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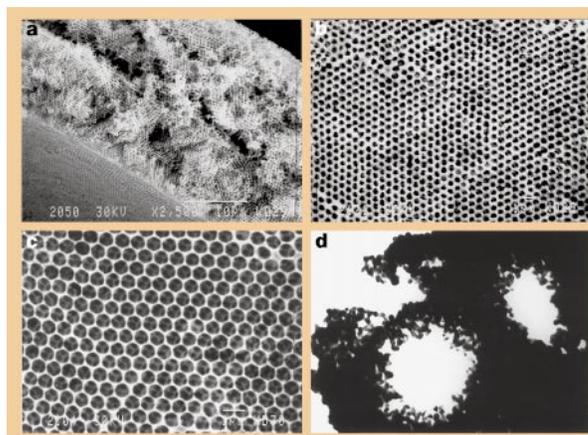
Materials

A class of porous metallic nanostructures

Colloidal crystals are ordered arrays of particles in the nanometre-to-micrometre size range. Useful microstructured materials can be created by replicating colloidal crystals in a durable matrix that preserves their key feature of long-range periodic structure¹. For example, colloidal crystals have been used to fabricate structures from inorganic oxides^{1–5}, polymers^{6,7}, diamond and glassy carbon⁸, and semiconductor quantum dots⁹, and some structures have photonic properties^{4,8,9} or are patterned on different hierarchical length scales⁵. By using colloidal crystals as templates, we have synthesized a new class of metallic materials with long-range nanoscale ordering and hierarchical porosity.

We formed porous metallic nanostructures by using colloidal crystal templates from monodisperse, negatively charged polystyrene latex microspheres 300 nm to 1 µm across. The close-packed crystals were assembled by filtration¹³ through a smooth polycarbonate membrane with pores (50 nm) that retained the latex and the gold particles but allowed a high flux of water. The diluted latex particles were slowly deposited into densely packed layers about 35 µm thick. Colloidal gold particles 15–25 nm across were then slowly deposited in the

Figure 2 Electron micrographs of the structure of porous gold obtained with 630-nm latex templates. **a**, Side view of the flake, showing long-ranged ordered arrays of pores, both on the surface and through the flake. **b**, A typical area on the surface of a calcined sample, showing fusion, domain boundaries and crystal defects. **c**, A sample obtained by latex dissolution. **d**, Transmission electron micrograph at the edge of a flake obtained by dissolution, showing the mesoporous particulate gold structure.



interstices of the latex crystals by filtration, forming a mesoporous structure around the latex microspheres. This porosity allowed the solvent to flow through the deposit until the pores were filled by the gold colloid. Because of diffraction, the dried latex–gold flakes generate strongly coloured reflections that are much brighter than those of the original latex templates alone (Fig. 1a, b).

The three different procedures we used to remove the latex beads from within the composite yielded porous metal with different properties. Calcination for 30 min at 300 °C yielded flakes with the colour of metallic gold, but with multicoloured domains on the surface (Fig. 1c). Removing the latex templates at room temperature by oxidation with acid or by dissolving in trichloromethane gave brown flakes with brightly coloured reflections. All the samples were conductive, with resistance higher than, but of the same order of magnitude as, that of metallic gold foil.

Scanning and transmission electron microscopy revealed that the materials have a three-dimensional structure of ordered pores throughout the flakes (Fig. 2a). As in previous observations¹, monocrystalline hexagonal domains of up to a thousand identical pores are predominant on the surface, usually corresponding to three-dimensional, randomly stacked, hexagonal close-packed planes and face-centred cubic packing (Fig. 2b,c), although square arrays are occasionally seen. The lattice dimensions correspond to those of the original latex crystals, indicating that there was negligible

shrinkage of the metallic structure, in contrast to that seen for inorganic oxides^{1–4}.

The materials formed by calcination are macroporous, with a smooth, fused gold structure (Fig. 2b). In contrast, the solvent dissolution method preserves the original particulate gold structure around the large pores (Fig. 2d). In this mesoporous–macroporous material, the size of the small pores and the overall surface area are determined by the size of the gold particles. Materials with such controlled hierarchical porosity may be particularly suitable for catalytic applications, as they provide a combination of efficient transport and high surface area.

The lace-like structure of the flakes (Fig. 2c) is an almost exact replica of some three-dimensional wire-mesh photonic crystals¹⁰, but reduced by a factor of 20,000 to the sub-micrometre scale. The materials may therefore have photonic properties in reflectance mode in the visible-light region. In principle, the method can be improved to allow the formation of layers only a few pores thick, with interesting transmission properties. The simple ‘wet’ method can also be adapted to create materials from other metals, alternating layers of metals, or composite metallic–dielectric structures. Such new materials could be used in advanced catalysis or electro-optical devices, as well as in reflective, conductive or energy-collecting metallic coatings.

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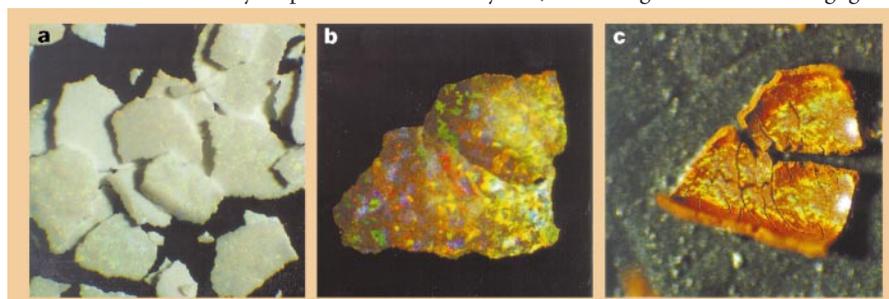


Figure 1 Optical micrographs of the materials formed with 630-nm latex at different stages of synthesis, in reflected polychromatic illumination. **a**, Original latex colloidal crystal templates. **b**, Latex–gold composite before removal of the template. **c**, Gold-only flake after calcination. Field of view: **a**, **b**, 1,800 µm; **c**, 900 µm. Further details of the methods are available from the authors.

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