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Silver nanowires: inclusion in and extrusion from a mesoporous template

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Silver nanowires both included in and extruded from a purely siliceous mesoporous support have been produced from silver ion containing precursors prepared through dry salt occlusion.

Ordered mesoporous inorganic solids have exhibited great capability for carrying the unique chemistry of crystalline zeolites to a larger pore regime. Inevitably, this has focused a lot of research work onto their application as chemical reactors, *via* the inclusion of catalytically active species in the pores.[1] Another area of contemporary interest has been the incorporation of transition elements such as Pd, Pt, Au and Ag to give continuous metal 'nanowires' within the channels.[2–5] This is one of a number of emerging synthetic routes for nanowire formation that include growth from templating solutions,[6] inside carbon nanotubes,[7] within porous alumina[8] and extrusion from zeolite crystals.[9] Among other potentially useful properties of metal nanowires it is envisaged that, through the optimization of synthetic procedures, a bundle of mesoscopically ordered, conducting, nanoscale wires, might be produced within a mesoporous support. The construction of such three-dimensional arrangements of reduced-dimensionality sub-units is one current approach proposed for overcoming many of the difficulties associated with the practical application of quasi-one-dimensional electronic systems.[10] Two common procedures are reported for achieving pore filling; the first involves solution impregnation with a metal salt, typically followed by a reduction process,[11] while the second uses chemical vapour deposition techniques.[12] This paper reports a third alternative: the adaptation of the phenomenon of salt occlusion, utilized in zeolites,[9,13–15] to incorporate silver within mesoporous materials.

The material chosen for this study was SBA-15 due to its arrangement of non-intersecting, one-dimensional channels. The siliceous form was prepared according to standard literature procedures and calcined at 500 °C.[16] Solid silver nitrate was manually ground together with a sample of calcined mesoporous material. The resulting homogenous powder was transferred to an alumina boat and heated, in darkness, at 250 °C for 12 h (heating ramp of 1 °C min^{-1}). To remove excess silver nitrate, the samples were quickly washed with a minimum amount of de-ionized water (*ca.* 10 cm^3), air-dried and finally heated at 300 °C for 2 h. Powder X-ray diffraction (XRD) was performed on a Siemens D5000 using CuK_α radiation (λ = 1.54056 Å), while transmission electron microscopy (TEM) analysis was carried out using a Philips CM20 operating at 200 kV, with samples mounted on a copper grid coated with carbon film.

Powder XRD (Fig. 1) was used to follow the disappearance of the silver nitrate and the emergence of silver as the reaction progressed. Before reaction, the pattern was that of commercially available orthorhombic silver nitrate (Fig. 1(a)).[17] However, following heating the pattern had changed, with peaks reduced in intensity and now corresponding to the rhombohedral phase of silver nitrate, formed during cooling after fusion (Fig. 1(b)).[18] The XRD of the samples following washing showed the first signs of elemental silver formation (Fig. 1(c)) and subsequent to heating at 300 °C a more intense pattern was observed (Fig. 1(d)).

Examination of the samples by TEM showed that the pore structure of the SBA-15 was robust enough to survive the occlusion process and so offers a good matrix in which to support an array of nanowires. Following reaction, the SBA-15 crystallites had a range of additional features: in some areas there was evidence of pore filling, either as continuous wires or individual nanoparticles, while at the surface there were larger nanoparticles and occasional nano-rods, -wires and -extrusions (Fig. 2 and 3).

The continuous filling of pores, while only arising in isolated regions of SBA-15 crystallites, usually occurred as clusters of parallel wires, with lengths in the order of hundreds of nanometres. The uneven filling of the crystallites cannot yet be unequivocally explained but may be attributed to one or a combination of the following: a lack of salt to fill all the channel space, removal of included material during the washing step, or the blocking of pores through structural degradation or incomplete calcination. The bunching together of the continuous nanowires, observed in some cases, was not unexpected and has been noted in previous attempts to fill the pores of SBA-15 with noble metals.[2–4] Such results provided physical evidence for the presence of a random microporous network linking the mesoporous channels of SBA-15: upon dissolution of the silica framework, the wires formed within the pores of SBA-15 remain clustered together, whereas they would have been expected to separate into individual filaments.[2–4,19]

Nanoparticles observed in the TEM varied in size from having dimensions equal to those of the pores (30 to 70 Å), to being upwards of ten times that scale. Particles with diameters comparable to the channel widths were generally ordered along

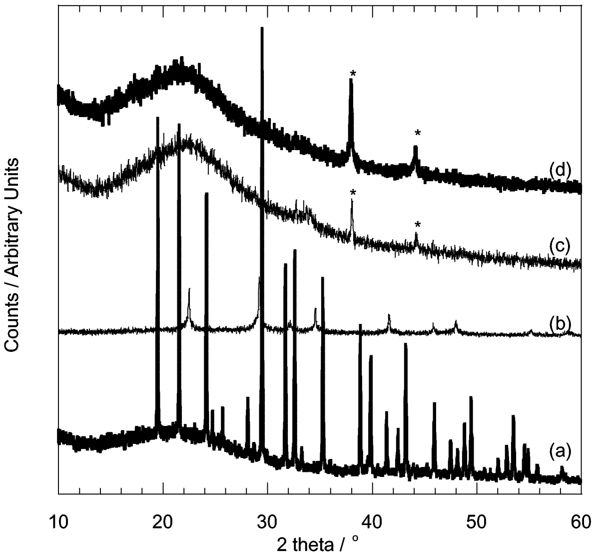

Fig. 1 Powder XRD patterns of the reaction between SBA-15 and $AgNO_3$: (a) orthorhombic $AgNO_3$ present before heating; (b) rhombohedral $AgNO_3$ phase formed after heating at 250 °C; (c) silver metal appears after washing; (d) the silver peaks (asterisked) increase in intensity after washing and heating at 300 °C.

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the direction of the pores, and are presumed to lie within the mesoporous material where their dimensions and organization are confined by the framework structure. In the case of the large particles they must either lie on the exterior of the crystallites or have disrupted the mesoporous structure within the crystallite.

In contrast to the intrapore wires and nanoparticles, outgrowths from the SBA-15 crystallites (Fig. 2) were only formed under the influence of the electron beam and were not present before the samples entered the microscope. This is known from the direct observation of their growth upon increasing electron beam intensity. The morphology of the extrusions varied widely, from being straight with uniform diameter, to curly with variable widths and lengths. From analysis of microscopy images this property has been directly related to their crystal structure, with straight protrusions identified as single crystal, while the more irregular forms are polycrystalline. Similar results have recently been reported for silver loaded, silver exchanged zeolites,[9,20] where the production of nanowires is proposed to result from the reduction and subsequent migration of silver cations under the influence of the electron beam. In the zeolite case, migrating silver accumulates in mesopores formed within zeolite crystals and from here the silver nanowires begin to grow, finally breaching the crystallite surface.

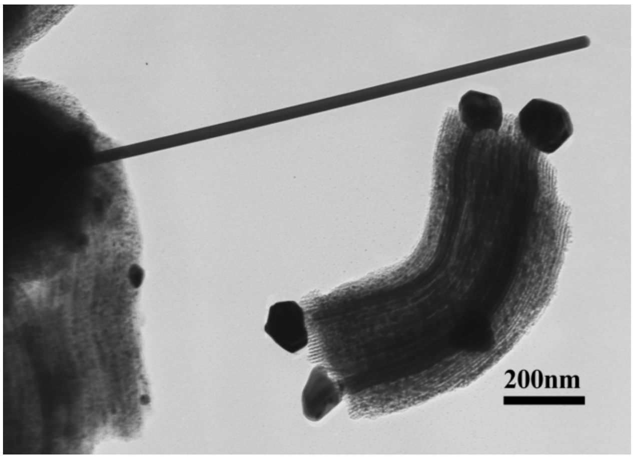

Fig. 2 A cluster of SBA-15 crystallites from which a straight metal nanowire has been extruded under the influence of the electron beam. The lone crystallite, in addition to its four large surface particles, shows pores filled both continuously and by individual nanoparticles.

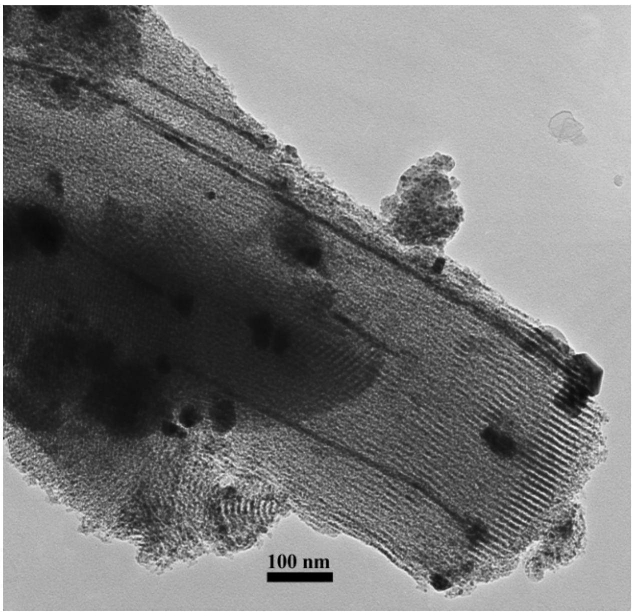

Fig. 3 An SBA-15 crystallite in which some channels are filled by continuous silver metal filaments.

In summary, the phenomenon of salt occlusion offers a potential new direction for the incorporation of metals into the channels of mesoporous supports. The procedure represents a simple, economical and quick alternative to the solution and chemical vapour methods previously reported. At present, results from all three techniques are comparable, but with further refinement, the prospects for using salt occlusion to produce a mesoscopically ordered bundle of conducting nanowires appear good. Uniquely, this technique has also led to the production of metallic extrusions from the mesoporous support in addition to intracrystalline wires. Obviously much greater control over the preparation of metal species within mesoporous hosts is required. Nevertheless, this result allows us to regard, perhaps for the first time, the idea of being able to link together crystallites, in which nanoscale structures have been confined, as genuinely plausible.

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