MATERIAL WITNESS

Greatest hits

Everyone loves lists. Or rather, some love them and others love to hate them, condemning them as invidious, unduly competitive or plain meaningless. But it's hard to deny one thing in their favour: a list is guaranteed to excite debate about what is valued in the topic it tabulates. That, it seems, was what induced the magazine *Materials Today* (**11,** 40–45; 2008) to draw up the "top ten advances in materials science over the last 50 years".

Being informed by the magazine's editorial advisory panel and 'leaders in the field', the list doubtless has some formidable authority behind it. All the same, you might anticipate that I am going to pour scorn on it. Not at all — it's a very attractive selection, which runs (briefly) as follows: the International Technology Roadmap for Semiconductors, scanning probe microscopes, giant magnetoresistance, semiconductor light sources, the US National Nanotechnology Initiative, carbon-fibre-reinforced plastics, lithium ion batteries, carbon nanotubes, soft lithography and metamaterials. The magazine's editor Jonathan Wood admits that some might be dumbfounded by the omission of organic electronics (yes) or high-temperature superconductors (no), but the list gives a nice sense of the scope of contemporary materials science.

And yet (here it comes)… Well, for one thing, like all such lists this one is biased towards the present. It's hard to justify such emphasis on nanotechnology, still unproven as a truly disruptive technology, at the expense of advances in more mature areas such as biomedical materials. Many immensely important materials, such as Kevlar (which Wood also mentions), synthetic zeolites and vapour-deposited diamond, fall off the podium simply because they have become so pervasive or routine to produce.

But although a discussion of what's missing can be instructive, it's perhaps more revealing to consider the trends that the list brings to light. For example, with the possible exception of carbon nanotubes, carbon-fibre composites are the sole representative of structural materials (indeed, in this regard carbon nanotubes are only an elaboration of the same thing). Many of the innovations here are concerned with ways of storing, sending, reading and manipulating data. It seems that the past five decades have seen materials science transformed from being about 'holding things together' to managing information flows. I'm not convinced that three decades ago one could consider that transition to have been made, which is again why the list seems a little amnesiac.

Another characteristic is how extraordinarily high-value-added these innovations are. I don't think I'm quite ready to demand a place for self-compacting concrete on the list, but it seems unlikely that such things were ever given a moment's thought when pitched against the dazzle of, say, metamaterials. One might say the same of PZT and cubic boron nitride. Along with high-pressure synthetic diamond, they fall right on the edge of the chosen time frame, but that in itself reminds us both how fertile the 1950s were for new materials and how different the priorities were then for those who sought them.

Philip Ball

BIO-INSPIRED MATERIALS

Unnatural life

The biologically inspired toolbox is well and truly open. From three-dimensional DNA assemblies to active catalysts inside the confines of a virus — biomolecules are finding a second, unnatural life.

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At the turn of the nineteenth century, Pieter Harting and George Rainey laid the foundations of a science called "synthetic morphology"[1]. The inspiration for the name probably came from Wöhler's discovery of urea synthesis in 1828, a breakthrough commonly perceived to mark the beginning of synthetic organic chemistry. The primary goal of Harting and Rainey's synthetic morphology was to explain and artificially imitate the formation of inorganic structures associated with living matter, such as those found in diatoms, pearls or butterfly wings.

But, what has become of Harting and Riney's synthetic vision today? Indeed, the questions initially stirred by the aesthetics of shells, feathers and scales are far from being answered and have expanded in many directions that promise to affect how we harvest energy, carry out reactions and study biological function. Whereas emphasis has changed from the early days of playful explorations, the original awe inspired by biological organization was vividly present at the symposium on 'Biomolecular and Biologically Inspired Interfaces and Assemblies' at the 2007 Materials Research Society Fall Meeting in Boston.

DNA and proteins are known in traditional biochemistry as informational macromolecules because the order of their subunits (nucleotides in nucleic acids and amino acids in proteins) is

highly relevant to their function. They are different from structural molecules such as cellulose, where the order of monomers is not essential for function. However, the boundary between these two categories is not clear-cut, as illustrated by the creative approaches of those attending the symposium. For Hanadi Sleiman (McGill University), DNA is a structural molecule — a building block that, together with rigid organic molecules at the vertices, can be used to make 3D polyhedral cages (Fig. 1)[2]. The DNA building blocks and linking organic molecules self-assemble into various structures, in which a blueprint is encoded in the DNA sequence. As a result, the informational component is not discarded.

The basic idea of using DNA to make regular arrays has been around since the pioneering work on nucleic-acid junctions and lattices of Nadrian Seeman[3]. Sleiman's approach promises to take this technology in new directions, by making dynamically controlled 3D DNA assemblies. To switch a DNA cage between different volumes, some of the polyhedron's sides would have to be adjustable in length. Sleiman achieves this by introducing internal loops on some of the sides (Fig. 1b) — similar to making knots to shorten a rope. The size of the internal loops is adjusted using 'eraser' strands. Förster resonant energy transfer is then used to measure the switch between different lengths (from ~5 nm to ~9 nm) of a prismatic cage. This versatile way to dynamically control DNA cages is potentially useful for drug encapsulation and release, regulation of the folding and activity of encaged proteins and creating 3D networks for catalysis. Alternatively, biomolecules that are hard to crystallize could be coerced into a regular 3D network with the help of such a DNA cage array.

Now, take a container woven from nucleic acids with proteins encapsulated, turn it inside out and you end up with something similar to a virus. A virus has a protein shell (capsid) self-assembled from hundreds of symmetrically arranged subunits, which encloses the viral genome. Many viruses have icosahedral capsids and, by virtue of symmetry and therefore of a well-defined local chemical environment, the internal surface of the capsid can be used to nucleate inorganic mineralization reactions, which can lead to the formation of a single-sized metal nanoparticle filling the inner void of the capsid[4]. In essence, these systems are not unlike the biologically grown calcium carbonate concretions that captured the imagination of Harting and Rainey 150 years ago.

Trevor Douglas (Montana State University) explained in his talk that

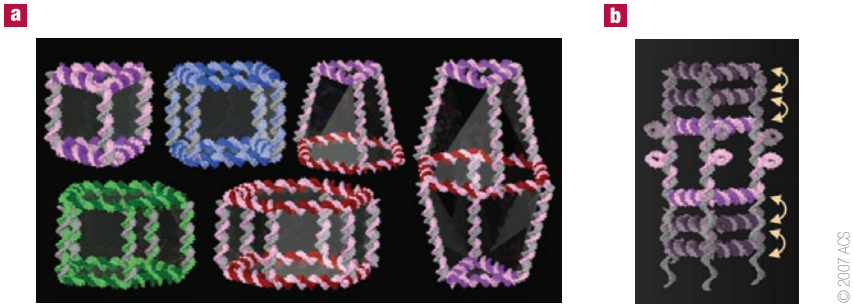
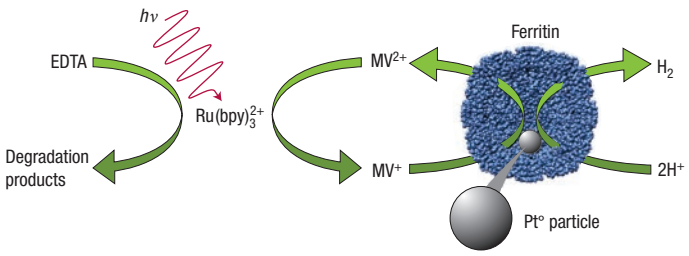


Figure 1 3D DNA assemblies[2]. **a**, The formation of a wide variety of polyhedra from the self assembly of single-stranded and cyclic DNA triangles, squares, pentagons and hexagons with rigid organic molecules at the vertices. **b**, The volume of a prismatic cage can be changed reversibly by introducing internal loops in the parallel edges of a prism.

such virus-confined nanoparticles may have superior catalytic properties. This discovery comes at a time when there is considerable interest in developing catalyst systems that can produce hydrogen efficiently using renewable sources such as solar energy. As an alternative fuel, hydrogen is attractive because its oxidation product is water. Douglas has developed a protein-cage-based system that catalyses the reduction of protons and produces hydrogen gas. The catalytic active sites comprise small clusters of platinum embedded into the well-defined protein cage of ferritin. The protein cage keeps the clusters intact and remains stable up to 85 °C. Hydrogen production is driven by visible light through a coupled reaction between a photocatalyst and methyl viologen — the latter acts as an electron-transfer mediator (Fig. 2). According to Douglas, hydrogen production rates are comparable to those of known hydrogenase enzymes and better than those previously described for platinum nanoparticles, proving that the biomimetic approach is advantageous in the design of nanoscale catalysts.

As if these diversions from the natural function of proteins and nucleic acids were not enough, the symposium witnessed the further expansion of the biomolecular toolbox to include unnatural amino acids incorporated in recombinant proteins[5], as reported by David Tirrell (Caltech), and anionic polymer/peptide condensates that exhibit self-healing properties, as explained by Samuel Stupp (Northwestern University). The Caltech team has discovered how to engineer a bacterium for high-fidelity incorporation of amino acid analogues at specific sites in recombinant proteins. Site-specificity is important because indiscriminate replacement could compromise protein function. Such an expanded set of genetically encoded amino acid analogues could lead to proteins with novel properties. The set of peptide amphiphiles described by Stupp are aimed at bridging the molecular and macroscopic realms in a way that is reminiscent of biology and may prove useful for regenerative medicine[6].

Where will these new materials that blur the borders of biology lead us?



TREVOR DOUGLAS

Figure 2 Light-driven hydrogen generation by coupled photocatalysis. A photoactivated electron donor, ruthenium tris bipyridine (Ru(bpy)$_3^{2+}$), reduces an electron mediator, methyl viologen (MV). A Pt nanoparticle confined to a protein cage then uses the reduced methyl viologen to produce hydrogen. The capsid-confined metal particle is more stable and has a better turnover rate than conventional particle catalysts. EDTA: ethylenediaminetetraacetic acid.

Perhaps one day we will be able to find the weight of a protein bound to the end of an oscillating DNA strand, as proposed by Ulrich Rant (Technical University München), or maybe phage display technology will yield groups of proteins able to selectively bind to explosives, as described by Justyn Jaworski (University of California, San Francisco).

This is a field where imagination and creativity are the uncontested rulers. For now, maybe it is best to remember Herbert Kroemer's (Nobel Prize in Physics, 2000) comment on new technology: "The progress from new technology to new applications is opportunistic rather than deterministic" and wait and see what happens.

References

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