Novel materials

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Materials have central roles in all fields of engineering; they define, through structures and devices, our interfaces to the physical and the virtual world. The emergence of new materials catalyzes transformative advances in civilizations, to an extent that eras of human development are often defined by the prevailing materials used in engineered systems, from the Stone, Bronze, and Iron Ages to the present times, aptly referred to as the Silicon or the Polymer Age. From an academic standpoint, the fundamental phenomena that define complex relationships between chemical compositions, structures, and properties in advanced materials serve as the basis for some of the most intellectually stimulating and dynamic areas of research in the physical sciences. This work has additional appeal because it is intrinsically interdisciplinary and combines essential aspects of traditional fields of study in physics, chemistry, and even biology, to an increasing extent, together with engineering processes and control strategies. Progress in materials science and in the engineering application of new materials is essential to the pursuit of solutions to societal grand challenges. Examples span those related to the development of sustainable sources of energy, from high-power magnets for wind turbines to designer semiconductors for solar cells; to the invention of technologies that improve human health, from metal alloys for lightweight prosthetics to polymer matrices for controlled drug release; to progress in intra- and interplanetary travel within realms of objective and virtual reality alike, from high-efficiency batteries for emissions-free vehicles, to carbon composites for fuel-efficient spacecraft, to atomically thin films for high-speed integrated circuits.

This Special Feature on Novel Materials presents a collection of perspectives articles, short reviews, and original research papers designed to capture some of the breadth and excitement in recent materials research. This representative set of topics intersects critical areas in electronics, biology, advanced manufacturing, and chemical synthesis, with interdisciplinary foci that combine scientific discovery with engineering applications. The issue begins with three articles on materials for classes of biomedical devices that offer capabilities with direct benefits in human health. The first article, by Ailianou et al. (1), describes fundamental studies of biodegradable polymers used in advanced vascular scaffolds designed for the treatment of coronary heart disease. These devices, known as stents, deploy into blood vessels where they provide structural reinforcement following procedures to remove obstructive plaques. Traditional metal stents, used on more than a half-million patients annually, remain in the body, where they present lifelong risks, most significantly because of their tendency to nucleate the formation of blood clots. Biodegradable polymers provide an alternative, in the form of stents that dissolve and disappear gradually after their function is no longer needed, thereby eliminating unnecessary device load on the patient. Such types of stents are rapidly replacing conventional counterparts. The findings reported in the Ailianou et al. article provide important insights into the morphological characteristics of the constituent polymers that confer the mechanical strength necessary for these and related applications. In particular, the authors discover that deformations caused by deployment of these stents align the polymer chains in a manner that increases their strength and prevents the formation of fractures. Such understanding has important practical implications for the engineering design of ultrathin, low-profile devices.

The second article focuses on materials designed to prevent the formation of clots and biofilms on the surfaces of stents and other implants. Specifically, Sunny et al. (2) introduce a composite coating that consists of a porous solid matrix filled with a liquid, to yield a repellent surface that prevents fouling. This system, as demonstrated in transparent coatings on endoscopes through a comprehensive set of animal trials, involves a design inspired by the slippery surfaces of the carnivorous pitcher plant, in which the liquid-infused material spontaneously forms a biocompatible, lubricating, "nonstick" overlayer. For endoscopes, the result is significantly enhanced antibacterial

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and antifouling properties, with an associated reduction in the need for time-consuming processes to clean the imaging lenses. The consequences include decreased time and cost for endoscopic procedures, with reduced risks to the patient and the ability to visualize previously obscure regions unobstructed and uninterrupted. Potential uses extend beyond camera-guided instruments, surgical tools, and biomedical implants, to icephobic surfaces that can improve the safety of aircraft, clog-resistant oil pipelines that can reduce the probability of spills, and marine antifouling hulls that can increase the fuel efficiency of ships.

The third article in this area, by Fang et al. (3), reports a materials solution to a long-standing challenge in classes of implantable devices that, unlike endoscopes or biodegradable stents, must provide reliable electronic functionality over the lifetime of the patient. In established technologies of this type, such as cardiac pacemakers and cochlear implants, the electronics reside in metal or ceramic housings. Interfaces to the body occur through point contacts established via electrode pads at the terminal ends of connecting wires. Recent research establishes materials strategies and device designs for flexible, conformal devices that can integrate directly with the curved, moving surfaces of critical internal organs, to provide qualitatively more sophisticated modes of operation in which the integrated electronic systems themselves, rather than wired electrodes, establish the biotic/abiotic interface. A key challenge in achieving stable, long-term function with such systems is in the development of thin, flexible coatings as structurally perfect, impermeable barriers to prevent penetration of surrounding biofluids into the active electronics. Results presented by Fang et al. (3) demonstrate that pristine, thin films of silica, thermally grown on the surfaces of device-grade silicon wafers and then physically integrated on top of flexible electronics platforms, can satisfy these demanding requirements, with projected operational lifetimes of many decades. This advance in materials science leverages a long history of innovations in crystal growth, purification, cleaving, and polishing techniques that underpin the capacity to manufacture silicon wafers with a nearly complete absence of impurities or crystal imperfections and with surfaces that have roughness measured at the atomic level. Silica that forms by oxidizing the surfaces of such wafers yield thin, electrically insulating layers of water-proof glass with similar levels of perfection and uniformity. Large-area films produced in this manner can reliably and reproducibly integrate with the most advanced forms of flexible electronic devices to yield impenetrable biofluid barriers. The outcomes enable long-lived biomedical implants that can bend and conform to the surfaces of critical organs, such as the heart or the brain, to provide clinically relevant modes of operation in stimulation and electrophysiological mapping that cannot be achieved with rigid, sealed electronic platforms and wired point contact interfaces that are available today.

The next two articles involve additional classes of materials with relevance to these and other types of advanced electronic systems. In the first article, Kang et al. (4) report methods for creating and purifying microscale sheets composed of phosphorous atoms chemically bonded together in a 2D construct, with thicknesses as small as a single atomic diameter. This material, known as phosphorene, has excellent semiconducting characteristics and remarkable mechanical properties. These features suggest potential uses in advanced electronic components, including transistors that might find roles in the types of flexible devices described in the previous paragraph. The methods introduced by Kang et al. rely on aqueous solution dispersions and centrifugation techniques to yield phosphorene with unmatched materials quality. The resulting high-performance "inks" can be delivered by low-cost printing techniques to substrates of interest for the construction of various types of electronic devices. Demonstrations include field-effect transistors with key properties that exceed those of devices formed with phosphorene synthesized in other ways.

The second article on electronic materials, by Kim et al. (5), summarizes recent progress in the development of light-emitting devices (LEDs) that have the potential to enable displays with brighter, more vivid colors and lower materials costs compared to those of technologies that currently dominate the consumer electronics market. The active materials include both organic and inorganic constituents, combined in ways that provide great versatility in their chemical compositions, crystalline structures, and associated properties. Although many of these so-called hybrid materials are historically old, rapid advances over the last three years in methods for chemical modification and physical deposition in forms optimized for operation in LEDs position these technologies as leading candidates for displays of the future, including those with paper-thin geometries and bendable mechanics. The materials and approaches for flexible and printable electronics embodied in the preceding pair of articles could be relevant in this context, as backplane driver circuits for these hybrid LEDs.

In any complex system, such as a display, materials-processing strategies and fabrication schemes are critically important. Although solution printing approaches such as those used for the phosphorene electronic inks in the paper by Kang et al. (4) are valuable, they are best suited for forming patterns of thin films in largely planar formats. Research over the last decade has established a broad range of materials and methods for printing 3D objects. The article by Janusziewicz et al. (6) reports progress on one of the most powerful and newest of these techniques. Here, specialized photosensitive polymers enable a process in which continuous exposure of a liquid precursor material to programmed patterns of light yields—in a continuous manner—3D objects in complex geometries, without the rough, layered morphologies that characterize parts formed using traditional methods. The resulting levels of uniformity in physical properties and degrees of precision in surface finish significantly exceed those of any alternative. The materials insight that underpins this technique is that the presence of oxygen can inhibit certain light-initiated reactions that cure liquid monomers into solid polymers. Janusziewicz et al. exploit this behavior by using an oxygen-permeable optical window that prevents growth of polymers directly on the window, where the oxygen concentration is high, but allows it to proceed unimpeded in adjacent regions where the concentration is low. Passing a sequence of patterns of light through this window in a coordinated fashion as it continuously moves through a liquid bath of monomer yields 3D parts with user-definable geometries. The high-speed nature of this process has the potential to expand the use of 3D printing beyond its traditional realm in prototyping, into high-volume, cost-effective manufacturing where the polymer materials will continue to play key roles in tailoring the resulting parts to satisfy application requirements.

In the article by Haines et al. (7), the authors demonstrate an interesting application of unusual, 3D polymeric structures formed by techniques of spinning and weaving rather than by 3D printing. Here, helical coils of oriented polymer fibers generate large and reversible changes in length as a result of thermal expansion under this type of geometric constraint, even with mild levels of heating/cooling. The underlying process involves winding/unwinding of these helical constructs such that actuators can be engineered as a kind of artificial muscle composed of individual strands, linear arrays of them, or 2D woven fabrics. Motion in such cases occurs through processes associated with intrinsic changes in the constituent materials, as a solid-state alternative to mechanical machines that rely on gears, pulleys, and motors for similar purposes. These materials-based actuators can deliver levels of specific work that exceed those of natural muscle by 50 times, and they offer the ability to create torsional actuation for rotational motions that can reach speeds of over 100,000 revolutions per minute. Such capabilities are of additional interest when considered in the context of the biomedical materials systems discussed in the first three papers (1–3).

The final article in this Special Issue provides perspectives on a strategy to produce 3D materials that is radically different from the 3D printing schemes and winding/weaving processes described above. In this piece, O'Brien et al. (8) outline fundamental considerations in the formation of systems by hierarchical organization, where structures that develop at one length scale are used as building blocks for a larger length scale. The corresponding processes range from formation of nanoparticles from atomic precursors, the organization of molecules on the surface of these nanoparticles, and eventually on materials built from nanoparticles, where the structure is guided by the results from the preceding length scales. This interconnected description reveals how the uniformity and control of one length scale profoundly impacts what can be achieved at each subsequent length scale. A goal of this work is to develop foundational concepts in materials science that can address the unique challenges associated with structural and compositional control in these unusual systems.

Our hope is that this overview and the associated collection of articles in this Special Issue can convey some of the vibrancy and excitement associated with modern research in advanced materials. The topics presented here are of interest not only for their basic scientific content in issues related to the growth of materials and structures, their intrinsic mechanical, chemical, and electrical properties, and the nature of interfaces between materials and biological systems, but also for their core relevance to engineering applications in areas ranging from biomedical devices to consumer electronics. The topical breadth, interdisciplinary content, and direct linkages to societal grand challenges suggest a bright and essential future for research on novel materials.

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2 Sunny S, et al. (2016) Transparent antifouling material for improved operative field visibility in endoscopy. *Proc Natl Acad Sci USA* 113:11676–11681.

3 Fang H, et al. (2016) Ultrathin, transferred layers of thermally grown silicon dioxide as biofluid barriers for biointegrated flexible electronic systems. *Proc Natl Acad Sci USA* 113:11682–11687.

4 Kang J, et al. (2016) Stable aqueous dispersions of optically and electronically active phosphorene. *Proc Natl Acad Sci USA* 113:11688–11693.

5 Kim Y-H, Cho H, Lee T-W (2016) Metal halide perovskite light emitters. *Proc Natl Acad Sci USA* 113:11694–11702.

6 Janusziewicz R, Tumbleston JR, Quintanilla AL, Mecham SJ, DeSimone JM (2016) Layerless fabrication with continuous liquid interface production. *Proc Natl Acad Sci USA* 113:11703–11708.

7 Haines CS, et al. (2016) New twist on artificial muscles. *Proc Natl Acad Sci USA* 113:11709–11716.

8 O'Brien MN, Jones MR, Mirkin CA (2016) The nature and implications of uniformity in the hierarchical organization of nanomaterials. *Proc Natl Acad Sci USA* 113:11717–11725.