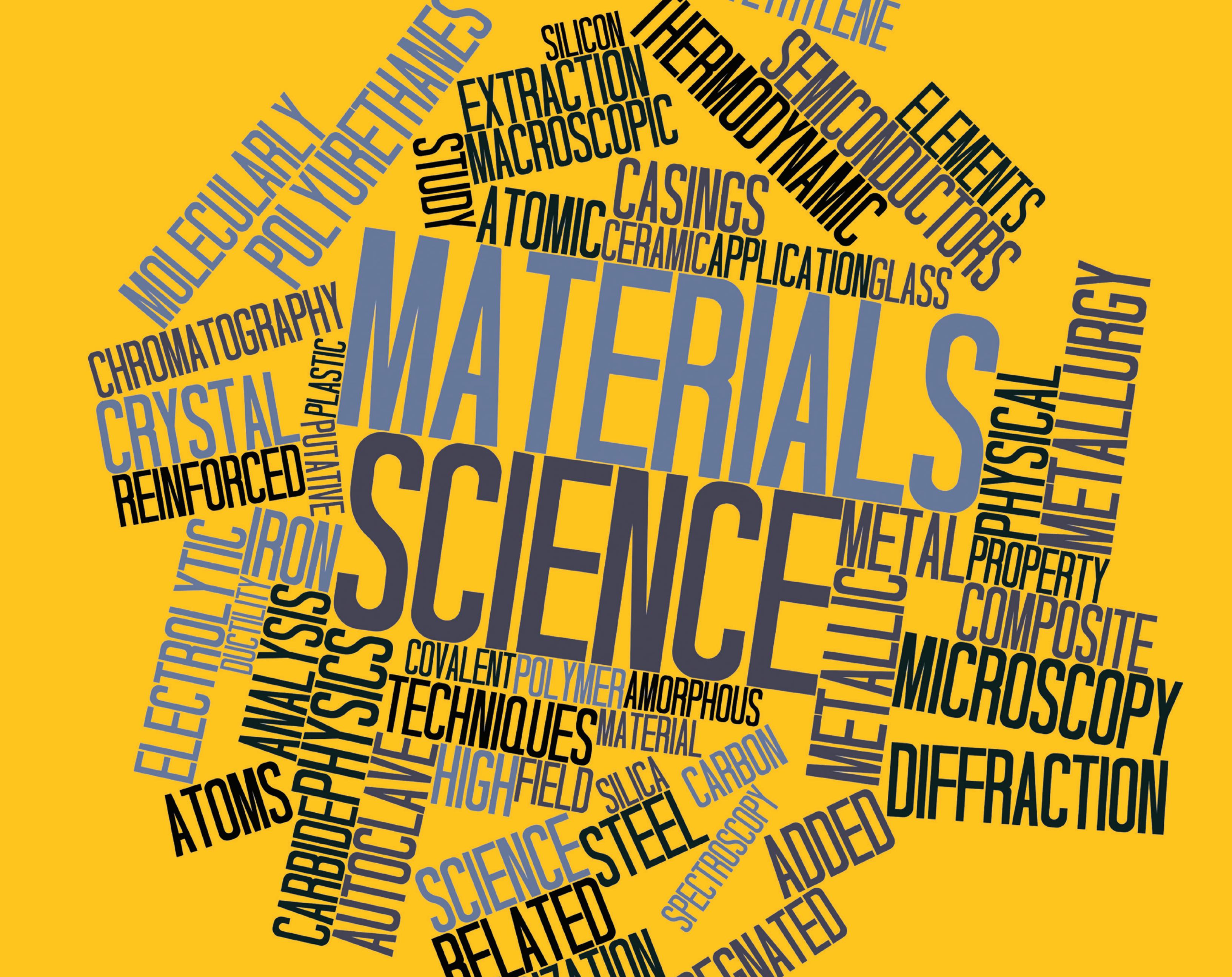

New Frontiers in the Chemistry of Materials Design and Applications

A white paper examining the latest developments in the creative design and fabrication of new and existing materials with applications in energy, electronics, coatings, and biomedical devices.

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New Frontiers in the Chemistry of Materials Design and Applications

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ABOUT THIS REPORT

ABOUT THE AUTHOR

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I. INTRODUCTION

Materials scientists rely on information from physics, chemistry, and engineering to design new materials; improve or modify existing ones; and develop new fabrication methods. The interdisciplinary nature of the field often means that graduates in materials science have a variety of skills that allows them to adapt to changing economic conditions.[1] According to the U.S. Bureau of Labor Statistics, jobs for materials scientists are expected to grow 5% — about 400 jobs — between 2012 and 2022. That growth is driven largely by the need for cheaper and safer materials for energy, electronics, and transportation.

This report will explore the frontiers of materials science, from design cues gathered from natural materials to materials designed for particular applications. Often, cutting-edge materials have yet to find their way to commercial products, but useful information can be found in how researchers create materials with properties needed for a given application and manufacturing process.

II. SYNTHETIC MATERIALS INSPIRED BY NATURAL STRUCTURES

Years of evolution have resulted in natural materials with properties like strength, iridescence, stickiness, and water repellency.[2] Synthetic materials with similar properties would be commercially valuable.[3] Spider silk, for example, is five times stronger than steel and three times tougher than Kevlar, a polymer used in bullet-resistant body armor.[4] But synthetic silk is harder to produce than other polymers. That's because natural silk is made from fine protein fibers, and more than 1,000 fibers are needed to make useable thread. Nevertheless, a group of small companies are developing methods of producing synthetic silk proteins and spinning thread that may make artificial fibers cost-effective for textiles and medical sutures, among other uses.[4]

COPYING THE SPIDER

Developers of synthetic spider silk are at various stages of progress

ORGANIZATION	TECHNOLOGY	INITIAL PRODUCT	DEVELOPMENT STATUS
AMSilk	*Escherichia coli*	Protein powder for shampoo, cosmetics	Already commercial
Araknitek	*E. coli*, transgenic alfalfa, goat, silkworm	Fiber for health care and more	Building pilot facility
KAIST	*E. coli*	Fiber stronger than Kevlar	Mulling partnership
Kraig Labs	Transgenic silkworm	Hybrid spider-silkworm fiber for textiles	Scaling up to commercial
Spiber	*E. coli*	Fiber and films for multiple uses	Pilot facility planned for 2015

KAIST = Korea Advanced Institute of Science & Technology.

Sometimes scientists recreate natural structures by using a natural material as a scaffold for a synthetic one. Scientists at the Georgia Institute of Technology covered grains of pollen from sunflowers in iron(III) isopropoxide. Heat-treating the coated grains destroyed the organic matter and converted the iron coating to magnetic magnetite (Fe_3O_4). The magnetic pollen grains adhered to a variety of surfaces with similar forces as natural grains, and the magnetic forces extended about one millimeter beyond the synthetic grains.[5]

Researchers also look for ways to make new materials by observing the formation of natural material. Sponges produce tiny needles called spicules that get their strength from alternating layers of mineral and protein. German researchers created synthetic spicules that were stronger and more flexible than natural ones by increasing the amount of protein in the needles.[6] The researchers also changed the mineral phase to be calcium-based instead of silica-based.

MOLECULAR AND NANOSTRUCTURE MIMICS: MUSSELS, GECKO FEET, AND LOTUS LEAVES

The molecular structure of natural materials also provides inspiration for synthetic materials. Mussels secrete a protein glue that helps them stick to rocks. A key component of this glue is an amino acid called 3,4-dihydroxy-L-phenylalanine (DOPA). While the exact attachment mechanism is unknown, it's thought that the catechol group in the side chain of the amino acid sticks to surfaces by forming covalent bonds to amines or thiols on some surfaces. The catechol may also form non-covalent interactions with metal ions.[7] Synthetic materials mimicking this adhesive are made by polymerizing dopamine or other catechol-containing building blocks.[8] These materials could be useful for underwater coatings that resist algal growth or for medical glues that remain sticky when wet.

However, unintended adhesion or catechol oxidation are two challenges when preparing mussel-inspired coatings. To overcome these obstacles, researchers have developed ways to protect catechol-containing polymers so that the group covering the catechols can be removed with light[9] or mild acid.[10]

GECKO FEET

For other natural materials, nanoscale structure provides interesting properties like adhesion or self-cleaning.[11] Advances in nanoscience allow scientists to mimic the characteristics of these materials as well.[3] Gecko feet contain three-dimensional structures of various widths that maximize adhesion to rough surfaces. Macroscale disks, or lamellae, on the pads of their feet contain microscale columns called setae. Increasingly narrow structures extend from the setae, branching until ending in nanoscale spatulae. Two gecko feet can contain about three billion spatulae.

Many research groups have made dry adhesives inspired by the hierarchical structure of gecko feet. In 2012, researchers developed a simplified method to produce a material with columns ending in tiny pads.[12] To improve the adhesion of their polyurethane coating, the researchers tilted the columns to mimic the directionality of setae in gecko feet. Both Tokay gecko setae and the artificial adhesive had similar ratios of frictional force to adhesive force when the materials were activated in their gripping direction.

Another interesting property of gecko feet is their ability to slough off dirt and regain stickiness. A recent study of synthetic coatings revealed that self-cleaning may involve features resembling macroscale lamellae. Building a coating that can clean itself as it brushes against a surface could help gecko-inspired adhesives reach practical applications in reusable tape or medical adhesive. Metan Sitti, at Carnegie Mellon University, and colleagues developed the first gecko-inspired adhesive that replicated the adhesion strength and self-cleaning ability of actual gecko feet on a smooth surface.[13] To determine how surface structures influence self-cleaning, the researchers built three different coatings of polyurethane pillars topped with mushroom-shaped pads. The coatings differed in the width of the pads and the spacing between the pillars. The researchers simulated dirt particles by covering each coating with silica beads of varying diameters. Then the scientists dragged the "dirty" coating along a glass surface to remove the beads from the surface of the pads. Coatings with pads smaller than the beads recovered almost complete adhesiveness after eight rounds of dragging. Coatings with pads larger than the beads regained less adhesion after repeated cleaning, but they maintained more stickiness immediately after contamination. The scientists then created a coating that had rows of pillars separated by wide grooves to mimic lamellae. A scanning electron micrograph of the surface after contamination and cleaning showed that most of the particles had fallen into the grooves, temporarily cleaning the surface of the pads until the gaps filled with particles. The particles remained on top of a coating with pillars but no grooves.

LOTUS LEAVES

Lotus leaves also have a nanostructured surface that provides inspiration for new materials. Epidermal cells create macroscale bumps on a leaf surface, and waxes create nanoscale roughness. These tiny features trap air in the valleys between each bump. Water droplets sit on top of the bumps and capture dirt as they roll off a leaf.

Materials scientists recreate this structure to make water-repellant and self-cleaning coatings.[14] Surfaces that repel oil would also have practical applications.[15] Lotus leaves provide little help in making oleophobic coatings, but another plant provides useful design ideas. The pitcher plant traps a meal of insects in a pool of fluid at the bottom of its elongated leaf pitcher, and the surface of the leaf helps bugs slide inside. The micro-textured walls of the pitcher hold fluid so that a layer of water forms on the surface. This fluid film repels oil on the legs of insects. Bugs step on the film, slip into the pitcher, and slide down the walls to the fluid at the bottom. Inspired by that natural material, Joanna Aizenberg, at Harvard University, and colleagues designed a fluid-filled coating that repels both oil and water.[16] They filled a

Teflon membrane with commercially available fluorinated liquids, like 3M's Fluorinert FC-70 or DuPont's Krytox oils. Blood and ice fell cleanly off the new surface, yet they remained stuck to superhydrophobic surfaces. Ants could not climb up the new surface, though they could ascend a Teflon membrane. The researchers used this approach to design an ice-resistant coating for aluminum.[17] Such coatings could be used to reduce damage on airplane wings, wind turbines, and electrical wires.

SELF-HEALING MATERIALS

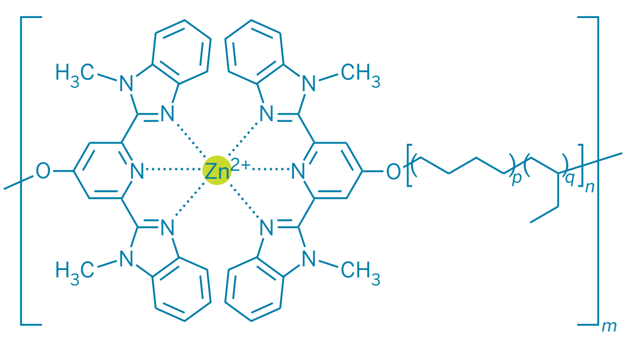
Materials used for coatings and structures inevitably degrade and fail. A common solution to this problem is making stronger materials. Another solution is inspired by the ability of biological systems to repair themselves when damaged.

In 2001, Scott R. White, at the University of Illinois, Urbana-Champaign, and colleagues developed an epoxy that repaired itself when cracked. The material contained microcapsules filled with one of two compounds: dicyclopentadiene or a ruthenium carbene Grubbs catalyst used for ring-opening metathesis reactions. Damaging the epoxy ruptured the microcapsules and mixed the contents. The catalyst reacted with the dicyclopentadiene to form a new polymer that filled the gap.

That idea sparked the growing field of self-healing materials.[18, 19] Since then, scientists have developed structural composites, adhesives, coatings, flexible polymers, ceramics, metal, and concrete that can heal themselves.

There are several approaches to building self-healing polymers. Some contain microcapsules of reagents, like the original design. Other materials replace the capsules with channels of reagents running through the material, mimicking the vascular system in a human body. Vascular materials repeatedly repair themselves after several wounds because the healing reagents refill the network. Capsule-based systems, on the other hand, cannot refill themselves.

Another design strategy involves building the healing ability directly into the molecular structure of the material. A group led by Stuart J. Rowan, of Case Western Reserve University, and Christoph Weder, of the University of Fribourg (Switzerland), designed a material to repeatedly heal itself when triggered by light. The researchers built short polymer chains that ended in large ligands. The ligands bound a metal ion, either zinc or lanthanum, and the chains essentially became high-molecular-weight polymer.[20]



The self-healing metallosupramolecular polymers are made from repeating units of a small polymer with ligands that bind to metals.

Shining light on the material broke the bonds between the metal and the ligand. The material, now a liquid, could flow into cracks and scratches. Removing the light caused the material to re-harden. Because the healing ability is intrinsic to the material's chemical structure, it could repair itself multiple times.

Materials that can heal themselves without an external stimulus like light are also useful. Intrinsically self-healing materials can be made with components that form reversible connections. However, weak connections that maximize self-healing also reduce the strength of a material. To solve this compromise between healing and strength, researchers at the University of California, Irvine, developed a self-healing polymer that contains two phases: soft polyacrylate-amide brushes extending from a hard polystyrene backbone.[21] The polymer self-assembles into nanoparticles, with the polystyrene component at the core of the particles and the brushes extending like a shell. The nanoparticles assemble into a thermoplastic elastomer that has both hard and soft domains. The amides on the ends of the brushes form hydrogen bonds with each other. Damaging the materials separates these connections, but the bonds easily reform to heal the material.

Another self-healing material repairs itself by reforming hydrogen bonds, though it is unique because healing restores mechanical strength as well as electrical conductivity. The researchers envision the composite as an electronic skin for robots or in prosthetic devices.[22] To make a conductive material, Zhenan Bao, at Stanford University, and her colleagues added nickel microparticles to a randomly branched network of polyurethane. The polymer forms hydrogen bonds to itself and to oxides on the surface of the microparticles. Electrical conductivity is restored to 90% of its original value within 90 seconds after damage; complete mechanical healing takes 30 minutes.[22] The researchers used the material to build a pressure sensor and a bending sensor, both applied to a small wooden mannequin.

III. MATERIALS FOR ELECTRONIC CIRCUITS AND DEVICES

Integrated electronic circuits like computer chips are commonly made from silicon-containing semiconductors. Electronics manufacturers produce smaller, faster, and cheaper products by tweaking the chemical composition of the semiconductors or changing how they are constructed into devices.

However, the performance of traditional silicon-based transistors, the workhorses of computer chips, becomes limited as the size of the elements gets smaller. New materials made from carbon or alternative semiconductors will be needed to improve device performance.[23] These "exotic materials" could also bring new properties such as flexibility and transparency to devices.

GRAPHENE

The discovery of two-dimensional sheets of carbon atoms called graphene electrified the scientific community in 2004, because until then, it was expected that individual sheets would roll into tubes instead of remaining flat. The honeycomb structure and atomic composition of graphene give the flat sheets interesting mechanical and electronic properties. Though a sheet of graphene is only one atom thick, the material conducts electricity as well as copper does, and it carries current quickly at room temperature.

The discovery of graphene brought talk of faster transistors and transparent touch screens, among other applications. Research into graphene has exploded for such applications as biomedical sensors, electronic components, and energy storage. Though many graphene applications are still under development, the material's scientific value was recognized when the two scientists who discovered it were awarded a Nobel Prize in physics in 2010.[24]

Commercially available graphene materials currently include flakes and printable inks.[25, 26] Production is growing, but the market could involve some risk. In early 2014, a financial regulator in the United Kingdom warned the country's investors that opportunities to buy the material as a commodity may be fraudulent, as products sold may be other forms of graphite, not graphene.[27] Today, graphene is being incorporated into flash memory devices[28] and integrated circuits to amplify current.[29] However, the material's lack of a band gap poses a significant obstacle to graphene's utility for current-switching transistors.[30] Without a band gap, electrons constantly flow through the material, and the current cannot be switched on and off. Therefore, researchers are considering other two-dimensional materials with inherent band gaps as candidates for future fast and thin devices.

The first integrated circuits made from any two-dimensional material were produced using molybdenum disulfide (MoS_2) in 2012 by researchers at the Massachusetts Institute of Technology. However, the quality of the material made with current methods affects its electron mobility.[31] Other two-dimensional materials include boron nitride and a recently discovered form of silicon called silicene.[32] Researchers at Drexel University discovered tri-layered materials made from an early transition metal, a main-group element such as aluminum or silicon, and a layer of carbon or nitrogen.[33]

ORGANIC ELECTRONICS

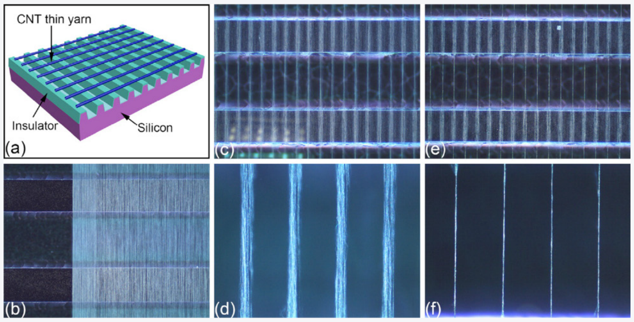
Polymers and small molecules can also be used to make electronics. Organic semiconducting molecules, whether independent monomers, short oligomers, or long polymers, have some common structural features. The carbon skeleton contains alternating single and double bonds, making a conjugated backbone similar to the one in graphene. Scientists tune the electronic properties of the molecules by replacing some of the carbon atoms in the backbone with heteroatoms like nitrogen or sulfur. Side chains (continued on pg. 9)

CARBON NANOTUBE DEVICES

Carbon nanotubes (CNTs) have been used to build electronic devices for more than a decade.[34] Like graphene, nanotubes conduct electrons faster and more energy-efficiently than silicon.

One challenge with building reliable devices from CNTs involved separating semiconducting tubes from metallic ones. Synthesizing or separating high-purity nanotubes still remains a challenge for large-scale CNT device production.[35] However, carbon nanotubes have been used recently to build rudimentary versions of common electronics: a computer and speakers for "earbud" headphones. Researchers at Stanford University built a carbon nanotube computer chip containing 178 transistors. To do this, they developed a method to destroy metallic nanotubes and pattern the semiconducting ones on a chip to prevent misalignment that causes computational errors. The CNT computer could count and do number sorting. That performance resembles 1950s-era computers, yet it was the most complex carbon-based electronic system yet realized at the time.[35]

To make speakers for earbud headphones, researchers carved grooves into a silicon chip. They filled the grooves with aligned carbon nanotubes and cut the film into strips using a laser. When treated with ethanol, the strips shriveled into 1-µm-thick strands similar to yarn. The researchers passed alternating current through the yarn to heat the nanotubes. This caused the air around the nanotubes to expand as it warmed and contract as it cooled, generating compressions of sound waves. The researchers reported that the headphones worked for more than a year.[36]



(a) A sketch of the CNT thermoacoustic chip. (b) CNT thin film across the 600 µm wide grooves. (c and d) Suspending CNT stripes with different magnifications. The stripes are 30 µm in width, and the pattern period is 120 µm. (e and f) As-fabricated thin yarn arrays with different magnifications.

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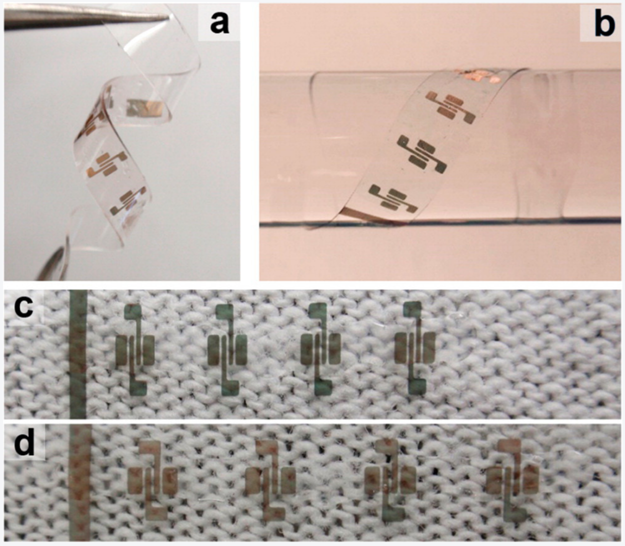
Flexible electronics are touted as the next generation of devices. Carbon nanotubes are ideal materials for these devices because they are bendable and strong. But making nanotubes into stretchable transistors is difficult because every part of a transistor has to move without breaking. Researchers at the University of Wisconsin in Madison recently built a flexible transistor using nanotubes.[37]



Demonstration of stretchabiltiy. FETs fabricated from CNTs transferred to strained PDMS twisted between tweezers (a), conformally wrapped around a glass rod (b), and adhered to a textile and stretched to 30% (c,d).

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The key was replacing a rigid layer commonly made from inorganic oxides with an ion-containing gel. The team attached a nanotube film to a piece of rubber, covered the film with gold electrodes, and topped the gold with the ion gel. The devices stretched to 57% of their original length when pulled, almost three times more than previous stretchy devices.

connected to the core or the edges of the molecule influence its solubility.[38]

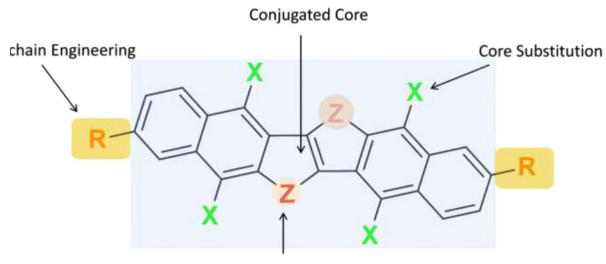

Illustration of a π-Conjugated System

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Flexibility is one of the main advantages of organic electronics compared to traditional silicon devices. Their "softness" and compatible chemical composition make these organic materials ideal for environmental or biological sensors that conform to rough, rounded surfaces.[39] Because they can be manufactured at room temperature, organic transistors can be placed on plastic or paper surfaces.[40] Silicon electronics, on the other hand, require high temperatures during processing. Organic electronics are also cheaper to produce than their silicon counterparts, and they are already being used to manufacture affordable solar cells being installed in East African villages.[41]

The most common commercial application of organic electronics is in light-emitting diodes (LEDs). Light bulbs made with metallic LEDs and their organic counterparts (OLEDs) are more energy-efficient than traditional light sources. The flexibility of OLEDs enables researchers to envision a lamp lit by an OLED shade instead of a bulb underneath.[42] Commercial electronics like some smartphones and a handheld game system already have OLED screens, and thin OLED televisions are expected in stores soon.

FLEXIBLE ELECTRONICS

Some researchers foresee a future of flexible electronics, driven by consumer demand.[43] However, materials for flexible electronics are still under development, and devices prepared using these materials are often research prototypes.

Flexible electronics can be made from semiconductors, like silicon, metals, or organic molecules, patterned on rubber films. Whatever the material, one challenge is maintaining the conductive contacts so that the circuits do not break when they are stretched or crumpled. One way to make a conducting polymer is to fill it with conductive materials like carbon nanotubes. But this addition typically stiffens the polymer and hampers its ability to flex. Researchers at the University of Michigan added gold nanoparticles to a polyurethane polymer.[44] Because of the small size of the nanoparticles, it was hoped that they would alter the polymer's stretchiness less than larger structures. The nanoparticles were covered with thin shells of negatively-charged citrate to help them stick to the positively-charged polymer. The researchers built a conductive film with alternating layers of polymer and nanoparticles. When they watched the structure of the material as it stretched using a transmission electron microscope, the researchers noticed that the nanoparticles formed chains. This behavior was only thought to happen in liquids, so this design principle could be a new way to build flexible electronics.[44]

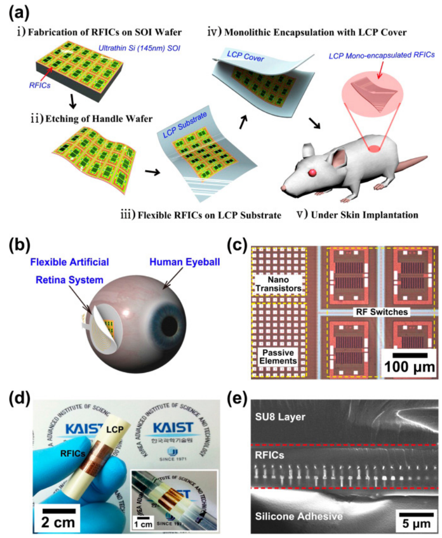
An electronic pressure sensor was reported to be the thinnest and lightest flexible device made as of mid-2013.[45] Researchers built the device starting with a 1-µm-thick foil of polyethylene napthalate. They covered the polymer with an insulating layer of aluminum oxide, organic semiconducting molecules, and gold pads. The complete device was one-fifth the thickness of plastic kitchen wrap and one-thirtieth the weight of a sheet of office paper. Researchers suggested it could be placed on human skin to monitor uncomfortable pressures during medical procedures. Flexible circuits might also be useful for medical monitoring devices that conform to the curved surfaces of the eye, brain, or heart.[46]

Another thin device might be used to monitor pressure in eyes for glaucoma. Metallic oxide semiconductors are patterned on a layer of poly(*p*-xylene). The polymer sits atop two dissolvable polymers on a standard glass or silicon wafer. Dissolving the polymers in water enables the circuits to be removed and wrapped around a human hair.[47]

Instead of using alternative semiconductors, other researchers are looking to make flexible electronics from silicon.[48] These devices can take advantage of the known fabrication methods and behavior of silicon devices. Silicon, however, is a rigid and brittle material, so materials scientists have devised several approaches to create flexible circuits using the material. These approaches rely on making thin slices of silicon that retain their semiconducting properties but gain flexibility due to their reduced thickness.

John A. Rogers, at the University of Illinois, Urbana-Champaign, and his colleagues used thin slices of silicon to make dissolvable, implantable medical devices in 2012.[49] The devices had silicon membranes as the semiconductor, magnesium for conductors, and magnesium oxide or silicon dioxide for dielectrics. A silk cocoon covered all the components. This dissolvable device was implanted in mice near a surgical wound. The researchers activated resistors in the device using radio waves. The resistors generated heat, killing bacteria near the incision. After three weeks, a small amount of silk was the only remnant of the device.

In 2013, a research group led by Keon Jae Lee, at the Korea Advanced Institute of Science and Technology, developed a method to build complex flexible silicon circuits designed to stay in the body for years.[50] They built an entire silicon circuit using standard techniques, and then they transferred a slice of



Silicon Circuits - (a) Schematic illustration of the process for fabricating in vivo flexible RFICs. (b) Artistic conception of a thin and flexible subretinal implant system. (c) Optical microscopy image of RF switches and other circuit components (nanotransistors and passive elements) on a flexible substrate. (d) Photograph of flexible RFICs on a LCP substrate. The inset shows that the flexible RFICs can provide conformal contact on curvilinear surfaces of three glass pipets. (e) Cross-sectional SEM image of the flexible RFICs on a LCP substrate.

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that circuit to a flexible liquid-crystal polymer. The researchers tested the performance of circuits implanted under the skin of rats for three weeks. They also soaked the circuits in a buffer solution at elevated temperatures, simulating conditions if they were implanted in a body for years. The production technique used is suitable for high-performance electronics that require many transistors. The researchers envision the method being used to make an implantable artificial retina that is attached to the back of an eyeball.

Other methods of producing flexible silicon circuits also rely on removing slices of a circuit from a silicon wafer. One method uses almost exclusively standard fabrication techniques and equipment, but could not produce extremely thin circuits.[51] Another method uses a less expensive form of silicon and reduces waste by enabling the wafer to be reused after a slice is removed. A 0.5-mm-thick wafer can yield six 25- to 50-µm-thick silicon slices, according to Muhammad M. Hussain, an electrical engineer at the King Abdullah University of Science & Technology in Saudi Arabia.[52]

IV. MATERIALS FOR ENERGY GENERATION, STORAGE, AND CAPTURE

Designing systems for renewable energy is a key avenue for research in many academic, government, and commercial laboratories around the world. In 2009, the Advanced Research Projects Agency - Energy (ARPA-E) began funding high-risk projects that could potentially transform energy storage and conversion. The agency has supported more than 285 projects since then, and a summit in 2013 showcased many projects involving specialized materials. Those projects included metal hydrides to store solar thermal energy and a liquid metal battery developed in an academic lab and commercialized by its inventor.[53]

Many renewable energy materials projects involve improving widespread technologies like solar panels and lithium-ion batteries. Another approach is designing materials to harvest energy from otherwise wasted sources (such as static electricity or physical movement) and to generate electricity to power small electronics. Materials development can be tightly connected to engineering research to maximize the efficiency of an energy storage or conversion system.

SOLAR PHOTOVOLTAICS

Solar cells based on crystalline silicon semiconductors dominate the commercial market for solar panels.[54] Alternative semiconductors could bring increased efficiency at reduced production cost. They can also be used to create flexible solar photovoltaics (PV), which would introduce new indoor and outdoor applications for solar energy.[55] Transparent solar cells attached to windows could turn skyscrapers into solar collectors.[56] Commerical thin-film PV panels are made using inorganic semiconductors of cadmium telluride (CdTe) or copper, indium, gallium, and selenium (CIGS). These solar cells weigh less than panels using silicon wafers, which reduces installation costs. But as these panels become more popular, the toxicity of some of the components raises concerns about their eventual disposal.[57] A study simulating the long-term leaching of metals from a commercial CIGS cell revealed that the panels released toxic cadmium under acid rain conditions.[58] Flexible solar cells made with organic polymer semiconductors, on the other hand, did not leach unsafe amounts of metals. However, Organic PVs convert sunlight to electricity less efficiently than silicon or inorganic semiconductors. But their low-cost materials and simple roll-to-roll manufacturing enables them to be used on large areas or irregularly shaped products like backpacks.[59]

BATTERIES

Lithium-ion batteries power our cellphones, laptop computers, and hybrid cars. The small size of lithium atoms means many atoms can be packed into a small battery that has a high energy density. The combination of small size, light weight, and high energy density fuels the popularity of these batteries. About 4 billion lithium-ion batteries were made during 2012, according to a battery expert.[60] Less than one in one million rechargeable lithium batteries will fail, though some fail by catching fire. Fully electric vehicles will need several hundred battery cells, and fire in one cell can spread to the others. The safety and energy density of batteries will need to be improved to further the spread of electric vehicles. A greater energy density enables vehicles to travel further between charging.

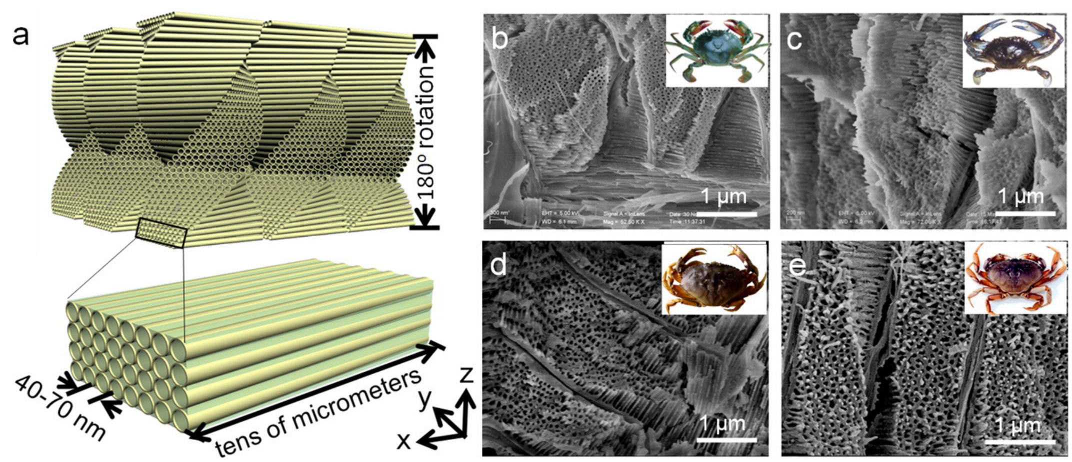
Charging a lithium battery causes positive lithium ions to leave the cathode, one of the two electrodes in the battery. They move through a micrometer-thin porous polymer separator and insert themselves in the other electrode, the anode. Typically, the anode is made of graphite and the cathode is made of $LiCoO_2$. Electrons move toward the anode through an external circuit to balance the charges. A non-aqueous electrolyte, such as ethylene carbonate or ethyl methyl carbonate, bathes both electrodes.

Materials scientists are working to improve the energy density of lithium batteries by changing the materials used for the two electrodes. Polymers can replace flammable organic solvents in the electrolyte to improve safety as well. For the cathode, side reactions between the material and the electrolyte can reduce the amount of charge that a battery holds over time.[61] Polymer coatings can reduce corrosion of lithium manganese oxide cathodes, like $LiMn_2O_4$. Cathodes using $LiFePO_4$ are considered the safest material, but they have poor conductivity. These cathodes are often made from nanoparticles to improve lithium ion diffusion.

Building cathodes with elements other than cobalt can reduce the cost of a battery. As a first step toward making a cathode containing all earth-abundant elements, researchers started with an iron nitridophosphate, a material that contains sodium, iron, phosphorous, oxygen, and nitrogen.[62] They ground the material into a powder and burned it with lithium bromide. Lithium replaced the sodium ions. The scientists used this material as the cathode in a small button-cell battery, like those that power watches. The material had about 80% percent of the energy capacity of current lithium-ion batteries.

Replacing a graphite anode with silicon could, in theory, improve the energy density of a battery by a factor of ten. However, silicon anodes swell and contract as lithium slips in and out of them during charging and discharging. This generates cracks that reduce battery life. Materials scientists have developed several tricks to prevent these cracks. One approach is inspired by self-healing polymers. Researchers at the Korea Advanced Institute of Science & Technology developed a sticky coating based on mussel adhesive to hold silicon nanoparticles together.[63] These polymers would serve as binders for nanostructured anodes because current polymers do not bind to silicon well. Researchers at Stanford University covered millimeter-sized silicon particles in a stretchy, randomly branched polymer held together by hydrogen bonds.[64] A battery constructed with the material had a charge cycle ten times longer than one made with current silicon particle anodes.

Another way to reduce cracks is to put the silicon in structures like carbon nanotubes that can flex to accommodate the swelling. Yi Cui, at Stanford University, identified an environmentally friendly source of carbon nanostructures: crab shells.[65] Cui and colleagues processed stone crab shells to obtain 65-nm-wide hollow nanofibers of calcium carbonate. The scientists filled the fibers with silicon and tested the material as an anode in an electrochemical device. The material retained 95% of its capacity after 200 cycles.



Structural model and SEM images of crab shell templates. (a) Structural model of twisted plywood nanochannel arrays in crab shell templates showing the hollow channels created by removing organic nanofibers in crab shells. The hollow channels are arranged parallel to each other to form horizontal planes stacked in a helicoid fashion, creating a twisted plywood structure. (b–e) SEM images of the biotemplates from a Chinese hairy crab shell, a blue crab, a stone crab, and a Dungeness crab, respectively, demonstrating the universal nature of the nanochannel arrays in crab shell templates.

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Lithium-sulfur batteries are under development as another alternative to current lithium-ion batteries. These batteries, with lithium anodes and sulfur cathodes, could have up to five times greater theoretical energy density than current commercial lithium ion batteries. The abundance of sulfur means high-energy batteries could be produced at low costs. Although these batteries remain largely experimental, researchers have recently reported the development of materials that extend the batteries' lifetime or increase their storage capacity. Researchers at the Chinese Academy of Science developed three new materials for these batteries: a cathode made from graphene oxide coated in sulfur, a stretchy polymer binder, and an electrolyte containing an ionic liquid to prevent sulfur leaching from the cathode.[66] A test battery built with these materials had a charge density of 300 watt-hour per kilogram of battery after 1,000 charging cycles. Conventional lithium-ion batteries store about 200 Wh/kg, and the U.S. Department of Energy's target for electric vehicle batteries is 400 Wh/kg.

Jeffrey Pyun, at the University of Arizona, imagines cathodes for lithium-sulfur batteries constructed from sulfur-containing polymers that would be easy to manufacture on a large scale. Pyun and colleagues tested 2,032 different compositions of sulfur polymers to identify ones that could extend the life of lithium-sulfur batteries. The best material contained 90% sulfur by mass and it had one of the largest energy storage capacities ever reported — 1,225 mAh per gram of material. After 500 cycles, about half of the lifetime of a lithium-ion battery, the capacity had dropped to about 635 mAh/g.[67]

Polymers also play a role in improving battery safety. Replacing the flammable electrolyte with solid polymers could reduce fire risk, should a lithium-ion battery fail. However, one challenge in developing solid-state electrolytes is creating strong materials that also conduct ions. Conductive materials tend to be soft, but a polymer electrolyte also needs enough rigidity to separate the electrodes and keep the battery from shorting out. One approach to solving this problem is to make a di-block polymer that contains hard and soft domains. When doped with salt, the polymer segregates into soft areas surrounded by hard domains, an arrangement that creates a material with the appropriate properties.[68]

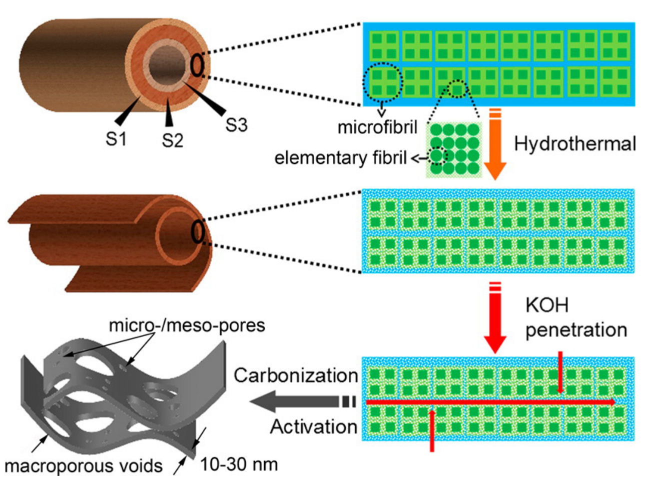
ELECTROCHEMICAL CAPACITORS

Electrochemical capacitors have been known for decades as a type of energy storage. They are used to deliver large pulses of power to commercial devices like lasers and cardiac defibrillators.[72] Capacitors could be used for long-lived, low-maintenance energy storage to capture energy from braking a hybrid vehicle, for example. They can be recharged faster and more often than batteries, though they hold less energy per weight. The simplest capacitor consists of two electrodes separated by a material called a dielectric. Energy storage comes from charge separation between the two plates: one holds a positive charge while the other gathers negative charges.

Materials scientists are looking to improve the energy density of capacitors. One way to do that is by using new polymers or nanocomposites for the dielectric.[72] Henry Sodano, at the

University of Florida, and colleagues developed a nanocomposite for the dielectric that stores more charge without reducing its operating voltage.[73] The researchers embedded nanowires of barium strontium titanium oxide in polyvinylidene fluoride. The polymer maintains the voltage, while the structure of the nanowires enhances charge storage. The material had similar operating voltage to commercial components, but stored 12 times more energy per volume.

Making electrodes from materials that hold more charge is another way to increase the energy density.[74] Because of its excellent conductivity, graphene is a potential candidate for electrodes in capacitors.[75, 76] Electrodes made from graphene-like nanosheets produced from processed hemp plant waste were used to make a capacitor.[77] To turn a plant into carbon nanosheets, researchers at the University of Alberta heated the bark-like layer of hemp to 180° for 24 hours. Two of the components of the bark break down during this time, and the third component, crystalline cellulose, begins to carbonize. Treating the carbonized material with potassium hydroxide and then heating it up to 800° creates porous nanosheets. The researchers built a capacitor with the nanosheets as electrodes and an ionic liquid electrolyte.



Hemp Sheets Schematic of the synthesis process for the hemp-derived carbon nanosheets, with the three different structural layers S1, S2, and S3

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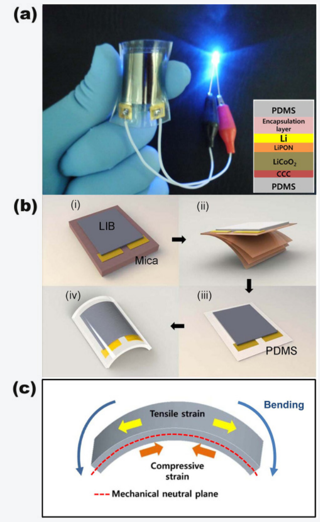
FLEXIBLE BATTERIES FOR FUTURISTIC DEVICES

Products like Google Glass demonstrate that wearable electronics are becoming a reality. As the number of types of wearable devices increases, there could be a need for flexible batteries that can be incorporated into clothing. Bendable batteries could also be used to power stretchy displays. Researchers developing flexible batteries are challenged with maintaining the device's performance, power, and cycle life while using materials that can withstand repeated bending, flexing, and twisting.[69] Solicore, a company based in Florida, uses a polymer-based electrolyte to producing flexible lithium batteries for smart credit cards containing a microprocessor.[68]

But many materials for flexible batteries do not provide as much energy as high-quality materials used in rigid lithium batteries. Responding to this problem, researchers in South Korea assembled a battery using conventional materials on top of a sheet of mica.[70] They peeled off layers of the battery using tape and stuck the thin sheets on flexible polydimethylsiloxane. The batteries stored the most energy of any flexible battery, and they discharged enough energy to power a flexible LED display. Cell phones, however, require more power than these batteries can currently store.



(a) Photograph of a bendable LIB turning on a blue LED in bent condition. The inset shows the stacked layers in the flexible LIB. (b) Schematic illustration of the process for fabricating flexible LIBs. A cultivated LIB on brittle mica substrate (i) is followed by mica substrate delamination using sticky tapes (ii), and then, the flexible LIB is transferred onto a PDMS polymer substrate (iii). Finally, the flexible LIB is covered with another PDMS sheet to enhance mechanical stability (iv). (c) Schematic image of the mechanical neutral plane generated from the counterbalance between tensile and compressive strain.

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Another group of researchers in South Korea redesigned batteries for textiles to improve their durability. The team created electrodes by electroplating nickel onto polyester fabric. The metal coated the individual fibers in the yarn, allowing the fabric to keep its mechanical properties while becoming conductive. Then the researchers coated each yarn in the fabric with a flexible polyurethane binder and standard composite used for lithium-ion battery electrodes. They then sewed the flexible battery into a sweatshirt, and it still functioned after 10,000 cycles of folding.[71] While this iteration of the battery can power an LED display, it still does not produce enough voltage for practical applications.

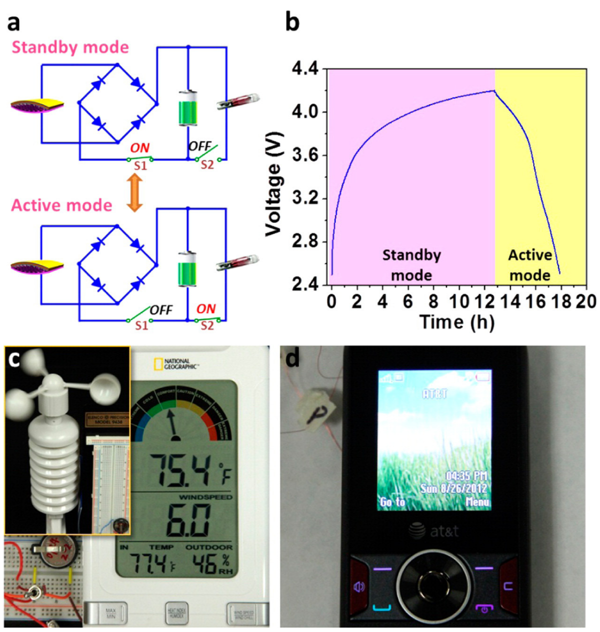
As materials for batteries and capacitors are developed, it is important to test the materials under conditions that reflect the electrochemical mechanisms underlying their function.[78]

ENERGY HARVESTING AND GENERATION

Many of the portable electronics we use today, such as mobile phones or implantable medical devices, require so little energy that they could be powered by seemingly insignificant sources: static electricity or physical movement, for example. Harvesting just 5% of the power generated by the heel of a brisk walker hitting the ground would be enough to power a mobile phone.[79]

Earlier this year, a team of researchers developed a flexible device to harvest energy from a beating heart.[80] The device relies on ribbons of a piezoelectric material, lead zirconate titanate, that generates electricity when compressed. The complete device had 12 groups of these ribbons layered between two electrodes. The researchers tested the devices by placing them on the hearts, lungs, and diaphragms of cows. They found that a stack of five devices produces enough energy to continuously power a typical cardiac pacemaker.

Other materials generate energy by using movement to cause electrical charges to gather on two materials. This charge build up is called the triboelectric effect, and the energy produced by the phenomenon could be used to power large networks of sensors.[81] Researchers at the Georgia Institute of Technology built a generator to turn motion into electricity.[82] They patterned a sheet of polydimethylsiloxane and a sheet of aluminum so that the surfaces of each material were rough. The scientists built the generator by placing the bumpy surfaces of the materials together, but they only connected the materials along the edges. That meant the middle of the materials bowed away from each other. Pressing on the center of the material packet pushed the aluminum into the polymer. A voltage was generated when the two materials sprang away from each other. A generator with 9 cm^2 area, tapped at 6 Hz by an



Power source module composed of an arch-shaped triboelectric nanogenerator (TENG). TENG and a lithium ion battery for driving portable electronics that need a regulated input power. (a) Schematic circuit diagram showing the switching between the "standby mode" and the "active mode" of the power source module. (b) Voltage curve showing the entire cycle of a lithium ion battery fully charged by TENG (standby mode), with the subsequent constant current discharge at 2 μA (active mode). (c) Wireless wind and humidex thermometer, as an example of a whole wireless sensor network system, is driven by two such power source systems (one for the remote sensor module and one for the receiver-display module). (d) Commercial cell phone powered by its original battery that was charged by the TENG.

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electric motor, produced enough power to turn on a light-emitting diode. After 85 hours, the material had produced enough power to charge a cell phone sufficiently that the researchers could make a call.

Other devices can harvest power from sliding, rotation, or vibration.[83] These devices could supplement power from solar or thermal energy, so that multiple energy sources could be tapped to provide power. This would enable power to be provided depending on the environment of a device.

V. MATERIALS FABRICATION FROM NANOSCALE TO MACROSCALE

Materials discussed throughout this report find their way to commercial applications if they can be manufactured into products. But manufacturing often involves more than combining ingredients to create a material with a desired chemical composition. The functionality of electronic and biomimetic materials often depends on nanoscale patterns on their surfaces. Solar panels or flexible displays also contain nano- or microscale structure, but obtaining optimum performance from these materials requires the tiny structures to be precisely reproduced across a large area. There are many ways to generate nanoscale patterns in materials and to replicate those patterns at large scale. This section will focus on two of those methods: lithography and printing.

LITHOGRAPHY

There are several kinds of lithography, but all methods essentially involve transferring a pattern to a surface. Lithography methods differ in the ways the patterns are created, the size of the features in those patterns, and the speed at which the patterns can be replicated.

Photolithography is the most common method used in the semiconductor industry, and its ability to quickly pattern small features across a large area is key to the industry's profitability.[83, 84] With this method, a surface is covered with a light-sensitive polymer called a photoresist. Ultraviolet light is shone through a patterned stencil onto the photoresist. The light removes material exposed by the stencil, transferring the pattern to the surface. Deep-UV lithography at wavelength of 193 nm can create features smaller than 50 nm on 60 to 80 wafers per hour.[83]

The ability to pattern smaller features could lead to more powerful computer chips, but equipment and production costs for photolithography increase as feature size decreases. Thus, researchers are developing other ways of patterning surfaces to simplify production and enable nanostructured surfaces to be used for a variety of applications.

Nanoimprint lithography uses a mold to emboss or shape a deformable material with features as small as 5 nm.[85] The molds can be created on large drums to enable large scale fabrication via roll-to-roll printing. Researchers in South Korea recently used this method to produce large-area water repellant surfaces inspired by the texture of rose petals.[86]

Another type of surface patterning, block copolymer lithography, relies on molecular self-assembly to create features a few to hundreds of nanometers wide.[87] This method begins with a polymer containing two chemically different domains. The domains segregate when the polymer is used to create a surface film. That segregation forms predictable patterns if researchers control the volume fraction of the two components, the rigidity of their structures, the strength of their connection, and the molecular weight of the polymer. These patterns can be replicated on a large scale using a technique called molecular transfer printing.[88] First, a copolymer and molecular inks miscible with each domain of the polymer are placed on a surface. The copolymer assembles into a pattern, and each ink localizes inside the domain of comparable polarity. A new surface is placed atop this patterned surface. The inks absorb, react, or interact with this surface, transferring a mirror image of the original pattern to the new surface.

PRINTING

Inkjet printing is a way to pattern materials on a variety of flexible substrates.[89] One way to make cost-effective medical tests involves printing patterns with wax on paper.[90] The hydrophobic wax pattern defines channels that guide a urine sample to areas of the paper that contain reagents for particular diagnostic tests. Flexible solar cells or light emitting diodes can be prepared by printing conductive inks or semiconducting polymers on plastic substrates, and the scale of production can be increased using roll-to-roll processing.[91] Printed electronics have been commercially available for more than a decade, and a desire for flexible devices is expected to help the market grow.[92] Academic research labs have reported printed lithium-ion batteries[93] and transparent paper-based transistors[94] that could be useful for renewable electronics. Recently, researchers at the University of California, Berkeley, made the first microelectromechanical system (MEMS) using inkjet printing.[95]

A MEMS is a 3-D electronic device that has moving parts and switches current on and off like a transistor. The printed MEMS was slower and less durable than a printed transistor, but it might be useful as a cheaper alternative to silicon MEMS in sensors and actuators.

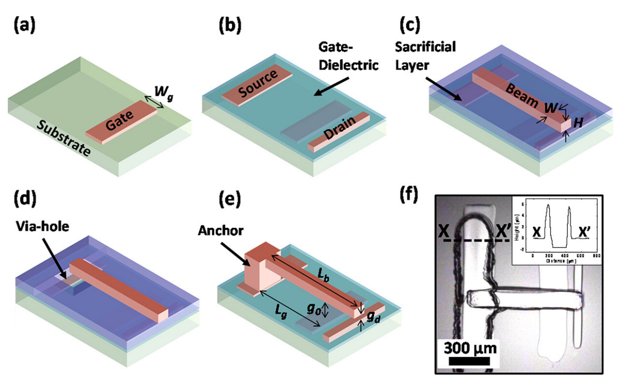

Illustration of the process used to fabricate the first MEM switches. (a) Gate electrode is printed onto an electrically insulating substrate using silver nanoparticle ink. (b) Thin film of cross-linked PVP is spin-coated to form the gate dielectric. Drain electrode and source pad are printed in alignment with the gate electrode. Additional drops of ink can be printed in the drain-contacting region to define a contact dimple. (c) Sacrificial layer of PMMA is spin-coated and source beam is inkjet-printed. (d) The source anchor region is defined by printing acetone to dissolve PMMA underneath one end of the source beam. (e) The source anchor is formed by filling the hole in the PMMA with inkjet-printed silver nanoparticle ink, and the structure is released by removing PMMA film with acetone. (f) Optical plan-view micrograph of cantilever beam after the anchor-region hole is defined by inkjet-printing PMMA; (inset) surface profile of the hole along XX'.

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3-D PRINTING

The growing popularity and availability of three-dimensional printers could bring a revolution in personal manufacturing.[96] The machines use powder, polymer, or edible inks to prepare product prototypes or manufacture small quantities of a finished design. Stratasys, a company based in Minneapolis, has produced more than 100 materials or composites for 3-D printers.[26]

In chemistry labs, 3-D printers could be used to make scaffolds for tissue engineering, custom microfluidic chips, and implantable drug delivery devices.[97] Researchers have used them to create lower-cost custom laboratory equipment like lab jacks and combs for electrophoresis gels.[98] The printers can also be used to make metal parts[99] or electrodes for lithium batteries.[100]

Applications for printed devices extend beyond flexible gadgets and sensors. At a printed electronics conference in 2011, an engineer from the aerospace company Boeing said printed wiring harnesses would help reduce the weight of copper wiring inside airplane wings. An outdoor advertising company thought printed displays would be cheaper than LEDs used at the time. And engineers with the U.S. Army were interested in printed electronics to make smaller and lighter weapons.[92]

VI. CONCLUSION

New materials are important to the development of renewable energy technologies, as well as energy-efficient electronic devices. However, it can take 10 to 20 years for a material to move from the research lab to market. An initiative proposed by the White House in 2011 aims to cut that time in half.[101] The Materials Genome Initiative will combine data, computational modeling, and experimental research to help federal agencies, industry, and academic researchers work together to develop new materials.

An effort by the Department of Energy announced in January 2013 is intended to fund research that addresses the availability of elements needed for clean energy technologies like LEDs, batteries, and solar cells. Government, industry, and academic scientists working with the Critical Materials Institute are tasked with developing ways to recycle components of clean energy technology as well as developing alternative materials that do not rely on obtaining exported rare-earth elements.[102]

As these initiatives get off the ground, other tools can help researchers develop new materials. Combinatorial screening can identify new functional materials when current knowledge limits further rational design.[103] Computational modeling can predict properties of new materials, and two web-based tools – one for inorganic materials, another for catalysts – aim to make those predictions as widely available as possible.[104]

The very nature of materials science is one of discovery, development, and repurposing. Many of the world's most pressing scientific problems involve the limitations of materials in use today. Overcoming these limitations inspires and provides opportunity for materials scientists to tap into the ingenuity and creativity gained by practicing in this interdisciplinary field.

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