

Breaking the mould: Casting on the nanometre scale

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The rational design of materials by organization at the atomic scale is attractive for delivering increased functionality, but there are practical difficulties in such precise construction. Nanocasting is an emerging technique that provides one way of solving the problem.

The concept of nanomaterials exemplifies the rational design of functional materials: Atoms are physically located in precise positions within interlocking regions structured on size scales ranging from one to several hundred nanometres. The dimensions of the internal structure are set by the desired functionality of the material, ranging from typical electronic wavelengths to magnetic coupling lengths to optical wavelengths. The advantage of nanomaterials is that they offer ways to deliver more efficient functionality on a smaller scale, or entirely new types of functionality that were previously unattainable. Plenty of evidence exists for new effects that can lead to advanced technology from such materials. Current commercial applications include super-capacitors for mobile energy storage, extremely sensitive molecular sensors, and advanced solar cells. However, the development of the field is held back by the difficulty of making such structures.

The most successful commercial nanofabrication that is pervasive in electronics is 'top down': essentially a large chunk of one material is carved up on ever-finer length scales to reach the target structure. Although incredibly successful, this is also

incredibly expensive, rising exponentially in costs as the size-scales drop. It also tends to be restricted to structures reached from planar precursors, falling a long way short of enabling arbitrary three-dimensional (3D) nanomaterials. The other prevalent paradigm, universal in nature, is 'bottom up' or self-assembly, in which the ideal nanomaterial is simply created by shaking a vat of organic precursors so they appropriately coagulate into a 3D network. The difficulty here is that although organic molecules have excellent assembly properties that can be directed, their functionality is limited to slow charge transport — owing to electrons hopping between molecules — and biomolecule manipulation rather than electronic, magnetic or optical functionality.

An answer to this impasse was literally written in the sands five millennia ago. The Mesopotamian civilization (or their progenitors) discovered that delicate but durable objects can be created by carving a mould into sand and by pouring in molten copper to cast it. As copper is harder, and therefore more suitable for toolmaking than the previously known silver and gold, this knowledge rapidly spread, reaching the Indus valley by 3000 BC (Fig. 1). The ancient process of casting has the

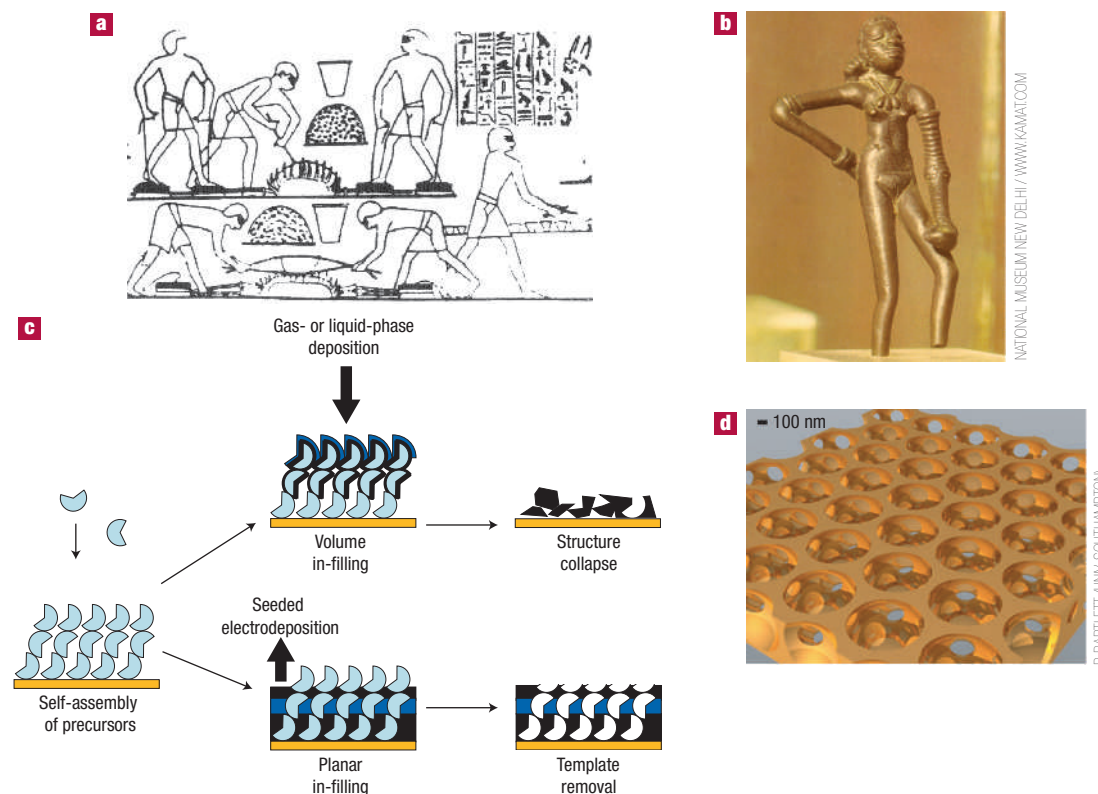


Figure 1 The old and the new. **a**, Egyptian tomb painting of the bronze casting process (~1500 BC). Reprinted from ref. 13, with kind permission of Springer Science and Business Media. **b**, One of the earliest known casts (~3000 BC) of a dancing girl in copper, from the Harappan civilisation in the Indus Valley (now in the Museum of New Delhi). **c**, Steps in nanocasting: production of a template and self-assembly into the target nanostructure, followed by (i) volume growth in pores through gas- or liquid-phase deposition, or (ii) surface-controlled growth through pores from the underlying substrate by electrodeposition seeded from the underlying substrate. The template can then be removed using etching, frequently resulting in structure collapse if the deposition has not successfully proceeded fully down to the substrate. **d**, A nanotemplated substrate as a Raman sensor.

unique attribute of constructing objects ranging from nanometres to kilometres across (Fig. 2). Casting is now an emerging approach for the formation of nanomaterials; it separates the two aspects of top-down versus bottom-up — that of making a desired structure on nanometre scales and of using particular atoms to do this. By making a mould or nanotemplate of a soft- or biomaterial, and then casting inside that template with the desired functional material, nanomaterials can be made elegantly, efficiently and economically. The resulting materials are already of interest for applications, but it is as yet unclear just how far this approach can go.

Casting as an industrial process is surprisingly recent given its ancient past. Considerably refined by Chinese technologists to make iron ploughshares, it diffused to India but was then lost for the next thousand years. After 1750 when casting steel was reinvented in England by Benjamin Huntsman, casting became one of the driving forces of the industrial revolution, as well as enabling the flourishing of the golden age of bronze sculpture. The early 20th-century smile flaunted casting for tooth filling, and industrial applications rocketed for munitions productions with the mass-scale use of explosives in the First World War. Currently, casting is being used back in its birthplace in Iraq in the form of munitions. However, only recently has the process been harnessed for producing nanoscale structures.

Production of moulds on the nanoscale can take a variety of forms, depending on the desired scale of the features. The simplest and mostly widely used are opaline materials, in which spheres of glass, minerals or plastic are stacked in a close-packed

array (Fig. 3), produced either naturally (exactly how this happens is still openly debated: whether precipitated or the product of decomposing microbes) or by artificial self-assembly induced, for instance, by capillary forces¹. Subsequent casting of these templates has been developed in a number of ways including chemical vapour deposition, molten metal filling, and precipitation of co-reactants. However, these frequently lead to problems of plugging near the surface preventing complete casting. Electrochemical casting avoids this issue because it proceeds from deep inside the mould up towards the surface, and combines lateral structuring with the flexibility of multilayer deposition (Fig. 1c). Although such structures are highly iridescent (if they have micrometre-scale periodicity), they inevitably incorporate defects in the stacking, which currently limits their application as full 3D-photonic-crystal nanomaterials. The commercial potential has recently been shown for sensor applications of nanotemplated gold films (structured as in Fig. 1d) as amplifying substrates for the surface-enhanced Raman scattering of molecules attached to them^{2–6}. Such fabrication exemplifies the cost benefits of nanotemplating: substrates can be produced at a thousandth of the price of top-down fabrication approaches.

Rather more precise templates on the 10–1,000 nm scale are provided from silica optical fibres that contain well-defined pores (so called ‘holey’ fibres, Fig. 4). These allow arbitrary arrangements of nanometre-wide tubes to be produced by pulling a stack of glass capillaries, or by soft-glass extrusion through an appropriate multi-holed aperture. Casting such structures — which have aspect ratios

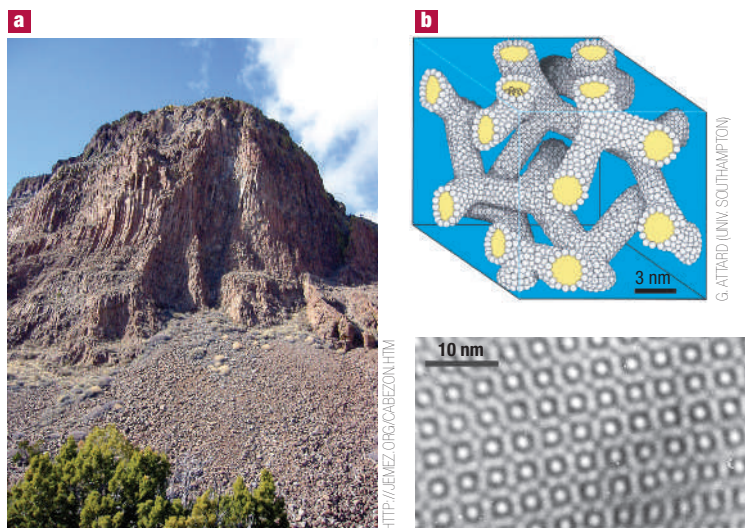


Figure 2 Casting on different scales. **a**, Kilometres: volcanic plug (Cabezon, USA). **b**, Nanometres: nanoporous platinum film, with precursor lyotropic nanostructure (above).

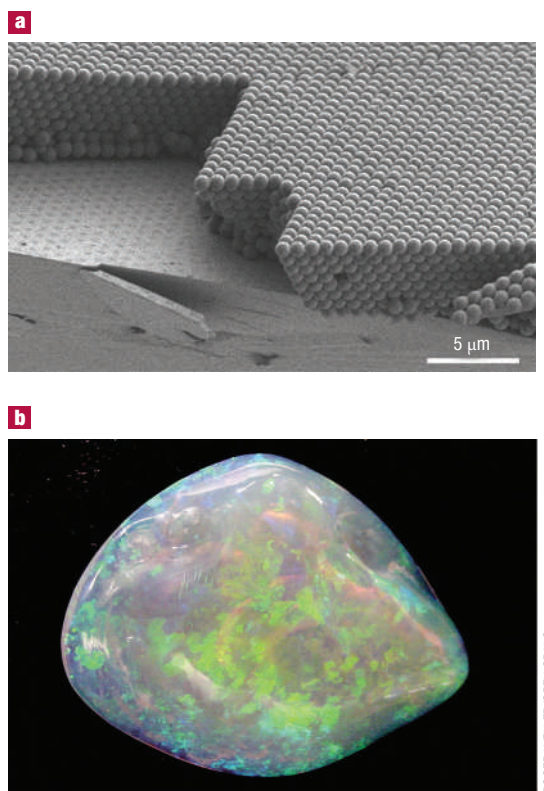


Figure 3 Opaline assembly. **a**, Opal built from 250-nm silica spheres¹, also naturally occurring producing **b**, iridescent polished surfaces.

exceeding 10⁹:1 — is extremely challenging, but has recently been achieved⁷ using high-pressure chemical vapour deposition (such single fibres make ideal pressure vessels), or by techniques using

supercritical carbon dioxide. Combining metals and semiconductors within these nanomaterials produces new functional electrophotonic properties.

One way to make templates on the nanometre-scale exploits the amphiphilic nature of soaps: lyotropic liquid crystals self-assemble depending on solvent concentration and temperature into an astonishing array of soft nanostructures. Sol-gel or electrodeposition in only the aqueous compartments of the structure are used to cast templates, resulting in nanomaterials that are impossible to produce in any other way^{8,9} (Fig. 2b). Such nanomaterials are being exploited as supercapacitors for energy storage, as well as sensitively controlled catalytic surfaces¹⁰. Phase separation in block copolymers is also a prospective template, but is complicated by the need to selectively etch out one of the phases before casting, while retaining the structural integrity of the nanostructure. More generally, there is a large array of bio-assembled nanostructures that can potentially be exploited to provide templates for nanocasting. Co-option of biotechnology for programmed assembly of soft templates combined with casting of metals or semiconductors has the potential to lead to sophisticated control of nanomaterial production.

The real advantage of separating out the processes of building a nano-architecture and afterwards filling it with the desired atoms, is the simplified production of functional nanomaterials. However, there remain limitations in nanoscale casting besides the production of suitable templates. Nanotemplates experience strong internal forces (such as capillary forces), which restrict casting processes to only those architectures that remain stable. On the other hand, removal of the template is not always easy, particularly at the smallest nanometre scales. Another problem is the deposition process inside such high-aspect-ratio structures, requiring new strategies for chemistry in high-pressure or supercritical environments¹¹. More importantly, for applications it is not always easy to combine nanocasting techniques to produce nanomaterials embedded in devices that exploit their functionality; much remains to be done on integration of such processes.

What are the ultimate limits of such an approach? Only three routes to templates have been outlined here: self-assembly of nanoparticles or molecules, and drawing/extrusion. Only by developing further these and other techniques can we learn to make more complex but well-defined nanostructures. Although our current nascent control of self-assembly will probably improve, single-step nanotemplate production is unlikely to satisfy all needs. A further development using these precursor 3D scaffolds, will bring in second-stage assembly based on nanoparticle attachment to specific points within a scaffold. We can envisage sequential and directed assembly of hierarchically derived nanostructures, followed by multiple casting steps involving different functional materials. More controllable yet would be to direct, in real-time, such assembly processes using illumination with spectrally tuned lasers that excite electrons at specific points within the structure, promoting localized attachment

of nano- or bio-particles. Target structures one can envisage include organized solar-cell nanomaterials combining organic semiconductors and carbon nanotubes in regular arrangements that maximize electron-hole extraction and photovoltaic efficiency.

The nanomaterials discussed so far are all based on making well-controlled robust films. Another popular route has been to build multi-component nanoparticles in colloidal suspension. For instance, promising avenues have used proteins or viruses that self-assemble into regular nanoparticles (such as tobacco mosaic virus, which forms 300-nm-long, 18-nm-diameter nanorods) that can be functionalized by surface deposition¹². To make 3D nanomaterials, these particles must then be assembled into precise spatial locations into the scaffolds formed by templates. The promise of such an approach is that modification of the genetic basis of the viral sub-units can lead to rapid exploration of new shapes and constructs. Significantly it is the production of useful functional properties from these assemblies that remains a challenge.

The increasing interest in research and exploitation of nanomaterials will continue for many decades, only blossoming when our technologies have reached the stage where we can rapidly produce target structures. There is little doubt that self-assembly of nanomaterials will have to mature to provide low-cost standardized nanostructures with useful functional properties. At the present time it is unclear which routes will come to dominate production as we are very early on this journey. Direct self-assembly of target nanomaterials remains extremely difficult due to the problems inherent in trying to integrate functionality into the precursors, which is then retained in the final structure. It is for this reason that nanocasting has excellent promise for the immediate future, harnessing self-assembly, but

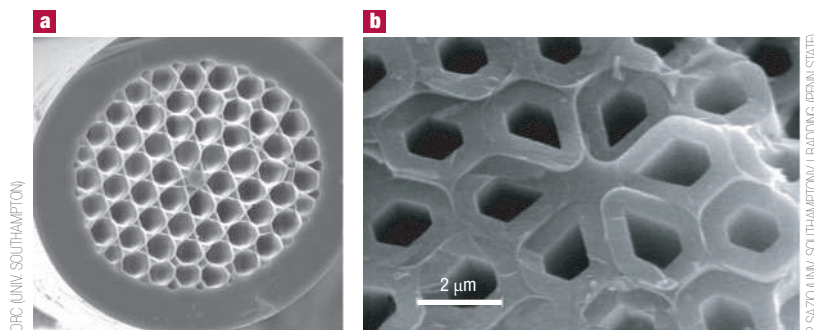


Figure 4 Porous silica. **a**, A precursor holey optical fibre (smallest features on the 10-nm scale). **b**, Germanium-filled fibre nanotemplate.

combining it with systematic ways to incorporate functional materials into the nanostructures. What is really promising is the low cost of both the production and the development, coupled with the speed of fabrication, hence allowing exploration of a very wide range of nanomaterials.

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