# Profiting from nature: macroporous copper with superior mechanical properties

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**Macroporous copper with a complex hyperbolic morphology and superior mechanical properties was produced by replicating the remarkable form of a sea urchin skeletal plate using templated electrochemical deposition.**

Nature is adept at producing remarkable structures, optimised in form and property for their designated function.[1] Looking for example at biominerals, morphologies are frequently entirely distinct from their synthetic counterparts, and are generated through the application of strategies including the use of soluble additives, directed ion flow and templating.[2,3] The superior mechanical properties of these materials typically derive from their composite inorganic–organic structure, and organisation on a spectrum of hierarchical levels.[4,5] Replication of such natural structures in terms of form and function remains an enduring and challenging goal.

This paper reports on the preparation and mechanical characterisation of a macroporous copper sample identical in form to a sea urchin skeletal plate. Echinoid plates exhibit impressive mechanical properties for a material constructed from humble calcium carbonate, a factor due in part to their unique microstructures. Although each plate comprising the test of the sea urchin is a single crystal of calcite, examination on the microscopic level reveals a complex, sponge-like form containing channels of diameter 10–15 μm and bounded by continuous curved surfaces. The surface of the echinoid calcite is recognised to resemble a triply periodic minimal surface (TPMS), namely a cubic P surface, as shown in Fig. 1.[6,7] The Schwarz P surface has a pair of identical sub-phases on either side of the surface, *i.e.*, the volume fraction of each phase is 0.5.[7]

Minimal surfaces possess zero mean curvature, such that the principal curvatures are equal in magnitude but opposite in sign at every point, with triply periodic minimal surfaces also exhibiting periodicity in structure in three independent directions.[7] TPMS are common throughout the natural world, having been observed, for example, in surfactant–water systems, silicate mesophases, block copolymers and cell membranes.[7,8] The sea urchin plate structure provides another beautiful example, but on a significantly larger length scale. Recent theoretical studies have considered the properties of bicontinuous two-phase composite materials and it has been demonstrated that composites formed from two materials with differing transport properties, *e.g.* a good thermal conductor mixed with a good electrical conductor, exhibit optimal performance for the simultaneous transport of both properties when a TPMS structure is adopted.[9,10] Further studies of the multifunctionality of TPMS systems have shown that they are extremal when competition is set-up between the bulk modulus of one phase and the conductivity, thermal or electrical, of the second phase.[11]

The structure–function relationship of echinoid test plates has long been somewhat of an enigma. Although it was originally proposed that the fenestrated form would hamper the progress of cracks through the structure, it has been demonstrated that the mechanical properties of such a multiply connected porous material would be poorer than of a solid material of equal mass.[12] Speculation that a porous solid adopting the Schwarz P structure would be optimal for mechanical strength and fluid permeability[11] may however be key, since the porosity of the stereom allows mobility of cells through the structure,[2] as well as providing the mechanical support demanded of the test. Indeed, optimal stress distribution and significant strain reduction are predicted for materials exhibiting the smoothly curved surfaces of the Schwarz P structure.[7,13]

We here describe how a porous metal that adopts the Schwarz P structure, and which consequently shows superior mechanical properties as compared with a metal with similar porosity but non-periodic structure, can be prepared using templated electrodeposition. We have demonstrated previously the potential of

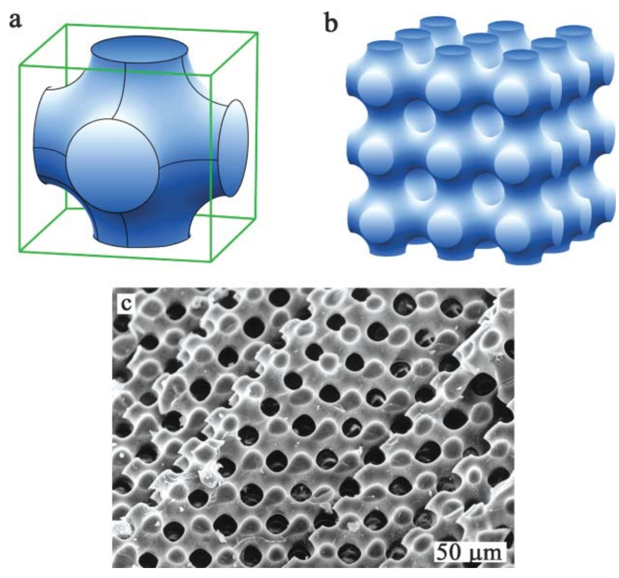


**Fig. 1** (a) Schematic of the primitive unit cell and (b) periodic structure of Schwarz's P surface and (c) cross section through a sea urchin skeletal plate showing resemblance to the P surface.

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using echinoid skeletal plates as templates to direct the formation of metals with bicontinuous structures, coating the surface to produce a fragile two-sided gold structure,[14] and producing a skeletal structure of nickel using electroless deposition.[15] Ha *et al.* also fabricated a structured tellurium photonic crystal using sea urchin skeletal plates as an initial template.[16] In contrast to our previous methodologies, electrochemical deposition provides access to perfect replication of the sea urchin structure, such that it is impossible to distinguish morphologically between the original calcitic material and product copper structure.

Copper replicas of sea urchin plates were produced *via* a two-step templating procedure. A methyl methacrylate/ethyl acrylate cast of a calcite urchin plate was first produced *via* infiltration of the monomer solution into the plate, curing, and subsequent dissolution of the $CaCO_3$ as described previously.[15] This porous polymer was a perfect negative structure of the original inorganic template, exhibiting a bicontinuous structure with pores of about 15 μm and smooth curved surfaces (Fig. 2a). Copper was then deposited in these porous polymers using an electrochemical method† and the polymer scaffold was finally dissolved in dichloromethane to yield a free standing macroporous copper sample. Direct electrochemical deposition in the calcite plates was not possible due to dissolution of the $CaCO_3$ at the low pH values generated during the procedure. Optical microscopy and SEM of these porous copper networks demonstrated perfect replication of the structure of the sea urchin plates in copper (Fig. 2b and 2c). Again the surfaces were smooth, and the structure resembled the Schwarz P structure.

The excellent mechanical properties of this porous copper structure were then demonstrated.† Mechanical studies were performed on a TPMS copper sandwich structure, which was prepared by placing the TPMS polymer template proud of the working electrode surface during electrodeposition, such that complete copper layers were formed above and below the membrane. The membrane was then dissolved to yield a sandwich structure. For comparative purposes, a non-periodic porous copper sample of comparable porosity was prepared by electrodeposition,

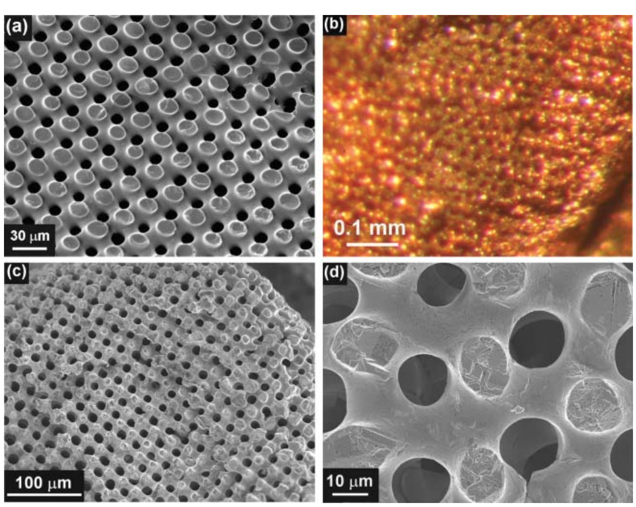


**Fig. 2** (a) Polymer replica of sea urchin skeletal plate; (b) optical micrograph of macroporous copper; (c and d) SEM images of the templated macroporous copper.

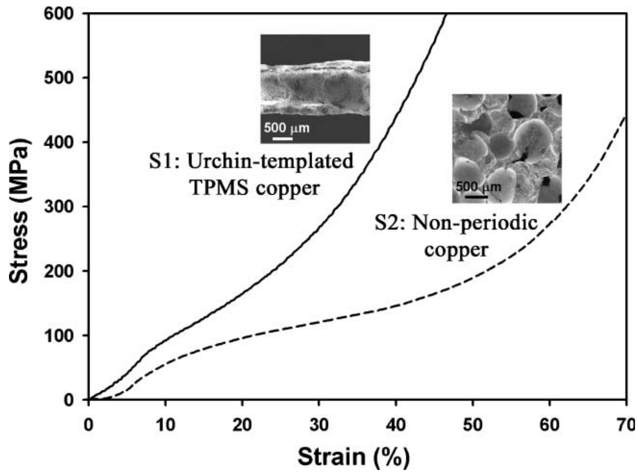


**Fig. 3** Stress–strain curves of porous copper samples. Insets are the SEM images of the samples. S1 is a 'sandwich' copper sample comprising TPMS copper coated with compact copper layers on the top and bottom and S2 was produced by copper electrodeposition using PMMA particles as a template. The surface area touching the punch during compression was monitored using a microscope. Each curve consists of >600 measurements, the estimated errors in the stress and strain are 5% and 3% respectively.

using 600 μm poly(methylmethacrylate) (PMMA) particles, placed on the working electrode, as templates. The measured porosity of the resultant sample, after removal of the PMMA using dichloromethane, was identical, within 0.1%, to that of the copper prepared in the TPMS polymer membrane.

Compressive stress–strain curves for the sandwiched TPMS copper network and the non-uniform copper network of matching porosity are shown in Fig. 3, along with SEM images of the two samples. As bulk copper is compressed it changes from an elastic to a plastic material, the stress at which this transition arises being termed the yield strength. It is noted that the porosity of the copper samples studied is lower than that of the cellular foams investigated by Gibson and Ashby[17] and that the values of the elastic modulus and yield stress are not in agreement with the simple scaling laws that apply to highly porous materials. The compression curve for the porous copper formed using PMMA particles as a template can be split in to three distinct regimes, as predicted for a foam of an elastic–plastic material. At low strain (<11%) the material is elastic; as the strain is increased a plateau is achieved, which corresponds to plastic yielding; and at high strain (>55%) the stress increases rapidly, owing to densification of the material.

The stress–strain curve for the copper exhibiting the TPMS structure not only indicates that this material has a higher elastic modulus and a higher yield stress but also that it lacks a defined plateau region. In the models of cellular foams the plateau region arises from plastic collapse at high strain points in the lattice—that is at the points where the cell walls intersect. The absence of a plateau region for the TPMS structure suggests that the force applied during compression is distributed uniformly over the material structure and is not focused at specific points in the lattice. This is therefore in perfect agreement with the finite element modeling of Rajagopalan and Robb[13] who demonstrate optimal stress distribution and significant strain reduction for materials exhibiting the Schwarz P structure.

 

In conclusion, we have fabricated macroporous copper with a bicontinuous TPMS structure using a templating route—profiting from the unique form of sea urchin skeletal plates. In accord with theoretical predictions, mechanical testing of this material shows that the TPMS structure endows it with a high compressive strength. The methodology is very general and it is envisaged that it can be extended to generate a range of composite materials with optimised properties.

## Notes and references

† A section of porous polymer was mounted on a copper sheet and the four sides of the polymer membrane and exposed parts of the copper sheet were sealed with wax. This working electrode was then immersed in a 1.0 mol $dm^{-3}$ $CuSO_4$ solution with counter and reference electrodes and copper electrodeposition was performed at a constant potential of −0.1 V and a temperature of 25 °C. Compression tests were conducted on a Lloyd material testing machine using punches with diameters of 6 mm or 12 mm and load cell of 30 kN. The base plate was homemade standard steel with a diameter of 12 mm. A Digital Blue QX5 computer microscope was employed to monitor size changes in the sample during compression.


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