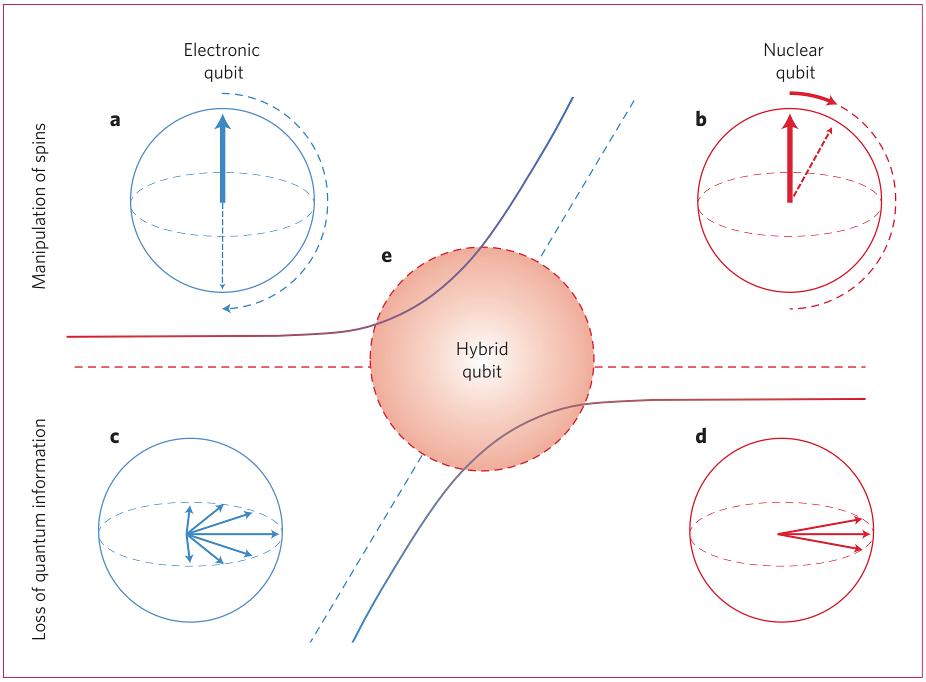

Figure 1 | A hybrid qubit. Both electron spin and nuclear spin can be used as qubits. **a**, Electron spins (represented by the thick blue arrow) can be flipped quickly. **b**, Flipping nuclear spins (represented by the thick red arrow) takes much more time. **c**, The electron spin state is quickly randomized (represented by the spreading of the vector directions) due to the environmental noise, resulting in a loss of quantum information. **d**, The nuclear spins are insensitive to the noise and the state vectors are less diffused, so that the quantum information is well preserved. **e**, Strong coupling between electronic and nuclear spins can mix them together, forming a hybrid qubit. It can have both long memory and short manipulation times.

widely used phosphorus donor in the semiconductor industry, a bismuth atom in silicon traps an additional electron, and the bismuth nucleus itself carries spin. However, the trapped electron spin and nuclear spin are strongly coupled together, and the strength of this coupling is much larger than for the case of phosphorus. The strong coupling enables a 50:50 hybridization of the electronic and nuclear spin (Fig. 1e) in a manner that makes it suitable for detection and manipulation using pulsed magnetic resonance techniques.

The hybrid qubit system combines the advantages of nuclear and electronic spins: it is characterized both by long memory times and fast manipulation rates. The results suggest they can store quantum information for hundreds of microseconds, and by isotopic purification of the silicon, this can be further extended to 4 ms. Although this is still significantly shorter than for the relaxation timescales for a phosphorus donor[3,4], the hybrid qubits also demonstrate a significant speed-up for the logic operations: flipping times of 32 ns were achieved, which is comparable to the flipping times of a pure electron spin state, and orders of magnitude faster than the nuclear spin operation time. As a figure of merit, the ratio of the memory time to the operation time can reach 10^5, which fits the requirement for quantum information processing and implies great application potential of the hybrid quantum bits.

Another distinguishing feature of the bismuth nuclei is that they have ten spin states[5,6], instead of only two (the up and down states) as in the case for the phosphorus nucleus. More spin states give rise to more complex level structures of the donor, particularly in the strongly coupled regime explored by Morley and colleagues. This work therefore opens a door for designing more sophisticated control schemes to realize precision spin dynamics, and may lead to more appealing applications for bismuth-doped silicon materials in the near future. ❐

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PHOTONIC CRYSTALS

Sustainable sensors from silk

A biocompatible method for fabricating three-dimensional photonic crystals opens up unique opportunities for structurally coloured biodegradable materials, but also for implantable biosensing and targeted therapeutics on the microscale.

Jennifer MacLeod and Federico Rosei

The challenge of developing sustainable approaches to materials design spans all aspects of the material's lifecycle: the synthesis and fabrication must be 'green', the material itself must be non-toxic and it should degrade to innocuous products at the end of its useful lifespan (Fig. 1). Writing in *Nature Photonics*, Sunghwan Kim and co-workers recently demonstrated the controlled fabrication of an inverse opal — a type of photonic crystal — from fibroin, a silk-derived protein that meets all the criteria for sustainability[1]. Furthermore, silk inverse opals (SIOs) are biocompatible and show promise as active layers for resorbable label-free biosensing.

The fibroin from which Kim *et al.* fabricate their photonic crystals is obtained from the cocoons of *Bombyx mori*, the domesticated silkworm. Although spider silk, such as the dragline silk of *Nephila clavipes*, can exhibit remarkably high toughness, exceeding that of Kevlar[2,3], for the extraction of fibroin, the silk of *B. mori* has the distinct advantage of being produced in relative abundance. Through a simple procedure involving only sodium carbonate and lithium bromide as reagents, the authors extract an aqueous solution of fibroin directly from the *B. mori* cocoons.

Photonic crystals — the structures on which the authors apply their fabrication technique — are engineered optical media whose properties arise from a periodic modulation of their refractive index in one or more dimensions[4]. In inverse opals, this modulation is imparted by a periodic lattice of voids[5]. Kim *et al.* use a simple casting technique to fabricate their SIOs. The extracted fibroin solution is poured over a self-assembled colloidal crystal of close-packed poly(methyl methacrylate) (PMMA) spheres and left to dry. The PMMA is then dissolved, leaving an inverse lattice of fibroin.

The SIOs reported by Kim *et al.* represent a notable example of control over the optical properties of functional materials. In particular, the periodic variation of the refractive index between the lattice and the voids imparts 'structural colour' to the crystal, which manifests as the type of iridescence occurring naturally in peacock feathers and mother of pearl. In engineered optical structures the colour is 'built' into the design of the material, and depends on both the spacing of the voids and their dielectric constant, which can be adjusted by filling with a different material. Kim *et al.* control the colour of the SIOs, both by varying the size of the PMMA spheres and by filling the voids with acetone. They then irradiate their samples with white light, and observe that the colour of their crystals changes according to the specified optogeometric parameters.

The combination of intrinsic structural colour with the biocompatible properties[6,7] of fibroin makes SIOs excellent candidates for applications in implantable biosensing. Together, the highly scattering nature of biological tissue and the light-absorption properties of one of its main ingredients, water, define a transmission window for light waves ranging from the ultraviolet to the near infrared. These constraints imply that suitable biosensors should be highly responsive, and that they operate in the range of visible light in addition to being biocompatible. Kim *et al.* demonstrate that the structural colour of SIOs can be detected even in the presence of up to 5 mm of overlying biological material. The sensitivity of the structural colour to the interstitial fluid in the lattice means that the SIOs can be used for *in situ* sensing of fluid composition. For instance, SIOs filled with glucose solutions with increasing concentrations exhibit a corresponding shift in the peak of their reflected spectrum. Although the shift observed for glucose is subtle (~20 nm for a change in concentration from 0 to 20%), other fluids may lead to more pronounced changes, and thus higher sensitivity.

A further emerging biomedical application of nanomaterials exploits the efficient generation of heat from metallic (plasmonic) nanoparticles under optical illumination, known as plasmon resonance-induced heating[8]. This type of hyperthermal effect can be used to systematically target and destroy unwanted tissues, for example, in anticancer therapies.

By 'doping' SIO with gold nanoparticles, Kim *et al.* take the concept of structure–property relations in their biomaterial architecture a step further. Profiting from wavelength-specific confinement effects in SIOs, they significantly increased the heating efficiency of the gold nanoparticles as compared with those embedded in an unstructured fibroin film.

This work demonstrates just a few of the possibilities that can arise from the combination of a carefully chosen raw material and a judiciously engineered design. The sustainability and biocompatibility intrinsic to fibroin bring numerous advantages to its use in photonic crystals. Applications beyond those demonstrated by Kim *et al.* are already within reach. In particular, fibroin has shown promise for bone regrowth; suitably functionalized fibroin films stimulated osteoblast-based mineralization *in vitro*[9]. Using a SIO as an osteologic substrate could allow for non-invasive optical monitoring of cell regrowth. The SIOs could also find use in other emerging applications, such as in environmental sensing, after being

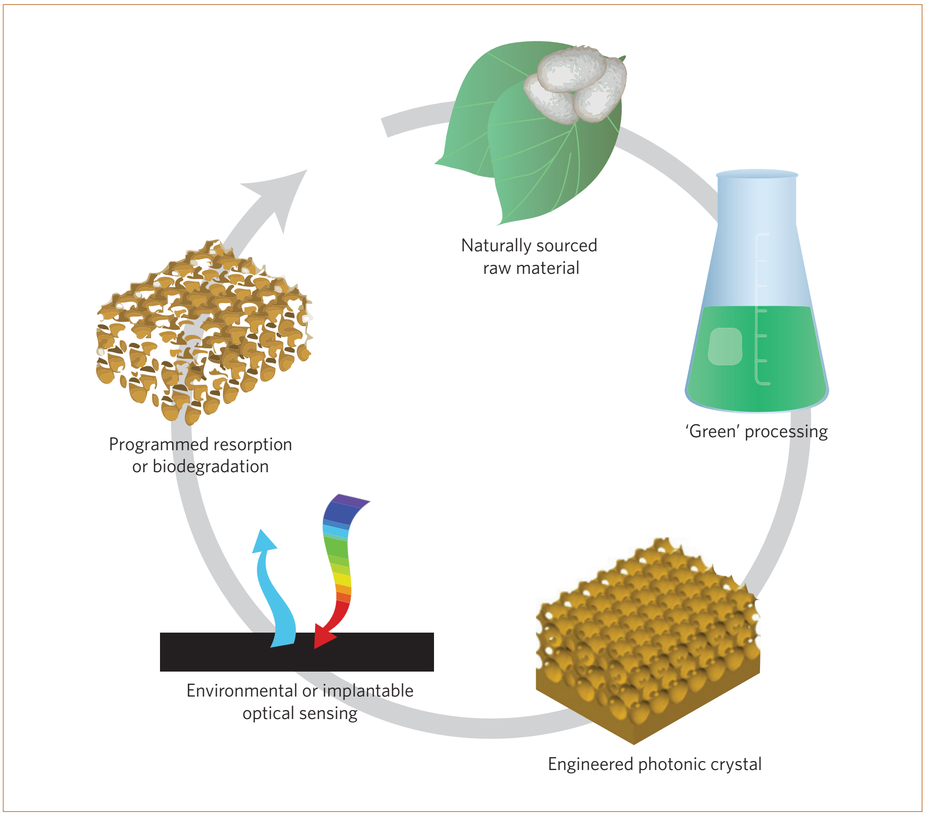

Figure 1 | General scheme for the fabrication of sustainable sensors from naturally sourced raw materials. Starting from a natural raw material, 'green' processing, involving a minimum amount of toxic reagents, is used to produce an engineered product, in this case a photonic crystal. The crystal is then used in a sensing application, and at the end of its useful lifespan it decomposes or biodegrades according to a pre-determined ('programmed') mechanism.

functionalized for sensitivity to certain gases. Further, the sustainability of fibroin is expected to play an important role, as the biodegradable SIO sensors would naturally decompose instead of requiring retrieval. Beyond fibrion, one can foresee a wealth of biologically derived raw materials, such as collagen or cellulose, with engineered functional properties that could lead to sustainably produced optical materials, suitable for a broad range of applications. For example, cellulose-based photonic crystals could potentially be used as a temperature indicator integrated into cups for hot drinks.

Certain challenges still need to be met before SIOs become feasible or fully sustainable in all applications. At present, the time between implantation and the onset of bioresorption of fibroin-based materials depends on the processing methodology, with longer-lived structures requiring non-aqueous processing[10]. Similarly, the logistics of how to functionalize the SIOs for use as high-sensitivity detectors need to be addressed. Yet, the potential advantages of using sustainable materials like fibroin to make photonic crystals — for a variety of applications — ensure that their future will be brighter than ever. ❐

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MATERIAL WITNESS

WATCHING ICE SPIN

PHILIP BALL

Mechanical analogies for the microscopic world have a distinguished history, perhaps most famously James Clerk Maxwell's vision of the luminiferous ether as a mesh of spinning vortices propelled by "gearwheel particles". J. D. Bernal used bags of ball-bearings to explore atomic random close-packing; for Osborne Reynolds several decades earlier, such a bag of spheres was a model for the fine-grained structure of the entire universe. And chemists have long used macroscopic physical models of molecules to intuit how they move and interlock.

The trick is to identify which elements of the macroscale apply equally to the microscale, where in general a different balance of forces — electrostatic, dispersion, capillary — holds sway. As Bernal understood, packing effects scale because they are purely geometric. The same is true for a macroscopic model of spin orientations described by Mellado *et al.* (*Phys. Rev. Lett.* **109,** 257203; 2012).

The researchers examine frustration arising in certain geometric arrangements of interacting particles. The problem is most easily seen for a two-dimensional array of magnetic spins that display antiferromagnetic interactions, so that adjacent spins aim to point in opposite directions. On a triangular lattice that configuration is impossible for all three neighbours in a unit cell — two neighbouring spins must inevitably be parallel rather than antiparallel.

This means the system has no unique energetic ground state. The same is true for the tetrahedral arrangement of hydrogen bonds in water ice: the number of configurations grows exponentially with system size, precluding a single minimal-energy state even at absolute zero. By analogy, some magnetic materials with a lattice of corner-sharing tetrahedra (the pyrochlore structure) exhibit magnetic frustration and have been christened spin ices.

To understand the relaxation dynamics of such compounds — the collective reorientations of spins as the system explores its rough free-energy landscape — Mellado *et al.* have built a macroscopic analogue of spin ice consisting of a honeycomb lattice of ferromagnetic rods about 2 cm long whose ends converge at (frustrated) three-fold vertices, hinged at their midpoint so that they can rotate vertically to flip their orientation.

When the spins are first oriented vertically by applying a strong magnetic field, and then allowed to relax, there follows a few seconds of 'negotiation' during which all the vertices acquire the various permutations of north–north–south (NNS) and SSN magnetic alignments, with no high-energy NNN or SSS states. Close video inspection of this relaxation process reveals that it has three stages. In the first ~0.07 s, many spins rotate from vertical to horizontal. Then some spins form head-to-tail linear chains; finally, the remaining spins become horizontal and rotate, then simply oscillate, until the kinetic energy is dissipated.

Such distinct dynamical regimes would be hard to see in microscopic systems — although in any case some of the behaviour, such as viscous dissipation at the hinges, does not translate to atomic-scale spin ice. The macroscopic system is also amenable to manipulation: changing the interaction strength, say, or adding vacancies. The researchers have even created a preliminary three-dimensional tetrahedral version from stacked layers. Regardless of how much of the behaviour applies to microscopic media, these systems look set to exhibit a richness of their own. ❐