spherical structures using preformed gold nanoparticles is as follows: While soaking the organic beads in the gold sol the nanoparticles enter the pores of the template where particle adsorption to the polymer surface occurs. The nanoparticles in the solution filling the pores deposit on the polymer walls during drying, resulting in a coating of the template. Long-term soaking of gold-loaded polymer beads in pure water led to desorption of the gold particles, as they were found to leach into the solution. The successful formation of porous gold spheres using the templating technique from the DMAP gold sol compared with the considerably smaller, collapsed and dense structures obtained by using the citrate gold sol can be explained by the different surface properties of the gold particles (increased loadings of gold nanoparticles have been achieved with DMAP stabilized gold)[12] and the substantial difference in concentration of these two sols (2.0 g L^{-1} and 0.1 g L^{-1}, respectively). For the DMAP gold the amount of material deposited inside the polymer beads is sufficient to maintain the porous structure during and after calcination, while the less concentrated citrate gold sol does not form a continuous layer on the polymer wall after impregnation, and hence collapse occurs.

As shown in the TEM image of an ultrathin section of the polymer template loaded with DMAP gold before calcination (Fig. 2a), the preformed nanoparticles impregnate the organic beads and coat the organic surfaces. After template removal the interior porosity remains (Fig. 2b and c), while the size of pores is reduced due to shrinkage. The diameter of the remaining pores for the DMAP gold spheres lies between 50 and 80 nm. Additionally, the size of the gold particles increases; partial melting and interconnection between particles can be observed for the samples calcined at 280 °C. Using a higher temperature for template removal increases the melting, and consequently decreases the specific surface area of the obtained gold spheres: The specific surface area for the gold spheres calcined at 280 °C is 55 m^2 g^{-1} whereas a calcination temperature of 350 °C gives a material with a specific surface area of 36 m^2 g^{-1}. A further increase in the calcination temperature to 500 °C led to the formation of a monolithic structure with only traces of the initial template morphology.

We have demonstrated the formation of macroporous gold spheres by bead template synthesis. Variation in the initial template bead diameter and the ability to synthesize highly concentrated metal sols of, for example, silver, platinum, and palladium[14] gives this method potential to form a variety of porous metal spheres with a range of diameters. This general procedure is expected to be applicable to a variety of different nanoparticles, for example, metal oxides, for the formation of porous inorganic spheres with controlled diameter.

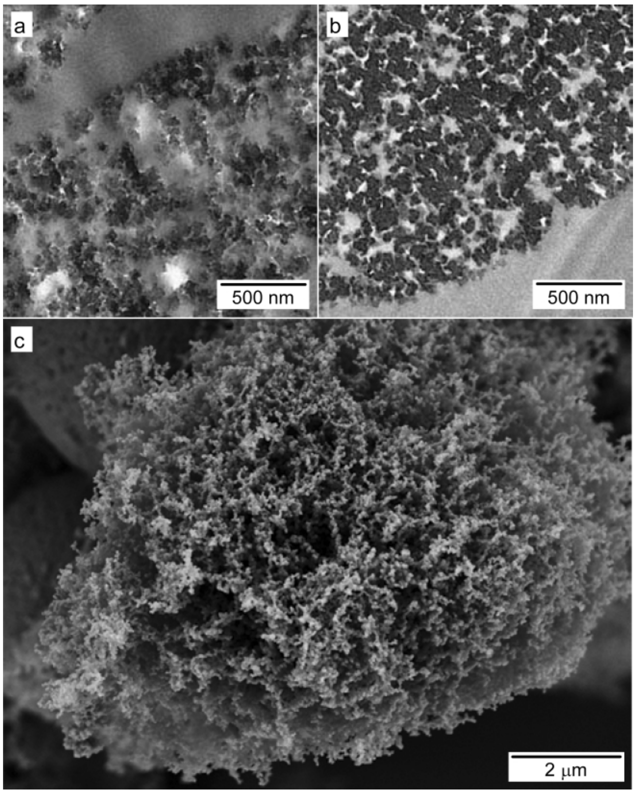

Fig. 2 TEM images of (a) the polymer template impregnated with the DMAP gold sol before calcination, (b) the final gold sphere after calcination at 280 °C, and (c) an SEM image showing the inner porous structure of the final gold sphere prepared using the DMAP gold sol.

The Max Planck Society and The University of Melbourne's MRGS are acknowledged for financial support. DGS acknowledges the German Academic Exchange Service (DAAD) for a one-year research scholarship (No. A/01/10817). Markus Antonietti is thanked for helpful discussions, Rona Pitschke is thanked for ultramicrotoming the samples and for TEM analysis. We are grateful to Frank Caruso and Andrei S. Susha for supplying the DMAP gold.

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