# Nanophotonics for a sustainable future

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Jennifer A. Dionne; Sahil Dagli; Vladimir M. Shalaev



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# NANOPHOTONICS for a sustainable future

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**Jennifer Dionne** is an associate professor of materials science and engineering and, by courtesy, of radiology, and **Sahil Dagli** is a graduate research assistant, both at Stanford University in California. **Vladimir M. Shalaev** is the Bob and Anne Burnett Distinguished Professor of Electrical and Computer Engineering at Purdue University in West Lafayette, Indiana.

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**As the field matures, its researchers are finding practical applications in solar-energy harvesting, chemical manufacturing, optical refrigeration, and energy-efficient computing.**

In the field of nanophotonics, researchers strive to precisely control light and its interaction with matter. A few successes include record-setting photovoltaic efficiencies, sensors capable of detecting single molecules and trace amounts of viruses and bacteria, and therapies that can kill tumors noninvasively. Futuristic technologies, such as solar sails for near light-speed space propulsion, quantum photonic computers, and sensors for deep-sea ocean exploration, are also in the works.



How do those technologies work? Nanophotonics researchers have devised methods to control the amplitude, phase, polarization, and localization of light. Some of the unique principles underpinning nanophotonics have been exploited for centuries. Artisans during the Middle Ages commonly used metal nanoparticles to tune the color of stained glass in windows. A more ancient example, dating from the fourth century CE, is the famous Lycurgus cup, whose glass appears green in reflected light but red in transmitted light. In both examples, the metal nanoparticles dispersed inside exhibit resonant absorption or scattering of visible light at specific wavelengths, which gives rise to the vivid color.

Yet the field of nanophotonics has grown rapidly only in the past two decades. A recent explosion of new materials—including two-dimensional compounds and their heterostructures and metallic, dielectric, and semiconducting nanoparticles—fueled the growth. Each of those materials can be assembled in all dimensions with near atomic-scale precision. Moreover, improved computation, machine learning, and sophisticated classical and quantum simulations have accelerated their design. Nanophotonics researchers can also leverage the same manufacturing techniques used to make computer chips with nodes that are just a few atoms long and other nanoscale devices at low cost.

Imagine a future with plentiful clean-energy harvesting to phase out fossil fuels, chemical manufacturing that does not emit harmful pollutants or produce wasteful byproducts, point-of-care diagnostics and sensors, and computers that operate at light speed and consume little energy. Advances in nanophotonics are poised to usher in that future, and in this article we describe the underlying physics.

## Materials palette

A material's optical response is directly linked to its electronic behavior. Metals and semimetals have free conduction electrons and exhibit different optical responses than do semiconducting and insulating dielectric materials, whose electrons are bound. Nanophotonics researchers tailor the shape and composition of nanostructures made of those materials to precisely control their optical response (see figure 1).

In the case of metallic nanostructures, a light field causes free electrons in the nanoparticle to oscillate in resonances called surface plasmons. The field of study focused on the fundamentals and applications of surface plasmon resonances is known as plasmonics (see the article by Mark Stockman, Physics Today, February 2011, page 39). The oscillating free electrons create an electric dipole that confines and amplifies electric fields in extremely small volumes called hot spots that are incredibly sensitive to the surrounding environment. Plasmonic behavior is also observed in metallic thin films, whose extended dimensions allow a surface plasmon to propagate along the interface between the film and its surroundings.

Doped semiconductors are also a common plasmonic material. As in metals, those plasmons rely on free conduction electrons, whose concentration and mobility can be tuned based on the material and its dopants. Because of their lower freecarrier concentration, compared with metals, many doped semiconductors exhibit lower-energy IR resonances and absorb less light.[1] Recent advances include creating robust and refractory plasmonic ceramic materials, such as titanium nitride and zirconium nitride. They have a high melting point and are chemically stable at temperatures above 2000 °C. That makes them capable of operating in extreme environments and enduring shock and exposure to contaminants. And they are well suited to being used as durable plasmon catalysts and compact sensors.

Dielectric resonances share many of the exciting properties of plasmon modes—they confine light to small volumes and strongly amplify electromagnetic fields. Light still induces a dipole moment in dielectrics, causing bound charges (rather than free electrons) to oscillate in the material. Yet dielectric nanostructures also possess unique features. For example, because of their positive permittivity values, they support strong electric and magnetic fields localized inside the dielectric rather than at its interface. In the presence of light that is not energetic enough to excite electrons over the bandgap of the material, dielectrics are also lossless. Therefore, unlike metals, their nanophotonic structures do not locally heat and can exhibit longer-lived resonances with sharper spectral linewidths, known as high quality-factor resonances.[2]

Atomically thin 2D materials are also emerging as an important class of nanophotonic components. They can span the entire range of electronic behavior. Transition metal carbides and nitrides—known as MXenes (see page 12 of this issue)—and graphene can act like semiconductors or metals and can support plasmons. Transition-metal dichalcogenides, such as molybdenum disulfide and tungsten diselenide, exhibit semiconducting behavior in the plane of the material and host excitons (bound electron–hole pairs). Wider bandgap 2D materials, such as hexagonal boron nitride, generally exhibit insulating, dielectric behavior.

Several of those materials can also host color centers—defects in the crystal lattice that serve as single-photon emitters.[3] Importantly, they can be exfoliated over large areas and stacked to form 3D heterostructures and so-called atomic metamaterials.[4] In thicknesses of up to a few nanometers, 2D materials can exhibit near-unity absorption and reflection, and their refractive indices are strongly tunable with applied voltage or light intensity. They also have electronic spins that can be directly excited by the photon spin and behave as optically addressable spin qubits and quantum sensors.

Periodic arrangements of subwavelength-sized nanoparticles from any of the above materials can give rise to collective optical responses distinct from the bulk material. Metasurfaces and metamaterials leverage that behavior to sculpt wavefronts of light. (See the article by Martin Wegener and Stefan Linden, Physics Today, October 2010, page 32.) By tuning the geometry of a nanoscale antenna unit cell, researchers have

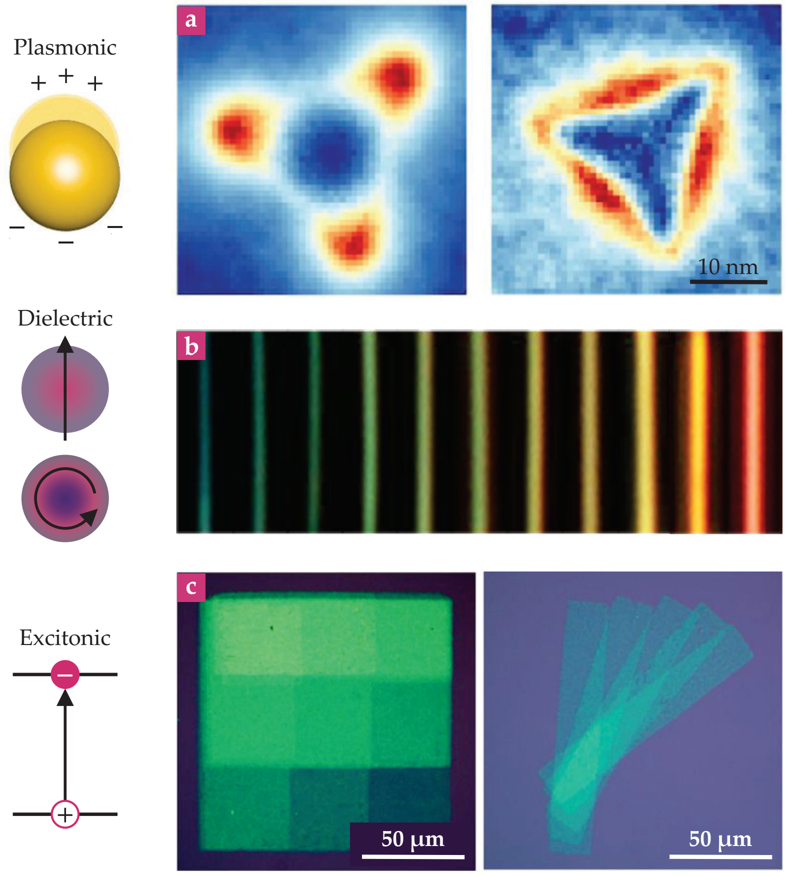


**FIGURE 1. OPTICAL RESONANCES.** At left (from top), a nanostructure can experience plasmonic resonances—charge-density oscillations—if it has free electrons, dielectric resonances if it has bound electrons, or excitonic resonances if it has bound electron–hole pairs. The resonances create an electric dipole that confines and amplifies the electric field in a tiny volume. **(a)** Experimental maps of the plasmonic modes in silver–palladium nanoprisms reveal the electric field's confinement at a prism's tips (left) and at its edges (right). (Courtesy of Daniel Angell and Jennifer Dionne.) **(b)** The colors on vertical strips of silicon dielectric nanorods change vividly as their radii in successive strips increase from 30 to 180 nm. (Adapted from L. Cao et al., *Nano Lett.* **10**, 2649, 2010.) **(c)** These photographs show the excitonic white-light reflectance of two-dimensional materials (left) and their stacked and twisted heterostructures (right). (Adapted from ref. 4.)

produced a host of flat optical devices, such as lenses, beam steerers, holograms, and lasers in ultrathin (submicron) and ultralightweight (milligram-scale) platforms.[5] Their 3D analogs—metamaterials—have produced sci-fi-like phenomena, such as negative refraction and invisibility cloaking, thanks to their complete control over the dispersion and propagation of light, from molecular to macroscopic length scales. (See Physics Today, February 2007, page 19.)

## Plasmon catalysis

Metal nanoparticles are common catalysts for producing the fertilizers, fuels, and materials that support modern society. For example, the iron-based catalysts of the Haber–Bosch process produce ammonia; platinum nanoparticles catalyze the

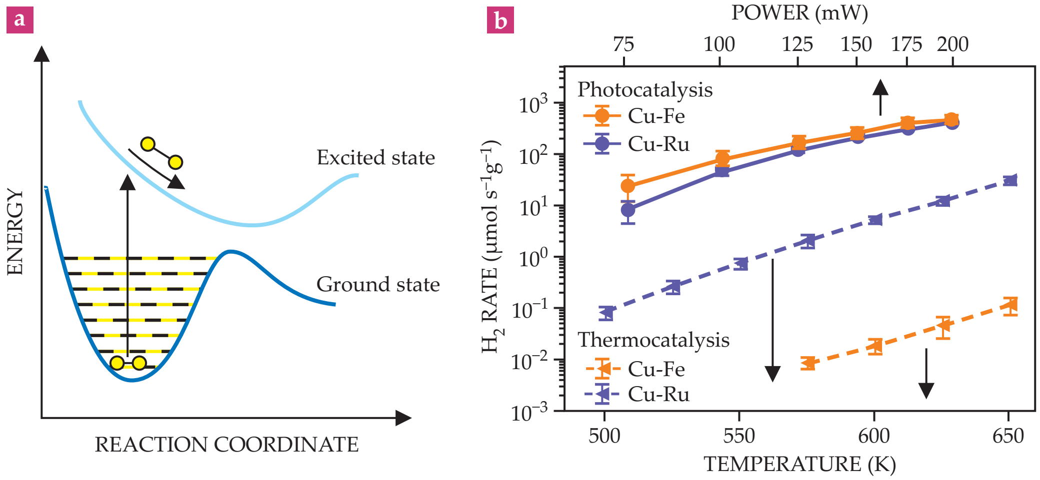


**FIGURE 2. PLASMON CATALYSIS. (a)** A molecular adsorbate on a catalyst initially sits at the equilibrium position on a ground-state potential-energy surface and requires a certain activation energy to dissociate. Photoexcitation of the catalyst (a plasmonic particle) deposits energy into the adsorbate and elevates it to an excited state, where it can react. (Adapted from ref. 6.) **(b)** Such processes can increase the reaction rates and product selectivity, as compared with thermocatalysis. In the case of hydrogen production from ammonia, the plasmonic element copper facilitates light absorption, whereas iron or ruthenium enables chemical conversion. (Adapted from ref. 7.)

reforming of naphtha for gasoline; palladium nanoparticles catalyze the formation of plastics and pharmaceutical intermediates; and gold nanoparticles catalyze solar-fuel generation and carbon dioxide reduction. To overcome the activation barriers of various reaction steps, metal-nanoparticle-catalyzed reactions generally operate at high temperatures that are typically achieved by burning petroleum fuels. But such thermal processes can form undesirable byproducts that require additional energy to separate and purify them.

Compared with thermal catalysis, plasmonic catalysis promises precision chemistry, in which reactions are simultaneously high yield, product selective, and free of greenhouse gas emissions.[6] Surface plasmons generate nanoscopically controlled distributions of electrons, photons, and phonons. They provide a chemical scalpel for sculpting reaction dynamics with a precision that is orders of magnitude higher than can be achieved using conventional thermo-, electro-, and photocatalysis. The plasmons offer such control through three main mechanisms.

First, strong electromagnetic fields at the surface of plasmonic metallic nanoparticles locally amplify the photon flux and can be used to improve the yields of countless chemical reactions. Second, localized heating associated with plasmonic near fields can increase chemical reaction rates and modify the products that are formed. And third, illuminating the surface can raise electron temperatures to several thousand degrees kelvin because electrons have a much smaller heat capacity than their host lattice.

Such hot electrons or holes, which are generated on plasmon decay, dissipate their energy using either molecular surface adsorbates or the catalyst lattice itself to heat the system to a few hundred kelvin. That feature of plasmon catalysis can not only influence the dissociation and desorption of small molecules but also open new, excited-state reaction pathways under optical excitation, as outlined in figure 2a.

Traditional transition-metal catalysts, such as iron, palladium, platinum, and nickel, have weak visible-frequency plasmon resonances. But they can be combined with plasmonic metals, such as silver, gold, and copper, to bolster the absorption of light while maintaining high chemical activity. Such bimetallic plasmonic systems generate catalytic activity that is highly dependent on the excitation wavelength and polarization state and on the particle's shape, size, and surface chemistry. Bimetallic systems can be created as a multinanoparticle antenna-reactor complex or as an alloy of the catalytic and plasmonic metals.

The many recent and exciting advances in plasmon catalysis are now bringing within reach sustainable hydrogen production, water splitting, ammonia synthesis, carbon capture, and $CO_2$ reduction. For example, Rice University doctoral student Yigao Yuan and his colleagues demonstrated the production of hydrogen gas from ammonia using an LED (see figure 2b); they employed earth-abundant iron as a catalyst rather than the more commonly used but less abundant ruthenium.[7]

Other exciting catalysis work is the exploration of selective reactions, including in producing the plastic (poly)ethylene from acetylene and in developing large-scale photoreactors for industrial materials, such as steel, whose manufacturing is responsible for 8% of all greenhouse gas emissions. A key challenge for the future will be developing reactors for efficient illumination of such catalysts, although several startup companies are making exciting progress.

## Solar-energy harvesting, storage, and cooling

In various parts of the world, the low cost and increasing efficiency of silicon and silicon-tandem solar cells make photovoltaic (PV) energy more economical than fossil fuels. As the use of solar PV technologies grows, researchers strive to increase the efficiency of solar cells to the Shockley–Queisser limit and beyond—ultimately to the thermodynamic, so-called Landsberg limit. Various plasmonic systems can trap incident light and concentrate it in or guide it across the solar cell. Such systems can also increase the efficiency of solar concentrators and solar upconverters, which convert photons whose energy may be below the bandgap of the solar cell to higher energy photons that can be absorbed.

What's more, nanopatterning the PV material itself to support dielectric resonances that trap light can help prevent nonradiative recombination. Some nanophotonic materials systems can even break the equivalence between emission and absorption—a principle known as Lorentz reciprocity—which further boosts solar PV efficiencies. Several of those fundamental discoveries are now commercialized; for details, see the review in reference 8.

The Sun does not shine around the clock, and societies will need scalable energy storage devices to fully move away from fossil fuels. Although battery technologies are rapidly advancing, they are not always cost-effective or practical. Fortunately, other options exist. A thermal storage medium, such as graphite, stores electricity through Joule heating. The heat can then be converted back into electricity using thermophotovoltaic (TPV) cells. Such cells are made of semiconductors with lower bandgap energies than silicon, such as indium gallium arsenide, which can absorb low-energy photons emitted from the thermal storage medium.

Ultrareflective mirrors placed on the rear of the TPV cell improve its efficiency by sending photons that were not absorbed by the semiconductor back to the thermal battery to be reabsorbed as heat. When such highly reflective mirrors are combined with semiconducting materials optimized for temperatures of 1900–2400 °C, the TPV devices can reach efficiencies[9] of 40%.

Beyond thermal storage, nanophotonic design can offer novel approaches to cooling. Air conditioning amounts to 15% of the electricity consumed by buildings in the US. To ameliorate that load, hot objects can transfer energy to colder objects until their temperatures equilibrate. Think of the universe as a heat sink. Heat gets transferred from Earth to the cold of outer space as blackbody radiation through the atmosphere's transparency window of 8–13 μm (see figure 3a). An ideal thermal emitter maximizes emissivity in that wavelength range to avoid trapping the heat in the atmosphere. That process becomes more challenging during the daytime, however, when Earth is heated by absorbed sunlight.

Nanophotonic devices cool an area using systems that reflect the visible range of sunlight but emit thermal radiation in the mid-IR. They do not heat up in direct sunlight and are able to cool down well below the ambient temperature. In initial demonstrations, researchers used a 1D photonic crystal composed of oxide thin films on a silver mirror, creating a Fabry–Perot cavity that maximizes emission from 8 to 13 μm. They then integrated a thinner set of films into the device to maximize the reflection of sunlight.[10]

Practically implementing such a passive radiative cooling device requires isolating it from the surrounding environment to reduce heat exchange through conduction and convection. Apparatuses with insulating materials or air gaps surrounding the radiative cooler can usually do the job. As the technology scales to rooftop installations to improve cooling inside buildings, materials such as paints and polymer films are being used to improve durability and reduce costs.

Those radiative cooling techniques can also be repurposed for energy harvesting.[11] As the device cools, it experiences a spatially varying temperature gradient that can be combined with a thermoelectric generator to produce electricity. Researchers recently powered an LED in a demonstration of the idea, sketched in figure 3b. Impressively, the demonstration took place at night and used the thermal gradient between Earth and outer space. Such technologies are opening opportunities for off-grid lighting in resource-limited areas.

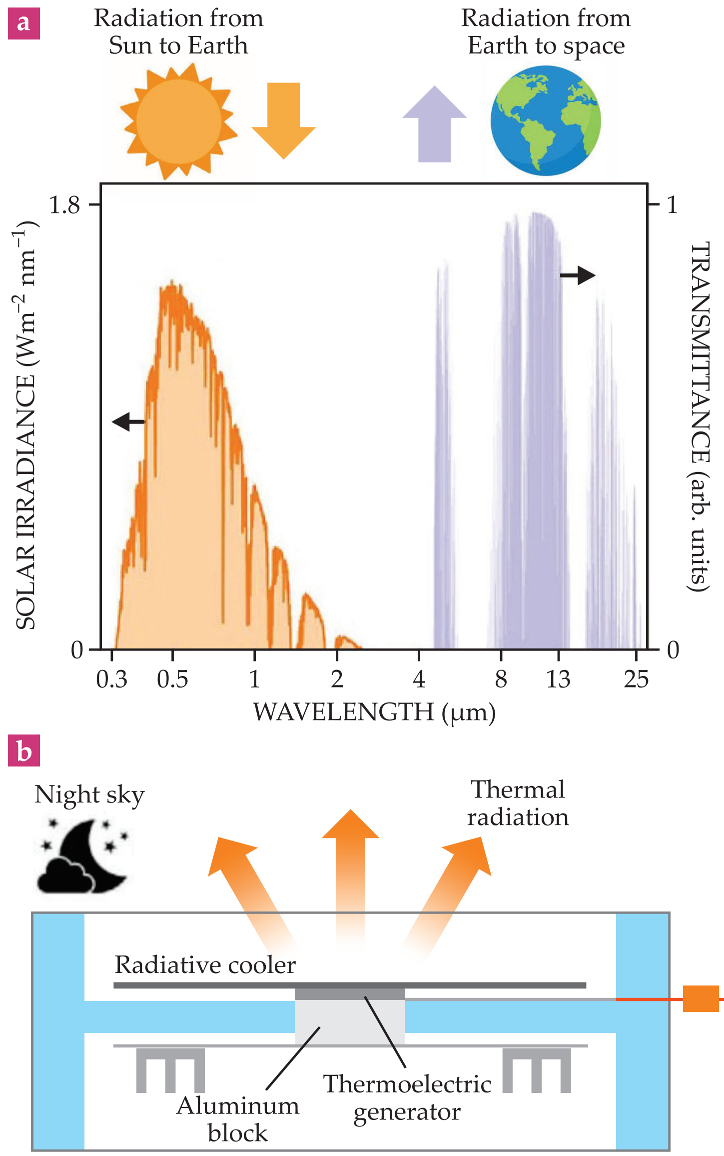


**FIGURE 3. NANOPHOTONIC SYSTEMS** can control optical absorption and thermal emissivity for various applications. **(a)** At left, the spectral energy intensity of solar radiation is plotted per unit area and per unit wavelength; at right, the thermal radiation from Earth is plotted. For photovoltaic applications, absorption should be maximized in the range of solar radiation. For radiative cooling, absorption should be minimized in the same range while simultaneously maximizing emissivity in the range of atmospheric transparency. (Adapted from ref. 10.) **(b)** Radiative cooling can be used to generate electricity when combined with a thermoelectric generator. Such systems produce electricity off the grid. (Adapted from ref. 11.)

## Environmental monitoring

Climate change threatens ecosystem health, food security, and quality of life. Nanophotonics provides a way to monitor that threat. For example, sensors of environmental DNA—the genetic material released by organisms into the environment—

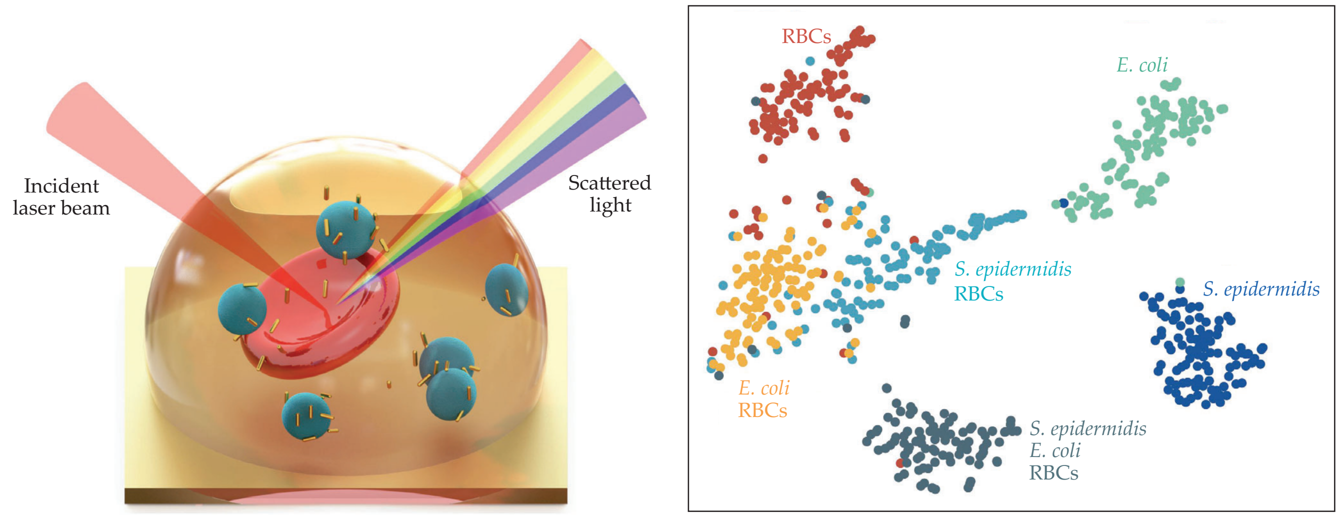


**FIGURE 4. NANOPHOTONIC SENSORS** can monitor the environment in real time at high resolution. Surface-enhanced Raman scattering (SERS) can amplify weak vibrational signals to detect the presence of molecules. A schematic (left) illustrates the scattering of laser light into a liquid droplet composed of red blood cells (RBCs; red), bacteria (blue), and plasmonic nanorods (gold). Combined with machine learning, SERS can detect *Escherichia coli*, *Staphylococcus epidermidis*, and other pathogens (right, in a two-dimensional projection of the data) in complex liquid samples, such as blood and wastewater. (Adapted from ref. 13.)

reveal details about the abundance and distribution of species and thus can provide an early indication of how invasive they may be. Such sensors can also detect toxins in the soil, air, rivers, and oceans, and they can survey areas for such extreme environmental conditions as wildfires and tsunamis so authorities can warn of threats to nearby communities.

The ability of nanophotonic materials to strongly concentrate electromagnetic fields allows them to behave as sensitive molecular detectors. In certain sensor designs, nanophotonic resonators are decorated with molecules that are specific to the analyte of interest. Binding those molecules to a target analyte modifies the optical signal because of subtle changes in the polarizability or refractive index of the resonator environment.

Recent studies have developed both plasmonic- and dielectric-based sensors of DNA, RNA, proteins, and metabolites. Indeed, SARS-CoV-2 rapid antigen tests rely on plasmonics principles—in particular, the color change that gold nanoparticles experience when antigens bind to antibodies. The tests' sensitivity can even be boosted to the single-molecule level when high-quality-factor structures, such as those hosting guided-mode resonances, are used.

Gas-phase molecules can be detected as well. For example, palladium nanoparticles in a hydrogen-rich environment can undergo hydrogenation; the resulting palladium hydride has a refractive index and thus resonant frequency that's distinct from pure palladium. Researchers have designed metasurface arrays of palladium nanoparticles that experience a large electric field amplification and yet have a narrow spectral linewidth. Sensors with that design can pick up hydrogen at parts-per-billion concentrations.[12]

That sensitivity is critical for rapidly detecting hydrogen embrittlement in materials used for hydrogen storage. Expanding the capabilities for gas-phase sensing could also lead to remote sensing, optical "e-noses" that pick up various gases and flavors, and sensitive atmospheric gas spectroscopy.

Beyond approaches that rely on surface functionalization, nanophotonics can detect, label-free, molecules and cells using vibrational spectroscopy. Techniques such as surface-enhanced Raman scattering (SERS) and surface-enhanced IR absorption do just that (see the article by Katrin Kneipp, Physics Today, November 2007, page 40). The analyte's specific structural information is encoded in photons that are inelastically scattered by symmetry-dependent phonons.

Although those vibrational spectroscopies have been limited historically by poor efficiencies, the inclusion of plasmonic and dielectric materials boosts their sensitivity to the single-cell and single-molecule level. SERS can amplify the optical signal by a factor of $|E(\omega)|^4/|E_0|^4$, where $E_0$ is the incident electromagnetic field, and $\omega$, the optical frequency. Such enhancements are routinely as high as $10^6$.

Unlike approaches that rely on fluorescent tags, the label-free techniques maintain high temporal resolution and do not interfere with molecular or cellular integrity. They can be combined with machine learning to identify dozens of bacterial cell species and strains, including their drug susceptibility—even in complex liquid samples, such as blood and wastewater (see figure 4).[13] Metasurfaces[14] are especially valuable in under-resourced settings for such applications as single-cell analysis and the detection of pesticides or plastics when a dedicated spectrometer is not available.

Nanophotonics is also making significant strides in larger-scale environmental monitoring, particularly in lidar technology. Lidar is a scanning and sensing tool that uses time-of-flight measurements of light pulses to map a surrounding area—similar to radar but with higher resolution. Not only has the technology found a home on air, space, and ground vehicles, but it is also increasingly crucial for autonomous systems, such as self-driving cars, robotics, and unmanned aerial vehicles. Additionally, it can be used to survey areas for hurricanes, wildfires, and other environmental threats to local communities.

Lidar is typically a bulky technology with limited mobility, largely because its laser light sources and detectors are configured on mechanically rotating mounts. Flat optical components based on metasurfaces are now capable of completing a number of tasks needed for lidar, such as beam deflection and point-cloud generation.[15]

Electrically reconfigurable metasurfaces are being developed for solid-state devices capable of full wavefront control. They require constituent materials whose refractive index is tunable with an applied stimulus, such as voltage. Liquid crystals, phase-change materials, epsilon-near-zero materials, quantum-well structures, and electro-optical polymers and crystals are all promising options.

Liquid crystals and phase-change materials offer a wider range of refractive-index tuning but can be limited in switching speeds. Electro-optical polymers and crystals generally have a narrower tuning range because of their weaker electro-optical coefficients, but they can operate at faster speeds. Metasurfaces having a high quality factor increase the field enhancement in the tuning medium, which in turn reduces the required voltage and improves device efficiency.

Recent advances in the field include the development of electro-optical and thermal metasurface devices capable of tunable beam steering and lensing. That work focuses on increasing the devices' field of view and switching speed and efficiency. By improving the systems' integration, researchers will also improve nanophotonic lidar's ability to extract information from the environment for such applications as remote gas sensing and high-resolution mapping.

## Energy-efficient computing

It's estimated that data centers consume 1.5% of the world's electricity. The energy cost for a single operation in a standard von Neumann architecture is bounded by $kT\ \ln(2)$, the so-called Landauer limit. Yet existing computing systems far exceed that thermodynamic limit and consume a million times more energy per operation; the dominant cost comes from the transmission of the signal through electronic interconnects. Nanophotonics researchers are exploring novel computing architectures that can reduce the power consumption without sacrificing computational complexity or speed.

Advanced computational tasks, such as image processing, often require analog-to-digital conversion in signal processing systems. That conversion requires power and time, but wave-based analog computing can bypass the need for it. Metasurfaces can perform mathematical operations on beams of light, which expedites computation in a relatively small footprint and with the capability of highly parallel operations. What's more, passive metasurfaces require no power consumption to operate.

For example, several metasurface platforms have been developed to detect edges—a critical step in defining features for image processing and computer vision. Near the edges of an object in a differentiated image, sharp changes in brightness are highlighted, while areas with more constant brightness are filtered out (see figure 5). Current metasurface processors detect those brightness changes in real time without relying on digital electronic computing.[16] And their compact size, or form factor, allows them to be integrated into many existing imaging systems.

More sophisticated metasurface designs are capable of also solving equations. The Fredholm integral equations, for example, were recently solved using a metasurface and a semitransparent reflecting plate. The device performed an iterative Neumann series to converge to a solution by reflecting off a semitransparent mirror and interacting repeatedly with the metasurface. The total time for the solution to converge was 349 fs—much faster than the speed of a conventional processor. Operating at visible wavelengths, the form factor of that nanophotonic device opens opportunities for chip-scale integration with other computing elements.[17]

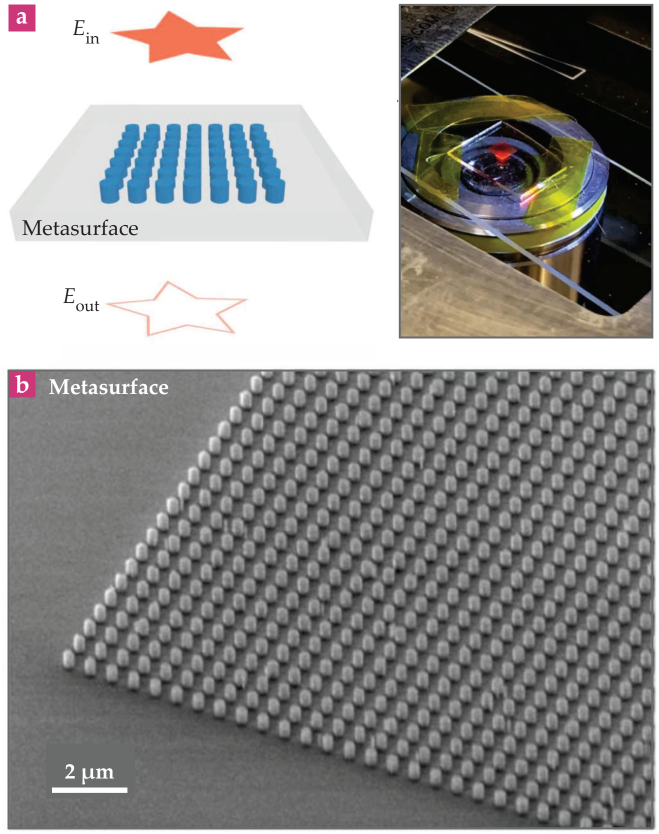


**FIGURE 5. METASURFACES** can enable energy-efficient computing. **(a)** They are engineered to detect the edges in an image, a star in this case. By taking a second-order spatial derivative of an incident electric field $E_{in}$, the metasurface—an array of silicon nanorods, each one effectively a dipole antenna—generates an output image whose edges are enhanced, and the rest of the image is filtered out. The adjacent photograph shows a fabricated metasurface on a glass slide, atop a microscope objective. **(b)** This scanning electron micrograph shows the structure of the edge-detecting metasurface. (Adapted from ref. 16.)

Beyond analog computing, nanophotonics is paving the way for breakthroughs in quantum information systems. Optical resonators magnify the interaction between light and the materials used for quantum information by an amount proportional to the ratio of the resonator's quality factor $Q$ and the mode volume $V$. For instance, various plasmonic nanoantennas and metasurfaces have been used to enhance and direct the emission from 2D transition-metal-dichalcogenide excitons at different valleys in the band structure and in different directions. The spatial separation of that emission is helpful for reading out the valley information as a quantum state.

Metasurfaces have also been used to enhance valley-specific photoluminescence and retain the valley polarization, even at room temperature. High-$Q$ resonators can enhance the light–matter interactions with longer resonance lifetimes. Low-$Q$ plasmonic nanoresonators, by contrast, have a different set of advantages: They offer broadband operation at much faster speeds.

Intriguingly, the spontaneous decay rates of quantum emitters coupled to broadband and ultrafast plasmonic nanocavities can be sped up and potentially outpace room-temperature quantum decoherence rates in matter.[18] That feature is especially critical for generating indistinguishable photons and entangled states. Plasmonics can therefore increase the rates of quantum processes to the extent that they become immune to decoherence. Furthermore, it promises to bring the operation of quantum photonic systems to the terahertz range by offering variable bit rates.

## On the horizon

Leveraging advances in materials science and machine learning, researchers continue to develop ways to advance chemical manufacturing, solar energy, environmental monitoring, computing, and communications. An ever-growing suite of new materials is expanding the realm of possibilities, based on unique light–matter interactions. In parallel, new algorithms and machine-learning models keep improving researchers' abilities to design better optical systems.

The advantages from those nanophotonic advances abound: Plasmonic photocatalysis is likely to improve the selectivity of chemical production and facilitate reactions that would be energetically unfavorable otherwise. Nanophotonic-enhanced PVs could be integrated directly into buildings and windows, while radiative cooling devices revolutionize our cooling infrastructure. Nanophotonic-enhanced vibrational spectroscopy, meanwhile, will rapidly detect viruses, bacteria, and toxins and will monitor our air, water, and soil in real time. Computing will be greatly advanced and far more energy efficient. In short, the physics of light provides almost countless benefits for the world we imagine in our future.

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