

Exploring Frontiers in Research and Teaching: NanoEngineering and Chemical Engineering at UC San Diego



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This **virtual issue** of *ACS Nano* highlights contributions of the faculty and students of the Department of NanoEngineering and Chemical Engineering Program at the University of California, San Diego.¹ Founded in 2007, NanoEngineering is the newest of six departments in the Jacobs School of Engineering. It comprises 26 research-active professors and a contingent of four teaching professors, whose area of focus is the core undergraduate curriculum in chemical engineering. The research interests of the department are highly interdisciplinary—it is known internationally for its strengths in nanomedicine, flexible electronics, and energy storage, with broad areas of overlap. A particular strength of the department that cuts across all research areas is computational materials science. This interdisciplinarity is, in part, a product of the diversity of the educational backgrounds of the faculty; most of us have undergraduate training in chemical engineering, chemistry, or materials science (approximately equally represented), with a smaller cohort from the field of mechanical engineering. Chemical engineering, in particular, is integral to the department and is central to its identity, with over 500 students enrolled in the undergraduate program (with a high-water mark of >200 bachelor's degrees in chemical engineers awarded in 2017). Although UC San Diego had been offering degrees in chemical engineering since the early 1980s, the program did not have the formal support of a department until 2007. When the Department of NanoEngineering was founded, it became the logical home for chemical engineering, which was already a popular program with high undergraduate enrollment. Moreover, there is intellectual complementarity between nanoengineering and chemical engineering, with an expansive frontier between them (Figure 1).

The department offers BS, MS, and PhD degrees in two programs: nanoengineering and chemical engineering. Its core strengths in research lie in the application of nanotechnology for healthcare and energy, broadly interpreted, and with many approaches represented. In the examples below, we have highlighted a few recent contributions of each of our research groups in the areas of nanomedicine, biomaterials, flexible and stretchable electronics, complex alloys and heterointerfaces, theory and computation, energy storage, nanophotonics and nanomagnetism, and photovoltaics. In the final section, we highlight our approach to teaching in chemical engineering and

nanoengineering. One of our principal motivators is continuous improvement in the nanoengineering curriculum and the adoption of video in asynchronous, remote, and active learning. In this Editorial, we give the reader a preview of what is to be discovered in this **virtual issue**, which we believe will contain something to satisfy the curiosity of most individuals within the broad readership of *ACS Nano*.¹

This virtual issue of *ACS Nano* highlights contributions of the faculty and students of the Department of NanoEngineering and Chemical Engineering Program at the University of California, San Diego.

Nanomedicine. Nanotechnology has the potential to change how diseases are managed in the clinic significantly, and UC San Diego's NanoEngineering and Chemical Engineering faculty have been hard at work exploring new and innovative ways of tackling some of the most pressing challenges in medicine. Prof. Liangfang Zhang's work centers on cell-membrane-coating nanotechnology, a biomimetic approach for functionalizing nanoparticle platforms.^{2–10} Synthetic nanoparticle cores, which can be loaded with therapeutic cargoes, are camouflaged with a layer of membrane that is derived from living cells, enabling the resulting natural–synthetic hybrids to take on cell-like properties (Figure 2a).^{3–10} For example, the Zhang group demonstrated that nanoparticles coated with platelet membrane can biointerface with different disease substrates, including damaged blood vessels and bacteria.¹¹ Membrane-coated nanoparticles can also serve as decoys that can be used for detoxification applications. Those coated with neutrophil membrane have been shown to neutralize inflammatory cytokines, significantly



Department of NanoEngineering
 NanoEngineering • Chemical Engineering

NanoEngineering	Frontier Areas	Chemical Engineering
<i>Molecular / Granular Approaches</i>	<i>Mesoscale Approaches</i>	<i>Continuum Approaches</i>
intermolecular & surface forces	electrochemistry	fluids, transport, thermodynamics
synthesis & characterization	nanoscale mechanics	measurement, analysis, & control
design of material	nanomedicine, energy storage, flexible devices...	design of process

Figure 1. Continuum of length scales, methodologies, and applications from nanoengineering to chemical engineering.

reducing the effects of arthritis in an animal model of the disease.¹² This approach has the potential to be applied across a wide range of conditions, including animal envenomation, bacterial infection, and exposure to chemical toxins or warfare agents.

Nanomaterials naturally exist within nature, and Prof. Nicole Steinmetz (a member of the ACS *Nano* editorial advisory board) focuses on leveraging well-defined plant virus nanoparticles for nanomedicine (Figure 2b).^{14–17} For example, her group has functionalized high-aspect-ratio potato virus X particles with a potent antitumor protein.¹⁴ Up to 490 copies could be loaded onto a single viral nanoparticle, and the resulting formulation was able to control tumor growth significantly in a breast cancer model.¹⁴ Certain plant viruses are also capable of strongly activating the immune system, and her group has taken advantage of this phenomenon for cancer immunotherapy applications. In particular, her lab has shown that local delivery of a nanoplatform based on the cowpea mosaic virus can lead to significant efficacy in aggressive animal tumor models.^{15,17} This approach takes advantage of an *in situ* vaccination effect, where systemic immunity can be generated to protect against tumor formation at distant sites.

Although the majority of nanomedicine platforms still rely on passive transport, Prof. Joseph Wang's work seeks to change this paradigm (Figure 2c). His motor-based platforms can be guided by external sources, such as a magnetic field, or they can be self-propelled by chemical reactions.^{18–36} The Wang group pioneered the use of motors *in vivo* and demonstrated their exceptional utility for oral applications. His group recently developed a micromotor pill platform, where a large number of the motors were packed inside a pill matrix for easy oral administration.³⁵ Upon dissolution in the stomach, the released motors autonomously propelled in the gastric fluid, facilitating enhanced delivery. For cancer treatment, the Wang group has also incorporated micromotors into microneedle patches, along with checkpoint blockade antibodies.³⁶ Upon penetrating the skin, the motors were activated and acted as pumps that drove delivery of the payload into the tumor.

The use of imaging to detect disease states and to guide treatment can greatly improve patient outcomes. Along these lines, Prof. Jesse Jokerst has developed nanoparticle platforms that leverage ultrasound and photothermal imaging for theranostic applications (Figure 2d).^{37–39} In one example, his bioimaging lab employed a silver/gold hybrid nanoparticle platform for the simultaneous treatment and imaging of bacterial infections.³⁷ Under near-infrared illumination, the nanoparticles exhibited a triggered release of silver ions, which are known to have potent antibacterial properties, and the gold core enabled concurrent photoacoustic imaging. The Jokerst group has also reported on a silica–iron oxide nanoparticle that was loaded with a protein-based growth factor to serve three unique purposes for stem cell therapy: maintaining cell

viability, magnetically guiding the cells to a target site, and providing imaging contrast.³⁸

Prof. Yi Chen is working on novel DNA-based nanostructures to enable precise delivery and gene-therapy applications.^{40,41} The natural pairing between complementary DNA bases offers exceptional versatility in generating three-dimensional structures with defined sizes and shapes.⁴⁰ In one of the Chen group's recent projects, gold nanowires were coated with a layer of DNA generated by rolling cycle amplification.⁴¹ Anchoring sequences were incorporated into the sequence of the DNA, which enabled the attachment of siRNA molecules for gene silencing. Taking advantage of the gold nanowire core, the researchers used ultrasound to propel the nanostructures directly through a cell's plasma membrane and into the cytosol. This method enabled significant gene knockdown, highlighting the promise of the approach for future gene-therapy applications.

The laboratory led by Prof. Vicki Grassian studies a range of applications in toxicology, particularly in biological⁴² and environmental⁴³ contexts. Using a variety of techniques in aerosol science, surface science, spectroscopy, and microscopy, the Grassian group has been working to achieve a molecular-level understanding of the surface chemistry of complex environmental interfaces (Figure 2e). In particular, the Grassian lab focuses on details of the heterogeneous chemistry of trace gases with particulate matter such as atmospheric mineral dust, dissolution and mobilization of iron-containing nanoparticles, optical properties of atmospheric aerosol, and the applications and implications of nanoscience and nanotechnology in environmental processes.

Cell-Instructive, Bioinspired, and Biomimetic Materials. The development and application of biomaterials is a multidisciplinary effort that thrives in an environment where engineers, physical scientists, biologists, and clinicians collaboratively develop technologies to address new medical challenges. NanoEngineering at UC San Diego has harnessed the spirit of interdisciplinary research and fostered advancements in the field toward clinical application. A major research focus in the department is engineering biomaterials spanning a range of length scales that encompass cellular and molecular engineering, drug delivery, and tissue engineering.

The development and application of biomaterials is a multidisciplinary effort that thrives in an environment where engineers, physical scientist, biologists, and clinicians are equal partners in addressing many of the new medical challenges.

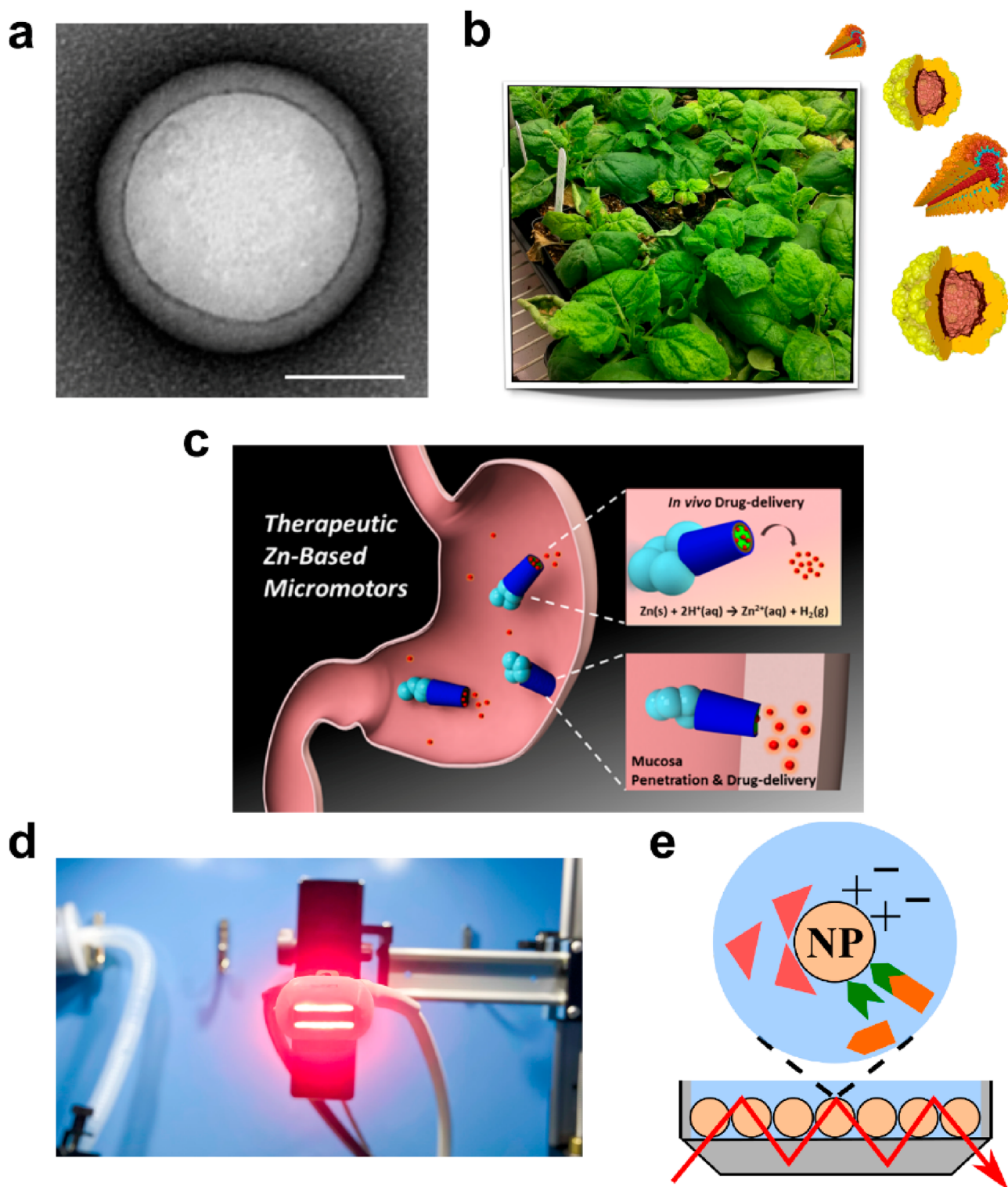


Figure 2. Nanoparticles used in medicine, imaging, and environmental science and toxicology. (a) Transmission electron microscopy image of a cell-membrane-coated nanoparticle from Liangfang Zhang's group (scale bar = 50 nm). (b) Nanoengineering gone viral: the Steinmetz lab produces plant-virus-based nanomaterials for nanomedicine and precision farming applications. (c) Wang group's demonstration of the first *in vivo* study of artificial micromotors using a live animal (mouse). Graphic summarizes work originally published in ref 13. (d) Jokerst group uses photoacoustic imaging and nanoscale contrast agents to improve medicine and to add insight into biology. Shown here is the lab's ultrasound transducer with integrated nanosecond optical excitation. (e) Development of spectroscopic probes to investigate nanoparticle surface transformations in different environmental and biological milieus for better understanding of nanotoxicity and nanotoxicity in the Grassian lab.

At the cellular and molecular levels, Prof. Nisarg Shah's research focuses on developing biomaterials as a means to

regulate cell function to restore biological homeostasis. The recognition of self from nonself is an essential quality of the

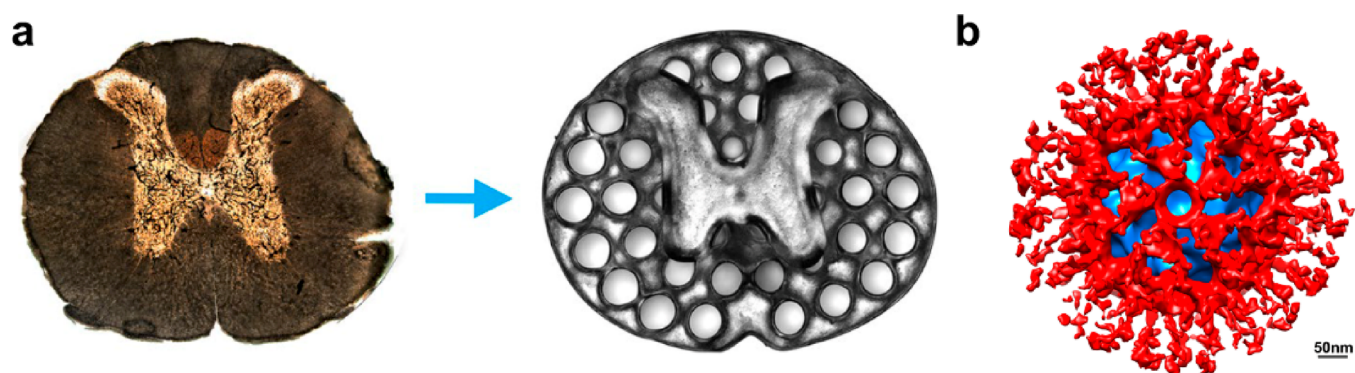


Figure 3. Polymeric biomaterials for tissue repair and drug delivery. (a) Three-dimensionally printed biomimetic scaffold for repairing spinal cord injury. Image related to work described in ref 46. (b) Cryo-EM reconstruction of a polynorbornene-conjugated viral nanoparticle (blue is viral nanoparticle, red is polymer). The polymer backbone displayed a unique molecular conformation and better protected the nanocarrier against immune recognition *versus* poly(ethylene glycol). Reproduced from ref 47. Copyright 2017 American Chemical Society.

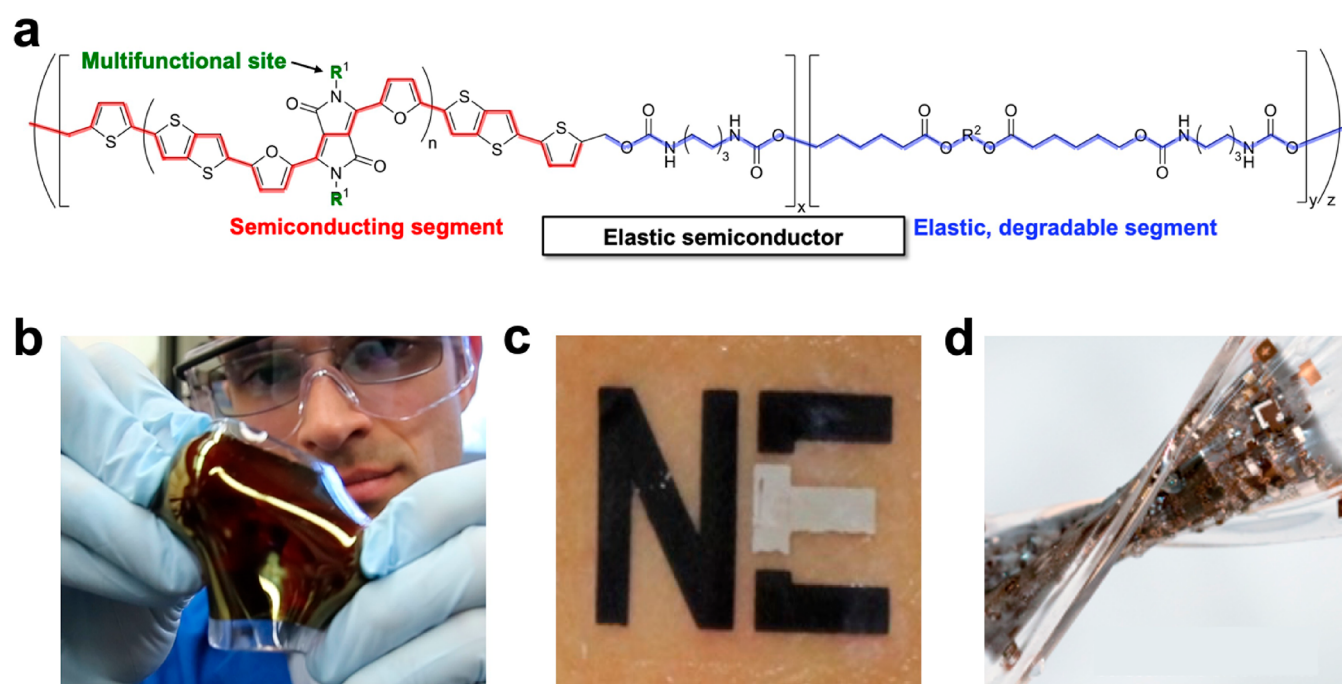


Figure 4. Stretchable materials and devices. (a) Chemical structure of an elastic semiconducting block copolymer produced in the Lipomi group for (b) applications in rubber-like electronic devices. Annotated version of structure in (a) first reported in ref 55. (b) Photo credit: UC San Diego. (c) Skin-worn chemical sensors produced in the Wang laboratory. (d) Three-dimensional integrated stretchable electronic devices produced by the laboratory of Prof. Sheng Xu, reported in ref 56. Photo credit: UC San Diego.

immune system that confers protective immunity against pathogens while suppressing activation against self-antigens.⁴⁴ The Shah research group develops polymeric biomaterials that regulate the fate of immune cells resident in tissues by providing cell-instructive cues to control their spatiotemporal behavior. By organizing functional features as chemical and molecular regulators, the biomaterials drive activation of immune cell specificities against pathogens and subsequently restoring the function of negative feedback of the immune system. Through biomaterials-mediated epigenetic and metabolic regulation, his group studies how immune cell subsets might be restored functionally and numerically to enhance immune protection against pathogens.⁴⁵

Another major research focus is on additive manufacturing and the assembly of biomaterials for tissue engineering and regenerative medicine applications. Prof. Shaochen Chen's

research group has focused on engineering biomaterials that integrate cell-material interactions at a range of length scales (from nano- to micro- to mesoscale), time scales (from femtoseconds to months), and biological dimensions (from molecular to cellular to tissue, Figure 3a). The Chen group's research has advanced both fundamental biomaterials science and biomechanics and developed new techniques to advance the translation of biomaterials in tissue/organ repair and regeneration.⁴⁶

An inherent problem for advanced biomaterials is the lack of scalability because most materials are fabricated using small-scale batch processes. Prof. Jonathan Pokorski's research group (Figure 3d) is leading the development of scalable manufacturing techniques to facilitate the slow release of biomolecules with protein/polymer depot formulations using traditional polymer-processing tools, such as extrusion or injection

molding, to fabricate slow-release protein/polymer blend devices. These devices can be in the form of microneedle patches, microparticles, or implants, depending on the therapeutic target. The ultimate vision for this research thrust is to develop protein-delivery devices that are inexpensive, eliminate the cold-chain, can be self-applied, and, most importantly, will improve therapeutic efficacy. The future of this project will involve the scaling up of implants and patches using injection molding techniques that could be used to distribute vaccine devices in resource-poor areas.^{47,48}

The development of materials through biomimicry at multiple length scales has been a central focus of biomaterials research in the department. Prof. Marc Meyers's research group has been studying mineralized biological materials, including shells, crab, exoskeleton, bird beaks, and feathers, focusing on the composite nature of the soft organic and hard inorganic compounds. The work of the Meyers group has produced insights into how nature has evolved these components to optimize multifunctional purposes. The hierarchical structure of these materials is at the crux of this enhancement. Microstructural features such as organized, layered organic/inorganic structures, and the presence of porous and fibrous elements are common in many biological components. Whereas the mineral constituents are weak by themselves, they interact with the organic matrix to produce materials with unexpected mechanical properties.⁴⁹

Flexible and Stretchable Electronics. The promise of distributed, wearable devices for healthcare has led to the development of new types of physiological sensors based on flexible and stretchable active materials and device layouts. Our work in this area leverages our strengths in chemistry and materials science, as well as a complementary approach based on continuum mechanics and device layouts. The work of the Lipomi group focuses on two types of materials for flexible and stretchable electronics (Figure 4a,b).⁵⁰ These materials are π -conjugated (semiconducting) polymers and a new type of composite sensor based on two-dimensional (2D) materials (graphene and hexagonal boron nitride, hBN) decorated with metallic nanoparticles.^{51,52} For decades, one of the principal motivating factors for research in semiconducting polymers was the promise of lightweight, thin devices for flexible (and possibly stretchable) applications, such as solar cells, displays, thin-film transistors, and wearable and implantable biosensors. However, the optoelectronic properties of such materials were usually measured on glass and silicon substrates; the use of these rigid substrates masked the highly variable mechanical properties possessed by these materials. In particular, the details of the molecular structure and solid-state packing structure greatly influence the modulus, toughness, and ultimate tensile strength of these materials. Unlike commodity polymers and engineering plastics, which have well-described mechanical behaviors, semiconducting polymers must retain their electronic function when deformed. The approach taken in the Lipomi group is vertically integrated and involves the synthesis of new polymers, prediction of properties by molecular dynamics (in collaboration with experts in our own department, such as Tod Pascal),⁵³ and fabrication of devices. So far, work in the Lipomi group has generated flexible and stretchable electronic materials,⁵⁰ including all-rubber solar cells, sensitive and high-resolution strain gauges, and purpose-synthesized conductive polymer to generate virtual texture in a wireless haptic glove in virtual reality.⁵⁴

The laboratory of Prof. Joseph Wang has a well-established program in the area of skin-conformable, wearable sensors. What differentiates this work from the majority of wearable sensor technologies is the ability to perform electrochemical analyses of (bio)chemical species, as opposed to mechanical or electronic signals. Wearable patches resembling temporary tattoos have been fabricated using high-throughput and inexpensive methods such as screen printing (Figure 4c). The Wang laboratory has used such devices to detect analytes noninvasively in a range of biological fluids, including sweat, tears, saliva, and interstitial fluid. Applications for this work include testing for biomarkers associated with various diseases, including diabetes,⁵⁷ Alzheimer's,⁵⁸ and Parkinson's.⁵⁹

The research of Prof. Sheng Xu takes a mechanics-based approach to generating stretchable, patch-like devices but uses new strategies to measure physiological quantities, which have previously been difficult to access from the skin surface. For example, using ultrasonic transducers embedded in epidermal patches, it was possible to measure the central blood pressure waveform from the peripheral vasculature.⁶⁰ One of the unique aspects of the work of the Xu laboratory is the generation of three-dimensional (3D) structure in nominally 2D patches. For example, with the strategic placement of vias using laser ablation and controlled soldering, along with sophisticated lamination techniques, it was possible to generate epidermal patches with a density of functionality that would be difficult or impossible to replicate in two dimensions (Figure 4d).⁵⁶

At the core of our activity in the area of flexible and stretchable electronics is an interest in the science of polymeric materials and soft matter. Jinhye Bae, a new assistant professor at the time of this writing, is interested in soft, actuable materials. In particular, the focus of the Bae laboratory is on the elucidation of the physics, mechanics, and dynamics of hydrogels⁶¹ and folded or buckled structures⁶² to develop new pathways of self-assembly. Future applications of this work are envisioned in medical devices and sensors.

Complex Alloys and Heterointerfaces. On the opposite end of scales from mechanical properties, the field of high-entropy alloys (HEAs) has garnered much research interest in recent years for applications in extreme environments. In the original theory of HEAs, the high configurational entropy of chemically complex, solid solution phases stabilizes them into a single-crystalline phase against the formation of the thermodynamically competing intermetallics. According to this theory, when the constituent elements are present in equiatomic amounts in a single phase, the maximum molar configurational entropy is obtained. It is somewhat generally accepted that this molar configurational entropy becomes significant when there are five or more components. Thus, HEA compositions typically comprise five or more chemical species mixed in equimolar (or close to equimolar) concentrations. High-entropy materials have attracted considerable interest due to the combination of useful properties and promising applications. Predicting their formation remains the major hindrance to the discovery of new systems. In a recent publication by Prof. Kenneth Vecchio's team (Figure 5a), in collaboration with a group from Duke University led by Prof. Curtarolo, a descriptor referred to as the "entropy-forming ability" was proposed for addressing synthesizability from first principles.⁶³ The formalism, based on the energy distribution spectrum of randomized calculations, captures the accessibility of equally sampled states near the ground state and quantifies configurational disorder capable of stabilizing high-entropy homoge-

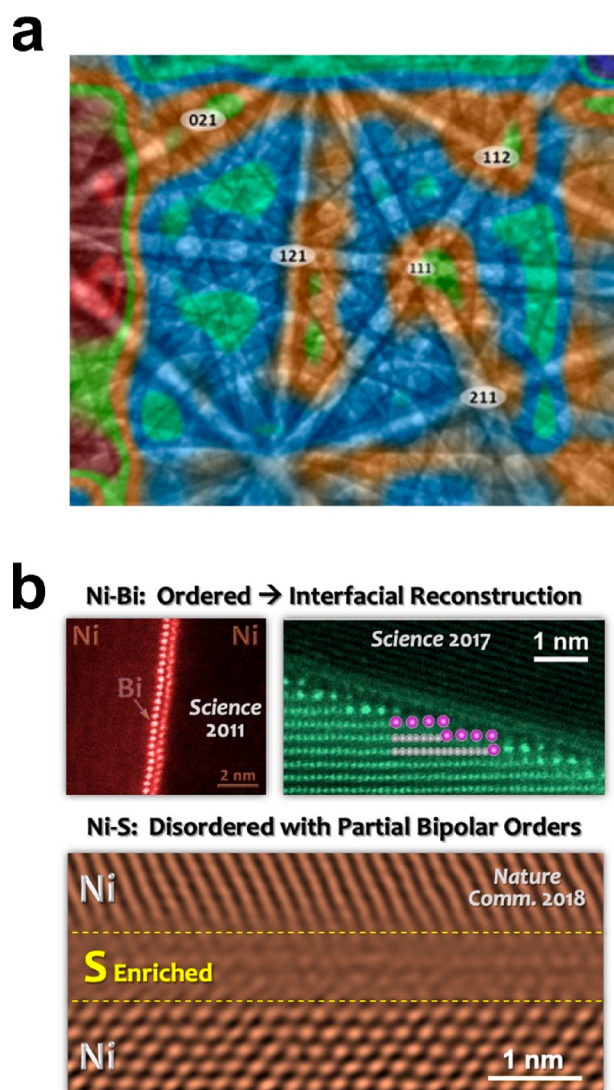


Figure 5. Complex alloys. (a) Heatmap highlighting the important regions for determining the correct space group (225) for the underlying NbC diffraction pattern derived from a convolutional neural network. Colorized representation of data originally reported in ref 64. (b) Two-dimensional interfacial phases have been discovered by Luo and collaborators in two classical grain boundary embrittlement systems, Bi- vs S-doped Ni. Annotated and colorized images are adapted from the data in refs 65–67.

neous phases. The methodology is applied to disordered refractory five-metal carbides—promising candidates for high-hardness applications. The descriptor correctly predicts the ease with which compositions can be experimentally synthesized as rock-salt high-entropy homogeneous phases, validating the model and, in some cases, going beyond intuition. Several of these materials exhibit hardnesses up to 50% higher than rule-of-mixtures estimations. The entropy-descriptor method has the potential to accelerate the search for high-entropy systems by rationally combining first-principles with experimental synthesis and characterization.

In collaboration with Vecchio and other groups, Prof. Jian Luo's group has made discoveries of new classes of high-entropy ceramics, including high-entropy borides, perovskite and fluorite oxides, and silicides, as well as single-phase high-entropy intermetallic compounds that fill a knowledge gap between high-entropy alloys and ceramics (Figure 5b).^{65–67} A

new and potentially paradigm-shifting perspective proposed by Luo *et al.* aims at expanding “high-entropy ceramics (HECs)” to “compositionally complex ceramics (CCCs)”, where the team has recently demonstrated that medium-entropy and/or nonequimolar compositions can often outperform their high-entropy, equimolar counterparts.⁶⁸

Prof. Luo and co-workers are also investigating solid interfaces and their roles in controlling the fabrication and properties of a broad range of ceramic and metallic materials. One current research goal is to develop the grain boundary counterparts to bulk phase diagrams as a new materials science tool. Recent studies constructed grain boundary “phase” diagrams *via* phenomenological and statistical thermodynamic models and atomistic simulations. Here, a grand scientific challenge exists because general grain boundaries have five macroscopic (crystallographic) degrees of freedom (DOFs). In collaboration with the group of Prof. Shyue Ping Ong, a most recent breakthrough study uses genetic algorithm-guided deep learning to map out grain boundary properties as functions of temperature, bulk composition, and five crystallographic DOFs in a seven-dimensional (7D) space.⁶⁹ This accomplishment had previously been considered to be a “mission impossible” *via* conventional experimental or modeling approaches.

Finally, a significant challenge within the world of materials discovery is accurate crystal structure analysis in electron diffraction. Prof. Vecchio's research team has developed a computer-based methodology that independently analyzes diffraction patterns utilizing a similar type of deep-learning algorithm (a subset of artificial intelligence and machine learning) as is used in facial recognition and self-driving cars. They demonstrated the method using electron backscatter diffraction (EBSD) patterns. Compared to other electron diffraction techniques, such as those in transmission electron microscopy, scanning-electron-microscopy-based EBSD can be performed on large samples and analyzed at multiple length scales and provides local submicron information mapped to the centimeter scale. The complex nature of the diffraction patterns often leads existing methods to find false structure matches in a user-selected list. As a result, the accuracy of the existing software's determination of the lattice type is dependent on the operator's experience and prior knowledge of their sample. The method developed by Prof. Vecchio's group is designed to function autonomously, as the deep neural network independently analyzes each diffraction pattern to determine the crystal lattice, out of all possible lattice structure types, with a high degree of accuracy (>95%).⁶⁴ A wide range of research areas including pharmacology, structural biology, and geology are expected to benefit from using similar automated algorithms to reduce the amount of time required for crystal structural identification.

Theory and Computation. With hardware advances as well as maturing software codes, theoretical computations are today an indispensable complementary toolkit in the nano-engineer's arsenal. Computations offer precise control over the “virtual” experiment conditions and can be scaled efficiently over modern supercomputers, such as those provided at the San Diego Supercomputer Center. Several research groups in the NanoEngineering department specialize in the application of such “virtual experimentation” to provide crucial insights in a variety of materials, from energy storage, to optoelectronics, to structural alloys (Figure 6).

One of the major themes in the NanoEngineering department is in using high-throughput (HT) first-principles

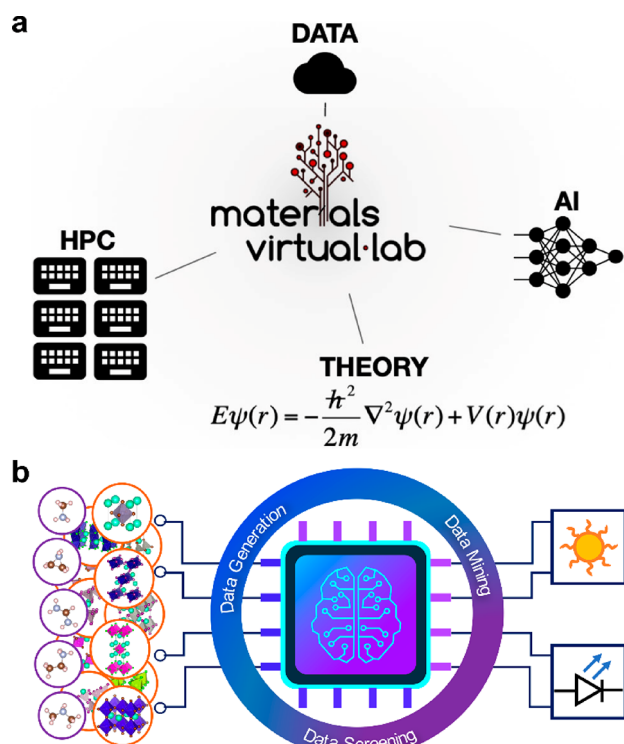


Figure 6. Theory and computation. (a) Activities of the Materials Virtual Lab of Prof. Shyue Ping Ong, which combines data, high-performance computing (HPC), artificial intelligence (AI), and theory to problems in materials for energy conversion and storage. (b) Laboratory of Prof. Kesong Yang applies high-throughput computational design for the large-scale design of novel organic–inorganic functional materials.⁷⁰ Reproduced with permission from ref 70. Copyright 2019 Royal Society of Chemistry.

computations to screen for technological materials efficiently. For example, the Materials Virtual Lab (Figure 6a) has also used structure prediction algorithms coupled with HT density functional theory (DFT) calculations to identify novel phosphor hosts for solid-state lighting, several of which have been successfully synthesized and confirmed.⁷¹ Similarly, Prof. Kesong Yang's group (Figure 6b) has recently applied HT DFT calculations to screen more than 4500 materials for lead-free hybrid halide semiconductors in the perovskite and non-perovskite structures, from which 23 candidates for light-emitting diodes and 13 candidates for solar energy conversion were identified.⁷⁰

A direct consequence of our ability to perform large-scale computations is an explosion in the quantity, quality, and diversity of materials data. The Materials Virtual Lab and Yang group are active developers and contributors to the Materials Project⁷² and AFLOWLIB,⁷³ respectively, two of the largest open databases of computed materials properties. In recent years, machine learning (ML) on large material data sets has emerged as a revolutionary paradigm for accelerating materials discovery and design. A major limitation of first-principles computations is their high computational expense and poor scalability, which constrains both the size (<1000 atoms typically) and number of systems ($\sim 10^6$ materials) that can be computed within a reasonable time frame. One application of ML is, therefore, in the development of surrogate models for material property predictions,⁷⁴ which can enable rapid screening of vast composition spaces for materials meeting a

performance metric (e.g., a specific band gap range for solar cells) or for performing simulations on complex materials systems (e.g., high-entropy alloys, containing millions of atoms). Yet another application of ML is in revolutionizing materials characterization. Prime examples of such an application are the Vecchio group's ML-based approach for rapid and autonomous identification of crystal symmetry from electron backscatter diffraction⁶⁴ and the Materials Virtual Lab's random forest models for accurate identification of coordination environments from X-ray absorption spectra.⁷⁵

Energy Storage. Cheap and safe energy storage is one of the key enablers of our digital age. The rechargeable lithium-ion battery, in particular, is a critical component in consumer electronics and is the leading candidate for the electrification of transportation. Furthermore, many clean energy sources, such as solar and wind, have variable energy outputs, and grid storage is a necessity to smooth out the output in response to demand. In the NanoEngineering department at UC San Diego, there are several research groups primarily dedicated to the development of advanced energy storage technologies, spanning the entire range from fundamental material discovery to novel devices and architectures.

On the material level, the Laboratory for Energy Storage and Conversion (LESC, Figure 7a) led by Prof. Shirley Meng focuses on three main areas in energy storage: (i) probing the bulk, surfaces, and interfaces of electrochemical active materials with a suite of *operando* experiments and first-principles computational methods; (ii) designing and optimizing new electrolyte materials for batteries under extreme conditions; and (iii) quantifying the inactive lithium in lithium metal batteries,⁷⁶ which could double the energy density of today's battery technology with long cycle life and safety. Recently, the LESC designed a new characterization tool, titration gas chromatography, which revealed the true nature of inactive lithium formed in batteries.⁷⁷

Similarly, the Sustainable Materials and Energy Laboratory (SMEL) led by Prof. Zheng Chen focuses on the design and understanding of novel molecules, nanostructured materials, functional polymers, and their hybrid materials for energy storage and conversion (Figure 7b). For example, the group studies electrolytes and electrodes that can enable lithium-ion batteries (LIBs) to work at extremely low temperatures (e.g., -60°C).⁷⁸ The SMEL also applies chemical engineering principles to develop reaction processes for recycling critical materials and treating water. For example, the group develops green and waste-free approaches to recycle layered oxide cathodes more effectively,⁷⁹ making energy storage more affordable and sustainable.

On the device end, the Electrochemical Materials Science Laboratory led by Prof. Ping Liu (Figure 7c) aims to develop low-cost, long-life, and fast-charging energy-storage systems to enable a renewable energy-powered electric grid and an electric-vehicle-dominated transportation system and to use rechargeable batteries as a multifunctional energy-conversion mechanism and a materials synthesis platform. Recently, the group discovered an oxide-based anode material that is capable of charging in seconds with an average intercalation potential of 0.6 V, leading to a long-life, fast-charging lithium-ion battery with >80% energy density improvement over commercial counterparts. In addition, a scalable, general platform for the synthesis of nanoporous metals was developed by leveraging a conversion reaction that has been extensively studied in rechargeable batteries.⁸⁰

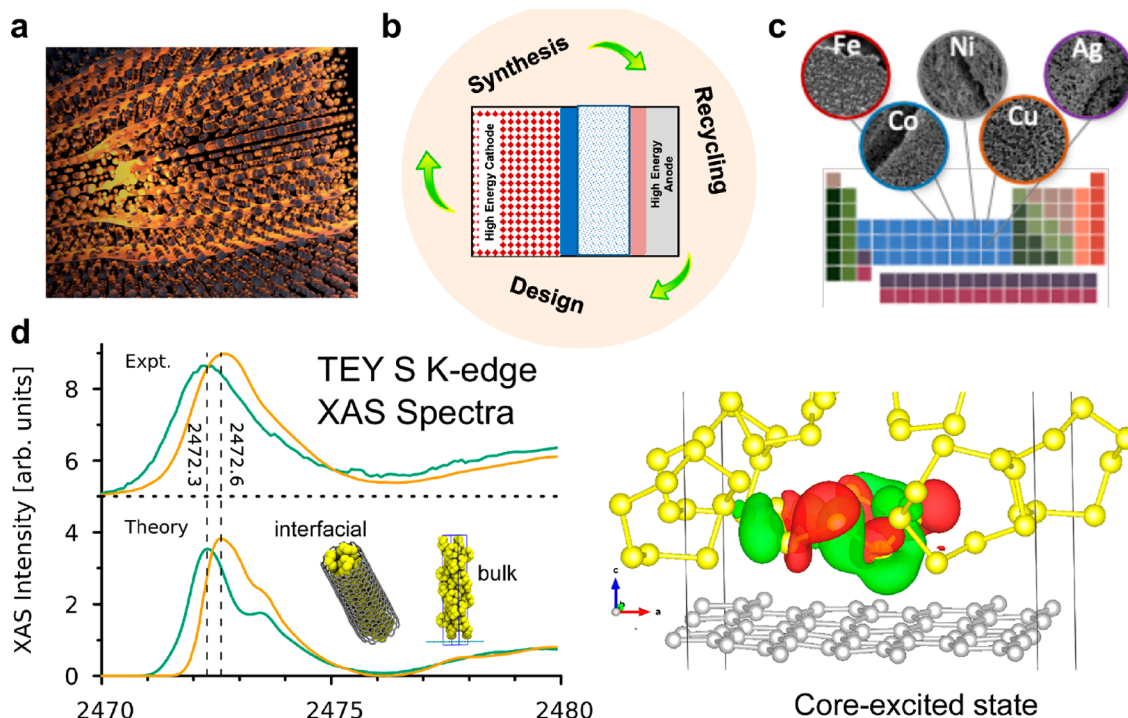


Figure 7. Nanostructured materials for energy storage. (a) Goal of Prof. Shirley Meng's Laboratory for Energy Storage and Conversion (LESC) is to design and to develop new functional nanomaterials and nanostructures for advanced energy storage and conversion applications. (b) Prof. Zheng Chen's group focuses on materials and process design for sustainable energy storage. (c) Prof. Ping Liu's group specializes in electrochemistry for energy storage. Depicted here is a general method for the synthesis of nanoporous metals by removing LiX from LiX/Metal nanocomposites formed through a chemical conversion reaction.⁸⁰ (d) Agreement between experiment and computational results of the total electron yield (TEY) sulfur X-ray absorption spectra (work of Prof. Tod Pascal). Reproduced from ref 81. Copyright 2017 American Chemical Society.

Increasingly, computation and theory are playing crucial roles in novel materials discovery as well. The Advanced Thermodynamics, Light–Matter Interactions and Simulations (ATLAS) Lab (Figure 7d), led by Prof. Tod Pascal, for example, develops computational and theoretical platforms for understanding the processes underlying microscopic systems to advance rational design strategies for nanomaterials relevant for energy storage devices, water filtration membranes and carbon sequestration. Notable recent achievements include a multiphysics framework for non-equilibrium simulations of biased electrochemical interfaces, revealing the core-level and vibrational spectroscopy fingerprints of dissolved lithium polysulfides,^{81,82} which are critical for the operation of lithium–sulfur batteries. These insights were subsequently leveraged by experimental collaborators to develop novel electrolytes for high-efficiency battery charging and discharging in extreme conditions.

Nanophotonics, Nanoplasmonics, and Nanomagnetism. Research in the NanoEngineering department is at the forefront of nanophotonics, nanoplasmonics, and nanomagnetism. One example is in the design and nanoengineering of novel optical probes for sensing and imaging. Prof. Andrea Tao's group uses shaped colloidal nanocrystals as a near-field antenna (Figure 8a), localizing light well below the diffraction limit.^{83,84} They invented a method to assemble colloidal nanocrystals onto commercial atomic force microscopy (AFM) tips probes, demonstrating unprecedented batch-to-batch reproducibility for tip-enhanced Raman spectroscopy.⁸⁵ Their massively parallel and scalable assembly technique presents a step forward in the realization of chemical mapping with

nanoscale resolution. Prof. Donald Sirbulys's group uses nanowires and nanofibers to create optical probes with unique mechanical properties. Using the evanescent field of a subwavelength optical fiber, Sirbulys's group created a nanofiber optic force transducer that leverages extremely sensitive plasmonic-dielectric coupling effects to measure small mechanical events (Figure 8b).⁸⁵ The high force resolution (sub-pN) of their nanofiber system is an order of magnitude better than AFM with a transducer size that is over an order of magnitude smaller. They demonstrated the performance of their platform by detecting sub-pN microflow forces from bacterial motion and recording acoustic signatures in liquid from micromechanical and biomechanical systems with a sensitivity of -30 dB (relative to $1 \mu\text{Pa}$). These nano-engineered sensing platforms fill voids in ultrasensitive instrument development and provide exciting systems to study new near-field light–matter interactions.

Expertise in the study and fabrication of 2D materials has paved the way for new device architectures. Prof. Eric Fullerton's group specializes in magnetic ultrathin films. In a recent collaboration with the Weiss group at UCLA, they demonstrated that ferromagnetic substrates functionalized at their surface with chiral molecular films exhibit spin-selective photoemission, where organic molecules serve as effective "spin filters".^{86,87} They have also fabricated stacks composed of 80 multilayers (0.34 nm thick Fe and 0.4 nm thick Gd) to produce skyrmion lattices. Skyrmions in thin films are cylindrical-like magnetic domains with nontrivial topologies that are pursued as building blocks for next-generation information technologies.⁸⁸ Prof. Ertugrul Cubukcu's and

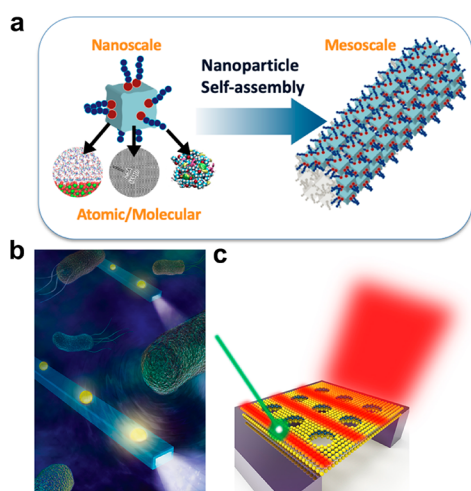


Figure 8. Nanomaterials for nanophotonic and optical applications. (a) Nanoscale Interfaces and Assembly Laboratory led by Prof. Tao works on the rational design of self-assembled nanoparticle materials for materials discovery, the development of structure–function relationships for low-density mesophases, and the investigation of emergent assembly behavior. (b) From the Sirbulys group, an artist's rendition of nanofiber optic force transducers detecting femtoNewton level swimming forces generated by bacteria. Image credit: Rhett S. Miller/UC San Diego. (c) Guiding visible light in an atomically thin semiconductor (Cubukcu group). Upon laser excitation, the monolayer emits photoluminescence. A portion of this light couples into the monolayer and is guided along the material. At the nanohole array, periodic modulation in the refractive index causes a small portion of the light to decay out of the plane of the material, enabling the light to be observed as guided mode resonance.

Prof. Oscar Vazquez-Mena's groups both use 2D nanomaterials in their device design. The Cubukcu group uses 2D transition metal dichalcogenides such as WS_2 in the fabrication of molecularly thin nanophotonic devices and has fabricated one of the thinnest optical dielectric resonators to date.⁸⁹ Only a few atoms thick, these resonators enable waveguiding of visible light by supporting by excitons at room temperature.

Faculty in this area are not only expanding the nanodevice toolbox but developing new fundamental insights into the novel electromagnetic properties of nanostructured materials. These insights are exemplified by research toward the discovery and study of fundamental light–matter interactions, specifically in metamaterials and plasmonic materials. The Cubukcu group recently reported a metamaterial absorber based on plasmonic nanoantenna arrays that supports resonances for sound (acoustic phonon eigenmodes) and light (photon eigenmodes) waves to enable phonon–photon coupling (Figure 8c).⁹⁰ These metamaterials can be pumped to exhibit laser-like acoustic phonon oscillations and cooling *via* a thermoplasmonic effect, which involves efficient conversion of optical energy to heat. Sirbulys's group recently fabricated a mechanically flexible, hyperbolic metamaterial that has near perfect absorption in the near-infrared while maintaining optical transparency in the visible.⁹¹ This capability is enabled by vertically aligned, close-packed nanotube arrays comprising alternating layers of aluminum-doped zinc oxide (AZO) and ZnO deposited by atomic layer deposition, meant to replace the planar metal/dielectric stacked architectures that do not exhibit mechanical compliance.

Tao's group has explored polymer-directed nanocrystal assembly for the formation of plasmonic nanoantennae that also serve as metal–insulator–metal nanojunctions that

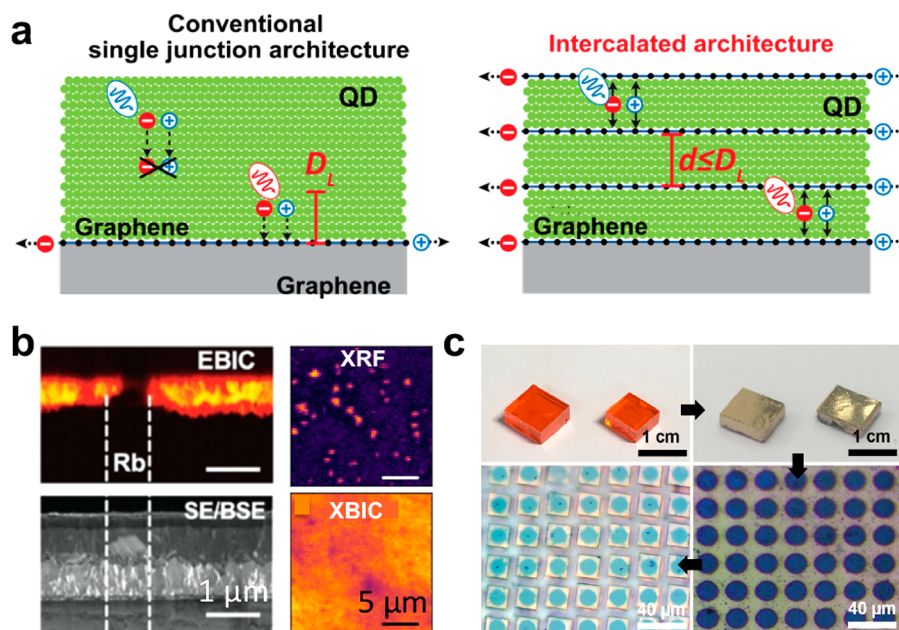


Figure 9. Nanoscale innovation in solar photovoltaics. (a) In an example from the laboratory of Prof. Vazquez-Mena, intercalated graphene layers can be used to ensure efficient charge collection from quantum dots (QD) in optoelectronic devices. Reproduced with permission from ref 94. Copyright 2019 Wiley-VCH GmbH & Co KGaA. (b) Photovoltaic forensics. The SOLar Energy Innovation Laboratory (SOLEIL) led by Prof. David Fenning advances photovoltaic material and device design leveraging unique nanocharacterization capabilities including electron- and X-ray-beam-induced current methods (EBIC/XBIC) and nanoprobe X-ray fluorescence (XRF), and secondary electron and backscattered electron (SE/BSE) to reveal performance-limiting defects. Left two panels reproduced with permission from ref 97. Copyright 2019 American Association for the Advancement of Science. (c) Photographs from Prof. Sheng Xu's work in the area of halide perovskite single crystals and the homoepitaxial growth of perovskite microarrays. Related work is reported in refs 98 and 99.

convert electronic energy into radiated light *via* inelastic electron tunneling.⁹² These nanojunctions take advantage of the highly crystalline, atomically defined facets of chemically synthesized Ag nanocubes to lower plasmonic losses and to facilitate efficient light generation.

Photovoltaics. Research in the department centered on materials for solar photovoltaics covers most material types, including silicon,⁹³ quantum dots,⁹⁴ perovskites,⁹⁵ and organics.⁵⁰ Nanomaterials such as colloidal quantum dots (QDs) excel in their optoelectronic properties, including direct band gaps tunable by size and corresponding strong light absorption. However, translating such properties into high photoconversion efficiency has been a challenge for QDs, lagging well behind bulk semiconductors due to poor long-range charge carrier mobility in QD films. For Prof. Vazquez-Mena, this deficiency is an opportunity to create novel architectures that are better suited for nanomaterials. A common trend in nanomaterials has been to try creating devices simply by replacing bulk materials with nanomaterials, while keeping the same device architecture. However, materials with novel properties may require novel architectures. Prof. Vazquez-Mena recently reported a novel architecture of ordered intercalated stacks of graphene and QDs (Figure 9a).⁹⁴ This architecture improves the charge collection in QD films, previously hindered by poor mobility, using graphene as transparent electrodes intercalated at distances below the QD diffusion length. This novel architecture enables efficient charge collection in QD films approaching 1 μm in thickness, well beyond the diffusion length limit, with quantum efficiency close to 90% in the near-infrared.⁹⁶ This efficiency is remarkable given the poor performance that QD photo-detectors typically show in the infrared.

It is an exciting time in the emerging field of halide perovskite optoelectronics and photovoltaics (PVs). These materials re-emerged onto the research scene in 2009 and have seen a meteoric rise in solar-to-electricity power conversion to surpass those of silicon solar cells. The “hybrid” nomenclature arises from blending an inorganic backbone that offers excellent electronic structure for solar with organic cations that enable simple synthesis at $\sim 100^\circ\text{C}$ —manufacturing them has the potential to be as easy as printing a newspaper. Their hybrid nature that enables this ability appears to be a blessing, but thus far it has also been a curse. Despite much effort, the durability of perovskite solar cells is still far from the rock-solid stability provided by commercial silicon-based technologies. Prof. David P. Fenning’s team has specialized in manipulating the materials chemistry of halide perovskites for PVs, using X-ray microscopy techniques that can analyze the composition of perovskites at nanometer scales to understand absorber formation, degradation, and device operation while circumventing challenges in traditional electron microscopy due to probe degradation. Fenning and co-workers found that, despite the impressive performance of perovskite devices, large nanoscopic variations exist in the stoichiometry in the most common thin film formulations of perovskite solar cells.⁹⁵ More recently, the team revealed that alloying in triple- and quaternary-A-site complex perovskites stabilizes the halide distribution and homogenizes film chemistry at the nanoscale, resulting in improved photovoltaic performance.⁹⁷

Prof. Meng’s research into perovskite solar cells (PSCs) has elucidated the complex chemical interactions in hole-transporting materials (HTMs) and at the interface between the perovskite and the HTM. Studying the commonly used

organic HTM, spiro-OMeTAD (2,2',7,7'-tetrakis(*N,N*-dimethoxyphenylamine)-9,9'-spirobifluorene), and its additives LiTFSI (bis(trifluoromethane)sulfonimide lithium salt) and tBP (4-*tert*-butylpyridine), the team showed that a 4:1 tBP–LiTFSI mixture resulted in full complexation of the constituents, as verified with Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy analyses. As a result, devices with a 4:1 mixture showed better performance and stability and less hysteresis than the common empirically optimized 6:1 tBP–LiTFSI mixture that has been widely applied in PSCs.¹⁰⁰ They also elucidated the mechanism underlying the aging-induced recovery phenomena of PSC devices with Ag electrodes. Perovskite solar cells using spiro-OMeTAD HTM and Ag metal electrodes showed an S-shaped bend in the current–voltage curves after fabrication, which disappeared after 24 h of aging, resulting in enhanced performance. The team found that Schottky barrier formation at the interface was the origin of the S-shaped bend in the device characteristic, and the aging-induced recovery was due to deoxidized spiro-OMeTAD and Ag–TFSI formation (Figure 9b).¹⁰¹

Compared with their more common polycrystalline counterparts, single-crystal halide perovskites show significantly reduced trap density, longer carrier diffusion length and lifetimes, improved material stability, and reduced ion migration. These favorable properties suggest single-crystal halide perovskite devices offer potential for high efficiency, long-term usage, and broadened applications. Prof. Sheng Xu and co-workers reported perovskite-on-perovskite epitaxy with control over film uniformity and thickness. The approach enables direct nano/microfabrication on the halide perovskite single crystals.⁹⁸ Micro- and nanostructured single-crystal halide perovskites with different geometries, orientations, and device structures can be obtained by sequential epitaxial growth for photovoltaic and optoelectronic applications. Xu also demonstrated that interfacial strain can be used to engineer structural stability and the electronic band structure of the halide perovskites.⁹⁹ This controllability in growth geometry, fabrication compatibility, and optical and electronic material properties provides a potential solution to deliver stable halide perovskite optoelectronics.

Teaching. Education is central to our mission as a department, and both of our undergraduate programs are certified by the Accreditation Board for Engineering and Technology (ABET). Whereas the curriculum in chemical engineering is well-established and its content is consistent with what can be found at any well-regarded program, the curriculum in nanoengineering exists only at UC San Diego. Given its interdisciplinarity and newness, it must be designed to respond to the dynamism in the field and the needs of potential employers. Input from our Industrial Advisory Board, exit surveys with students, our internal Teaching Working Groups, and external feedback from ABET auditors and review committees are used to improve our program in a continuous manner. Vice Chair of Education Andrea Tao has been a leader in curriculum development since the early days of the department and oversees these efforts.

Given the diversity of academic fields in which our faculty received training, it is critical that our courses in chemical engineering—the larger of our two undergraduate programs—are covered consistently and authoritatively. Our faculty includes four Teaching Professors, Vlado Lubarda,¹⁰² Justin Opatkiewicz,¹⁰³ Aaron Drews,¹⁰⁴ and Alyssa Powell,¹⁰⁵ who

are specialists in the pedagogy of chemical engineering. Indeed, for all of our degree programs, innovation in teaching methodology is encouraged, and several faculty members engage in styles of instruction consistent with current research on active learning.¹⁰⁶ This work is supported by the extensive use of video,¹⁰⁷ with several instructors using YouTube^{104,108,109} or equivalent repositories for delivering lectures asynchronously (for students off campus or in different time zones) or to produce material intended as prelecture viewing for “flipped classrooms”. In fact, it is our view that experience with video increased the resilience with which we were able to respond to the recent closure of our campus due to COVID-19. It is likely that this experience—at UC San Diego and elsewhere—will spur innovation and lead to a wider acceptance of technology in remote and hybrid styles of instruction.

Conclusion and Prospects. Since its inception in 2007, the Department of NanoEngineering at UC San Diego has grown to 30 full-time research and teaching faculty, whose research interests cover a range of topics in nanoscience and nanotechnology. In fact, our department and *ACS Nano* share the same birth year, and much of our best work has found a home in the journal. We believe the selection of papers in this *virtual issue* showcases the breadth of the department in its activities in research and teaching.¹ We would especially like to highlight the role of chemical engineering in our history and as an intellectual foundation that underpins our research and pedagogy. Indeed, it has been profoundly fruitful for those of us with training in chemistry and materials science to develop systems of nanoscale materials and to understand them through the lens of transport, kinetics, and computation—that is, the toolkits of our colleagues trained in chemical engineering. Similarly, the rich history of topics and teaching methods used in chemical engineering continues to inform our development of the nanoengineering curriculum. We believe this intersectionality is apparent in this Editorial, and that there is quite literally something for every reader of *ACS Nano* within this *virtual issue*.¹ We invite the reader to peruse it and to engage with us in person, in the literature, and on all electronic platforms.

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Notes

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