MATERIALS OF THE FUTURE

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Contents

Summary

The development of new techniques for seeing and manipulating matter from the atomic scale upwards has enabled an increasing element of rational design to be incorporated into materials innovation, enabling materials to be tailored to particular tasks. In particular, these technical developments are shrinking the size scales at which engineering can be conducted. Concomitantly, materials science has experienced a trend away from structural materials towards functional ones: from materials that perform some passive structural role (generally supporting a heavy load) to ones that perform some active function, such as generating an electrical current or closing a valve. This change makes materials increasingly important for a wide range of technologies, notably medicine and information technology. The materials of the future will therefore arise from collaborative efforts between scientists ranging from electronic engineers to chemists to cell biologists.

1. Introduction

Ages defined by their prevalent materials seem now to be passing with disconcerting speed. The Stone Age can be stretched, depending on one's terms of reference, over 20 millennia; the Bronze Age lasted for over 20 centuries. But one could argue that the Plastic Age began and ended during the twentieth century, and the Silicon Age could be over within the lifetime of many of those who saw its dawning. If the current time represents the Age of Materials, as some have suggested, that is surely because the appearance and demise of new materials is happening at a phenomenal rate. All of this leaves us decidedly myopic when trying to gaze into the crystal ball of the future.

Discussions of future technologies—indeed, of the future in general—must either be prosaic extrapolations of current capabilities, or science fiction. This article will err on the side of the former, while acknowledging that for each ensuing decade the probability that it will overlook something of great importance is at least doubled.

This can be illustrated with reference to the case of carbon nanotubes (described in more detail in Section 9). Before the 1990s, no one had even postulated that these super-strong filaments of graphite-like carbon exist. That in itself is worth remarking on, since it is commonplace now for theorists to speculate about materials that *might* exist, to calculate their putative properties in inordinate detail. But even though the soccer-ball-shaped carbon molecules called *buckminsterfullerene* (now one of a family of hollow "fullerenes") were predicted in the 1970s and discovered in 1985, no one extrapolated to tubular versions. Yet in the 8 years that have now passed since the discovery of carbon nanotubes, they have furnished an entirely new arena of research, have eclipsed the fullerenes as the most promising and interesting form of "nanostructured" carbon (that is, a form of pure carbon sculpted at the nm scale), and are now discussed in the context of molecular wires for microelectronics, single-molecule transistors, ultra-strong carbon fibers, probosci for the most powerful microscopes, high-capacity storage cylinders for hydrogen fuel, etc.) If written 10 years ago, (1990), this article would have missed them totally.

Specific materials systems aside, one can be little more confident in making some prognostication of the possible future trends in materials science and engineering. First—and this is not a semantic detail—the discipline will need a new name. Already there is concern that this stolid, post-Second World War label does scant justice to a field that embraces (amongst others) cell biology, computer science, geophysics, organic chemistry and mechanical engineering. It is truly now a discipline that surveys the behavior of matter in all its guises, short of the extreme energy scales that remain the domain of particle physics. Two of the prime reasons for this expansion of breadth are associated with *scale* and *function*.

The materials devised and created today have important structural features on all length scales between the atomic and the macroscopic (the "everyday" scale discernible to the human eye). Sometimes just a single scale tends to dominate: for the nm-scale crystals that act as "quantum dots" for optoelectronic information-processing devices (which employ both light and electricity as their input and output), it is the size of the crystals that sets the wavelength of light absorbed or emitted. In other cases, the material might acquire important properties from structures over a range of scales. This is typical, for example, of natural materials such as bone, wood and shell—all of them sophisticated composite materials whose superior properties make them attractive models for synthetic products.

One of the key concepts under the umbrella of *scale* is hierarchical structure, which implies that the structure is defined over a multiplicity of length scales. The architectural prototype is the Eiffel Tower, which gains a high strength-to-density ratio by a repeated application of the triangulated crossbeam principle (which an engineer knows as a Warren's truss) over four distinct length scales. (Here, as so often, nature points the way: Warren's truss is seen in the metacarpal bones of a vulture's wing.) But

a hierarchical structure need not simply repeat the same motif at increasing magnification: in bone, for example, each level of structural organization bears no resemblance to the one before.

Traditional methods of materials synthesis will not generally allow for simultaneous control of structure over several length scales. At scales below ~1 μm, this sort of control requires various kinds of chemical expertise. Making nm-scale particles of some inorganic material might involve finesse in colloid science. Organic chemists might then be able to advise on how to attach molecular linkers to the surface of the particles so as to join them together. In any event, this sort of microscopic manipulation is a far cry from the hot-pressing techniques with which a ceramics technologist might be familiar.

The second consideration is *function*, and this forces us to re-evaluate the whole meaning of the term "material." Colloquially, it conjures up some substance that performs a structural role: a steel girder, a cement bridge, a cotton sheet. But increasingly, materials are acting like machines: they *do* things. Materials that emit light, that swell and contract when prompted, that stimulate bone growth or release drugs—all are active substances, qualitatively unlike the passive materials that have traditionally formed the core of the discipline. It then becomes a matter of opinion where "material" ends and "device" begins, or what distinguishes a materials researcher from a computer engineer or a biomedical scientist.

Many of the advanced materials in development today betray a desire to be invisible—not to muscle in on daily life like a garish plastic chair or a chrome-plated staircase, but to carry out their role as unobtrusively as possible. Vibration sensors and switches made from "smart" materials that respond to stimuli in their environment will make aircraft cabins quieter without anyone knowing they are there. Fractured bones will be held in place not by metal plates that will forever trigger airport alarms, but by sutures that slowly dissolve as the bone regrows. Cumbersome and eye-fatiguing televisual screens might give way to electronic ink: microstructured particles that redistribute themselves on a flat white field, looking almost indistinguishable from ink on paper. The world of advanced materials has its Herculean aspects, such as ceramics that withstand awesome temperatures; but it is more often a Lilliputian and modest neighborhood where the job gets done more cleanly and quietly.

2. Synthesis and Processing

How will the materials of the future be discovered and made? We are faced with the curious situation that two current trends in materials synthesis are taking the process of innovation in opposite directions. On the one hand, there is a greater element of design than ever before—materials are planned as if at the drawing board. For example, one can now rationally design and then fabricate organic or inorganic materials perforated with microscopic pores of a well-defined shape and size. This design process may sometimes permit of a modular approach, in the same way that an electronic circuit consists of modules such as amplifiers or pulse generators. A polymer for use in optoelectronic technology might be given some side chains that absorb light at a certain frequency, others that release charged particles when stimulated by the absorbed energy, still others that transport or trap these charges, and so forth.

On the other hand, one of the major innovations of the 1990s in the arena of materials synthesis and discovery was the development of combinatorial methods. These entail the creation of a huge library of materials whose compositions are blends of several different components or substances, mixed at random or in gradually modulated steps. These libraries are analogous to (and sometimes visibly resemble) a color chart for commercial paints, in which each unique hue is composed of a mixture of several different pigments.

Figure 1. A Combinatorial Array (Library) of Ceramic Materials Prepared by Mixing Four Elements in Different Ratios. These are all potential superconductors, and each block will be tested individually to discover its properties

By blending chemical elements in different ratios, or assembling molecular units at random into new molecules, one samples different materials over a whole region of

"composition space." The challenge is then to find an effective, rapid and sensitive way of screening these candidate materials in the hope of discovering one that performs in the manner desired—a superior phosphor, say, or a catalyst, dielectric or superconductor. Combinatorial synthesis may be intellectually less satisfying than rational design—it amounts to little more than trial and error writ large by automated technology—but the accurate, quantitative prediction of materials properties from theory alone remains severely challenging, and so the combinatorial approach may be the most pragmatic for many situations.

It is also important to appreciate that serendipity is as important to the materials scientist as ever it was. One of the most important new materials of the 1990s is the mesoporous form of silica known as MCM-41, created by researchers at Mobil's research laboratories in the early part of the decade. "Mesoporous" denotes the fact that the silica is laced with long cylindrical channels ~10–100 nm across; and the critical feature is that these are uniform in size, and arranged in an orderly fashion, packed hexagonally as if in a honeycomb.

Figure 2. MCM-41, A Porous Form of Silica Permated by Cylindrical Channels of Uniform Size. These can range from ~10–100 nm in width, depending on the method of preparation

This makes MCM-41 a scaled-up version of the aluminosilicate zeolites that are widely used in the chemical industry as highly selective catalysts and "molecular sieves"—their smaller pores are the width of small molecules. MCM-41 is now simply a member of a much broader family of ordered mesoporous inorganic materials: others have slit-like pores or three-dimensional connectivity between pores, and their walls can be made of oxides other than silica. An understanding of the formation process, which involves templating by spontaneously assembling clusters of surfactant molecules, has now led to a strong element of rational design in the creation of these materials. But the initial discovery was unexpected, and stemmed from studies directed at the creation of new types of (small-pore) zeolites.

Rational design of materials has emphasized the importance of the interface with chemistry, in particular because developments in the field of supramolecular chemistry have a great deal to offer the materials scientist seeking control of structure on the scale of nanometers or less. Supramolecular chemistry is the "chemistry beyond the molecule." Whereas the traditional synthetic chemist strives to assemble atoms into a specific molecular geometry, the supramolecular chemist typically uses whole molecules as the fundamental building blocks, and devises ways of assembling them into organized structures and arrays, generally using non-covalent interactions, such as hydrogen bonding or metal-ion coordination chemistry. This makes synthesis possible at a scale extending upwards to meet that at which the engineer can carve structures from monolithic materials. Thus, to make the kinds of microstructures required for, say, electronic circuitry or micromechanical engineering, one now has the choice of adopting either a top-down or a bottom-up approach. Examples later in this section should serve to illustrate the possibilities this presents. One consequence is that the very meaning of the word "material" becomes ill-defined. Supramolecular and colloid chemistry can afford assemblies of diverse components, some of which are single molecules. The term "integrated chemical systems" has been proposed for heterogeneous molecular assemblies of this type that are designed for a particular function. Perhaps the central point is that "materials" are no longer to "chemistry" as "bulk" is to "molecular": much of the action is taking place somewhere in between, at the mesoscopic scale of nanometers to micrometers—the dimensions typical of many of the structures in living cells. Many of the advanced materials of the future will surely be engineered at this size scale.

How will they be put together? Several considerations are leading to a shift away from energy-intensive, "harsh" conditions of synthesis and towards what one might call "soft processing" technologies: solution-phase chemistry (often with water as the solvent), low temperatures, ambient pressure. In part, this trend is driven by environmental considerations: a reduction in energy consumption and in the use of hazardous solvents. In part, it is dictated by the kinds of synthetic procedures pertinent to supramolecular chemistry, which employs gentle inter-particle forces, rather than the strong (and therefore somewhat intransigent) bonds that maintain the integrity of individual molecules.

It is certainly true that toxic organic solvents, high temperatures and ultrahigh vacuums have been widely used in the synthesis of advanced materials—in semiconductor processing, for example. But the recognition that the solvation properties of benign

fluids, such as water and carbon dioxide are markedly different in the supercritical state, has led to their introduction as solvents for several industrial chemical processes that might otherwise utilize organics. Water's critical point, where the distinction between gas and liquid disappears, is at 374 °C and 218 atmospheres. Substances that are sparingly soluble in liquid water may become appreciably so in the supercritical fluid, and vice versa. Reaction rates also differ significantly: many organic compounds, for example, can be efficiently oxidized in supercritical water. Carbon dioxide, with its lower critical temperature of 31 °C, is a more amenable supercritical solvent, and has been used, e.g., in the fabrication of nanoscale particles of various materials, including drugs.

Liquid water too, is finding increasing use as a solvent. Electrochemical processing from aqueous solution can deliver thin films of technologically useful oxide ceramics such as barium, strontium and lead titanate, and lithium niobate. Electrodeposition has been used to make complex many-layered "superlattices" of metals and ceramic materials, which are more conventionally fabricated using high-temperature vapor deposition methods. And hydrothermal methods, which employ moderate temperatures and aqueous solutions comparable to the conditions of some geological processes are used in zeolite synthesis amongst other things, and have been proposed for the fabrication of diamond films.

3. Biomedical Materials

One place where the new face of a functional, nano-engineered materials science should be felt most keenly is in the hospital. We have, since time immemorial, been able to do little better in effecting mechanical repairs to the body than if it were an inanimate machine. Thus, prostheses of wood or metal have evolved into robotic limbs of immeasurable benefit to the recipient, but nonetheless a tacit submission to the traditional idea that the ways and materials of engineering have little or no overlap with those of biology.

This disjunction becomes all the more stark in the case of artificial organs, and it is perhaps remarkable that a heart imitated by a plastic air-blown pump, or a kidney by a plastic membrane filter, does so well! Such synthetic devices are by no means crude in engineering terms: the Jarvik-7 artificial heart, for example, has complex laminated polymer walls designed to minimize an inflammatory response and to incur low friction and wear as it inflates and deflates. This device has been used to sustain many patients awaiting urgent cardiac transplants. But nothing of the kind will suffice for long-term use.

In biomedicine, "minimal visibility" of materials was long equated with inertness: as long as a material in contact with the bloodstream did not provoke an allergic, toxic or inflammatory response, it was deemed adequate. But to an organism, utter passivity is not at all the same as invisibility. An inert material is typically regarded as a wound, triggering the creation of scar tissue at the interface. To truly look like a biological material, an implant must be active, capable of a kind of communication with the surrounding cells. That is why, for example, artificial blood vessels made from polymers such as polytetrafluoroethylene (in a porous form comparable to the Goretex

fabric) may be given a lining of the protein heparin, which prevents blood clotting. The epithelial cells of real blood vessels release heparin to combat thrombosis, and the same end is served by immobilizing heparin at the surface of synthetic vessels.

The same broad principle is being employed in materials that simulate bone. Here, one finds a tidy illustration of the many, sometimes conflicting, demands placed on a biomedical material. Clearly a bone replacement must be strong and lightweight. Metals such as stainless steel and titanium have good fracture-resistance, but are considerably denser than real bone. The material must also be corrosion-resistant, and if, as in hip joints, it is liable to be subjected to movement against another hard surface, wear resistance is crucial. Flexibility similar to that of real bone is also an important attribute. And if the material takes up too much stress in its load-bearing capacity, it can induce dissolution and weakening in surrounding bone.

Small wonder, then, that the best bone replacement materials are composites that derive the right combination of properties from several distinct substances: e.g., fiber-reinforced polymers. A porous microstructure is important both mechanically, and to allow ingrowth of new tissue, so that the implant can develop an intimate interface with freshly grown bone. Natural coral has been used as a master for making molds with the required porosity.

Yet even this falls short of providing a material that can bind smoothly and securely to real bone, as an implant is commonly required to do. Again, inertness is in this respect a hindrance, not a help. The formation of fresh bone demands a surface that is conducive to the bone-depositing osteoblast cells. Bioactive ceramics are materials that actively encourage this regrowth. These "bioglasses" are typically mixtures of silica with sodium, calcium and phosphorus oxides, which appear to be capable of mimicking the behavior of the calcium phosphate (hydroxyapatite) component of real bone. Osteoblasts will create crystallites of a carbonate-containing variant of hydroxyapatite, a precursor to the deposition of true bone, on the surface of the bioactive ceramic, and this helps to weld together the new bone and the implant. Composites of bioactive ceramics with metals or polymers can achieve an attractive combination of strength, flexibility and compatibility with natural tissue.

If even "mechanical" biological structures like blood vessels and bone display this complexity of interaction with the surrounding tissue and fluid, what are the prospects for developing materials systems that have a more active biological role, like that of the liver, the cornea, the spinal cord or the brain? While some organs have a function that one might hope to mimic crudely in purely artificial devices, there are others whose job can, at present, be conducted only by the living cells themselves. We simply do not know how to make an artificial nerve cell or neuron that interfaces seamlessly with the real thing.

Therefore, the ultimate in biomedical materials engineering is to find ways of growing the biological tissue itself: to grow new organs in culture, seeded by the cells of the intended recipient. This is called tissue engineering.

The process, as yet still hypothetical, is something like the following. Rather than

having to await a suitable donor and then run the risk of transplant rejection, a person suffering from kidney failure has a smattering of cells removed from her kidney. These are scattered within a porous polymer material shaped like a kidney, and the cells are stimulated into growth by the right amounts of nutrients. Slowly the cells multiply and colonize the scaffold, which is gradually dissolved away as the tissue forms around it. The cells are provided with the hormones that promote the formation of a network of blood vessels, ensuring that the nutrient-bearing "blood" gets distributed throughout. The final product is a fully grown kidney, complete with blood supply, ready to be implanted in the patient and fully compatible with her immune system.

Some researchers even speculate that, given an appropriately shaped scaffold seeded with cells of the requisite tissue types, an entire artificial arm could be grown in culture to replace one lost in an industrial accident. Once grown, it is simply stitched into place.

This is not as far-fetched as it sounds. Already, tissue engineering has been used to grow skin that can then be used for treatment of severe burns. At least two US companies have developed synthetic skin: Advanced Tissue Sciences have produced Dermagraft, grown from tissue-forming epidermal cells on a thin mesh of a biodegradable polymer, while Graftskin, using a collagen matrix, is the product of the company Organogenesis.

Figure 3. Graftskin, Artificial Skin Grown from Cultured Cells on a Scaffold of Biodegradable Polymer

The key to these advances is a suitable polymer scaffold: the material should be broken down slowly by the cells into non-toxic by-products. A copolymer of lactic and glycolic acid is a favorite material (approved by the US Food and Drugs Administration), which

is degraded to carbon dioxide. Liver cells have been cultured in such supports. The formation of blood vessels (angiogenesis) can be encouraged by doping the scaffold with the protein called angiogenic growth factor, which does just what the name implies. Similarly, bone growth in a biodegradable scaffold may be stimulated using bone morphogenic protein.

Many organs are not, however, just a mass of cells. They might contain several different tissue types interwoven in a complex geometry that is essential to proper cell-to-cell communication. For example, the hepatocyte cells of the liver are mixed in with tissue-forming fibroblasts. Hepatocytes cultured in isolation do not function so efficiently. The right blend might be achieved by growing the two cell types on surfaces treated with a thin layer of cell-adhesion molecules. Techniques of microlithography, discussed in Section 6, may be used to imprint a microscopically patterned film of adhesion molecules on the surface, and hepatocytes will then stick only to the patterned areas. Once growth is underway, the intervening spaces can be made adhesive too, and fibroblasts deposited in these interstices. Studies of this kind have shown that there is an optimal patterning scale at which the hepatocytes function best.

Biomedical materials are therefore moving in two related directions. The first is towards greater biological integrity: synthetic materials are being developed for their ability to interact with cells in beneficial ways, so that the interface of the natural and the artificial is as unobtrusive as possible. The ultimate extension of this approach is then to remove the interface altogether: to grow real biological materials, assisted by supports and scaffolding that direct and stimulate the growth before, in the ideal case, being destroyed by the very tissues whose formation they have promoted.

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Biographical Sketch

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