

Nanoplasmonics: The physics behind the applications

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The field of nanoplasmonics is young but rich in phenomena that have inspired practical uses in physics, biomedicine, environmental monitoring, and national security.

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Nanoplasmonics is the study of optical phenomena in the nanoscale vicinity of metal surfaces. At first glance, that operational definition may be puzzling, given the common presumption that electromagnetic radiation cannot be concentrated, focused, or confined to a region whose size is less than half the light's wavelength. Indeed, it appears obvious that the minimum volume of an optical field localized in a cavity—bounded by three pairs of ideal mirrors, say—is $(\lambda/2)^3$, where λ is the wavelength. That's about $0.01 \mu\text{m}^3$. The question, therefore, is this: How can an optical field be localized seven orders of magnitude tighter, on the scale of 1 nm^3 ?

The answer lies in what happens to nanoparticles made of conducting metal such as gold when they are subjected to an external optical wave, as sketched in figure 1. The particles should be smaller than the metal's skin depth—how deeply the optical radiation penetrates the metal. That depth is roughly 25 nm for coinage metals, copper, and alkaline metals over the entire optical and most of the IR region. On the minimum end, the particles should not be smaller than the so-called nonlocality length l_{nl} —the distance that an electron with Fermi velocity $v_F \sim 2 \times 10^6 \text{ m/s}$ moves during one optical oscillation. Since a half period is about a femtosecond, that nonlocality length is 2 nm. Thus nanoplasmonic phenomena unfold on a characteristic length scale between 2 and 20 nm. On that scale, an incident light wave is always a plane wave, and no focusing of light in the optical far-field is possible.

To first approximation, the electrons of the metal nanoparticle move freely and, driven by an external light's electric field, are periodically displaced with respect to the lattice ions. The displacement creates charges at opposite surfaces. Because those charges attract each other, there also exists a restoring force. The result is an electron oscillator, whose quantum is called a surface plasmon (SP) and whose frequency is determined by the restoring force and effective mass of the electron.

The frequency of the SP depends not only on the metal's composition but also on its size and shape, as illustrated in figure 2, and on the dielectric material that may surround it.^{1,2} Nanoparticles with elongated shapes acquire red- and blue-shifted SP modes because of the different distances between the charges at opposite surfaces; that, in turn, changes the restoring force. A surrounding dielectric screens the surface charges, causing the frequency to redshift. That is the foundation for some of the nanoplasmonics applications to sensing, as we'll see.

Stained glass

The resonant properties of plasmonic metal nanoparticles are readily apparent to the naked eye because the excitations absorb and scatter light at optical frequencies. The most ancient example is the famous fourth-century CE Lycurgus cup from the British museum, whose glass looks green in reflected light but ruby red in transmitted light. Those colors are complementary, evidence that there is little optical loss inside the glass. Investigation has shown that the dichroic glass contains nanocrystals of a gold–silver alloy at a fraction of less than 1%.

Such colloidal suspensions of gold and silver have been widely used in stained glass since the Middle Ages. Transmission through a silver colloid yields yellow light and transmission through gold yields ruby red. The magnificent colored light from the stained glass of the Sainte Chapelle in Paris is assumed to be largely due to the nanoplasmonic resonances.

Unlike glass-staining metal ions such as iron, chromium, copper, and cobalt, metallic nanoparticles, which both absorb and scatter, transmit light with an intensity that strongly depends on the incident and viewing angles. The Sainte Chapelle dramatically exploits the effect: At sunset, the grazing-angle scattering of light by gold nanoparticles in the windows creates a pronounced red glow that appears to slowly move downward, while intensities of blue tints from ions of copper or cobalt remain the same. The artistic impression, probably intended, suggests a stream of blood slowly flowing downward. (A photo showing the effect is available with the online version of this article.)

Faster, smaller, stronger

The three most important properties of SPs are the quality factor Q , the oscillator strength f , and the modal volume V_m , the nanoscopic volume in which the SP is localized. What's more, SPs have ultrafast dynamics, with plasmon relaxation times on the order of 10 femtoseconds and coherent evolution times even shorter, around 100 attoseconds, a property that makes them important for information processing and optical memory.

The quality factor is a measure both of how many oscillations an SP undergoes before it decays and of the concomitant increase in the local field amplitude when SPs are resonantly excited by an external optical field. More formally,

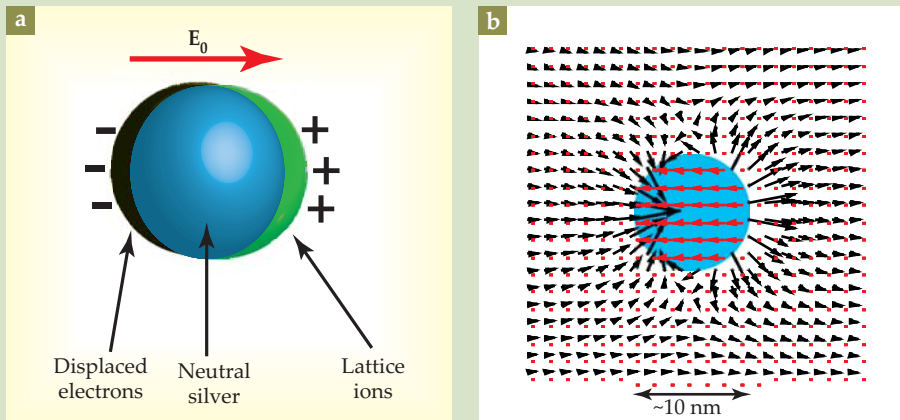


Figure 1. An instantaneous snapshot of the localization of an optical field in a nanosystem. (a) When an external light wave is incident on a 10-nm-diameter silver sphere, its electric field E_0 periodically displaces the sphere's electrons with respect to the lattice. The result is an oscillating electron density—a localized surface plasmon. **(b)** The electric field (black arrows) from displaced electrons is greatly amplified on opposite sides just outside the silver sphere, as calculated here for a resonant photon

energy of 3.5 eV. Inside the sphere, the electric field is uniform (red arrows) and is on the same order of magnitude as the local field just outside the sphere.

Q can be expressed in terms of the dielectric function through the real and imaginary parts of the metal's permittivity: $Q = -\text{Re}\epsilon_m / \text{Im}\epsilon_m$

For noble metals, Q ranges between 10 and 100. The resonant enhancement of the local optical-field intensity is proportional to a factor of Q^2 , between 10^2 and 10^4 . Importantly for many applications, that factor also indicates the enhancement of the absorption and emission rates for molecules adsorbed on the metal particles. For processes involving two photons, such as surface-enhanced Raman scattering (SERS), the enhancement scales as a factor of Q^4 and can thus be enormous—between 10^4 and 10^8 . An additional factor related to the geometrical arrangement of nanoparticles can raise the SERS enhancement higher still (see the article by Katrin Kneipp in *PHYSICS TODAY*, November 2007, page 40).

The oscillator strength for an SP is equal to the number of the conduction electrons in a nanoparticle, about 10^5 typically. In comparison, for a dye molecule or a semiconducting quantum dot f is about 1. The absorption cross section is proportional to f , and the scattering cross section is proportional to f^2 . The much higher f of plasmonic nanoparticles explains why they are such comparatively efficient scatterers and absorbers (compared to dyes or quantum dots), and that efficiency is key to their applications, especially in detection and sensing.

The modal volume V_m of SPs for a nanoparticle whose size is less than the metal's skin depth is on the order of the volume of the nanoparticle itself, typically 10 nm^3 . That sub-wavelength confinement of the optical energy is crucial to surface plasmonics and forms the basis for a plethora of applications, including optical filters, waveguides, and other photonic-circuit components (see the article by Thomas Ebbesen, Cyriaque Genet, and Sergey Bozhevolnyi in *PHYSICS TODAY*, May 2008, page 44) and exquisitely sensitive detectors.

Hot spots from surface plasmons

On the scale of a few nanometers, any optical wave looks like a uniform plane wave. And yet when the light is incident on nanoplasmonic particles, it gives rise to an inhomogeneous distribution of intense and highly localized electric fields. Such intensity spikes, which Lakshmi Pandey, Thomas George, and I first studied in 1996 and called "hot spots,"³ are now recognized as one of the most important and universal phenomena in nanoplasmonics. The large enhancement of the local fields at a hot spot arises from the multiplication of

the enhancement factors due to the SP resonance, the constructive interference of the fields from different SPs, and the enhancement due to specific morphologies associated with the nanoparticles, such as sharp tips and narrow gaps that can form between particles.

One of the most commonly found and widely exploited hot spots in nanoplasmonics is due to the so-called lightning-rod effect, a mostly nonresonant enhancement that generates a high local field at a sharp tip when the polarization of the exciting light is parallel to the tip's axis,⁴ as illustrated in figure 3a. The effect finds its most common application in near-field scanning optical microscopy, discussed below.

In disordered plasmonic nanostructures, such as the fractal, or self-similar, clusters of silver or gold shown in figure 3b, the hot spots are sites of very pronounced enhancements in the local field. Furthermore, a self-similar system composed of nanoparticles of vastly different sizes, arranged in a chain, generates an especially bright signal. As illustrated in figure 3c, the field enhancement in a system composed of just three silver nanospheres whose sizes form a geometric

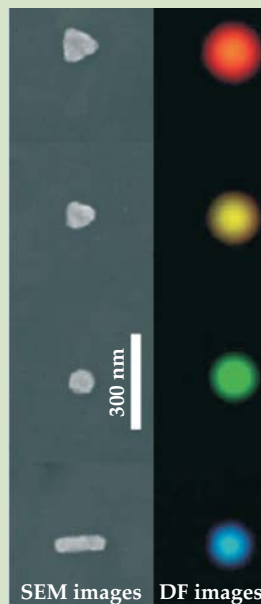


Figure 2. Plasmonic colors. These gold nanoparticles (left, imaged with scanning electron microscopy) are each about 30 nm wide and carved by electron-beam lithography into distinct shapes (two triangles, a disc, and a rod) on a silica substrate covered with 20 nm of indium tin oxide. The distinctly colored light emission from each (right, imaged with dark-field optical microscopy) illustrates that the metal's resonance frequency can be tuned simply by varying its size and shape. (Adapted from ref. 1.)

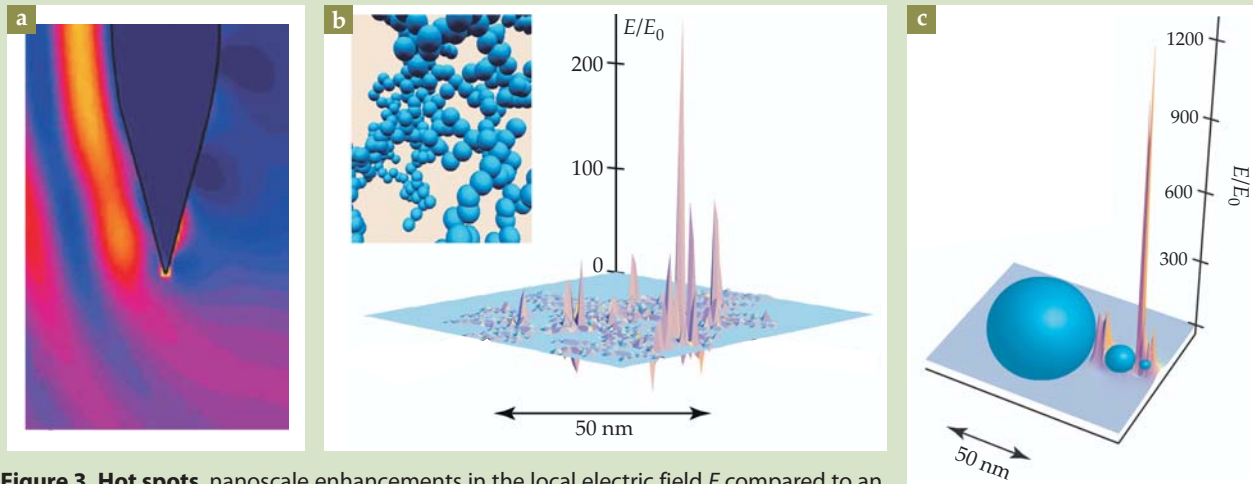


Figure 3. Hot spots, nanoscale enhancements in the local electric field E compared to an incident field E_0 , are calculated for certain metal nanostructures: **(a)** the sharp end of a gold tip excited by a vertically polarized laser field (adapted from ref. 4); **(b)** a fractal cluster of silver nanoparticles (inset) whose resonance enhancement and specific morphologies can magnify, at the hottest spot, the local fields by a factor of nearly 300 (adapted from ref. 3); and **(c)** a self-similar nanolens whose geometrical arrangement of spheres concentrates optical energy, from bigger spheres to smaller ones, in the tight gaps between them.⁵ In the hottest spot, the field is enhanced by a factor of 1200.

series can be as high as three orders of magnitude. The enhancement grows along the chain, from bigger to smaller spheres, with hot spots appearing in the tight gaps between them.⁵ In the case of SERS, that arrangement can enhance the signal by a gigantic 12 orders of magnitude using silver and 9 orders of magnitude with gold—potentially making it bright enough to observe single molecules.⁶

In what is detrimental to many applications, the local-field enhancement can be significantly reduced when the corresponding resonances are dulled by radiative losses in relatively large nanoparticles whose length scale is greater than the skin depth. One way to counteract such losses is to use interference of the dark and bright plasmonic modes, creating

so-called Fano resonances,⁷ after Ugo Fano, who first described them in 1935. At those resonances, whose spectral width is much narrower than that of ordinary SPs, the local fields at the nanoparticle surface are again extraordinarily enhanced.

Hot spots of surface plasmon polaritons

Surface plasmons are localized, collective oscillations of electron density. But when they couple with a photon, the result is what's known as surface plasmon polaritons (SPPs)—electromagnetic waves that propagate at an interface between a plasmonic metal and a dielectric. Those waves are transverse magnetic—that is, their magnetic field is perpendicular to their wave vector \mathbf{k}_{SPP} and in the plane of the interface. The

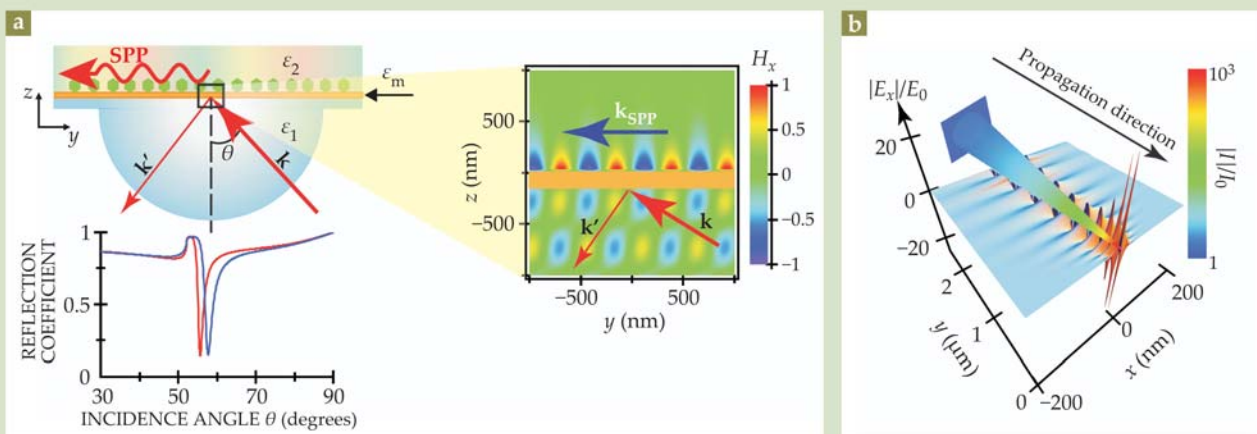


Figure 4. Surface plasmon polaritons (SPPs). **(a)** Light with wave vector \mathbf{k} can excite SPPs when the light is incident on a dielectric–metal system in the Kretschmann geometry, as illustrated here: A hemisphere of heavy glass with permittivity ϵ_1 sits under a film of gold metal with permittivity ϵ_m under a medium with permittivity ϵ_2 . The system's reflection coefficient (red) drops to a minimum at the angle θ that excites the SPPs on the bare gold surface. But when a monolayer of protein molecules (green) is adsorbed on the gold, as shown, the subtle change in ϵ_2 is sensed as a shift (blue) in the angle of minimum reflection. The adjacent image shows the instantaneous magnetic near-field H_x of the incident light and the SPP wave, viewed in cross section. **(b)** In a cone whose diameter tapers down to a sharp tip, the local enhancement in electric-field amplitude E (normalized to the incident field E_0) becomes adiabatically concentrated at the tip.⁸ The cone and the local field intensity along its surface are superimposed here on the local electric-field distribution. The scale of intensities $|E_x|/E_0$ is shown at right.

wave vector of an SPP is always higher than that of an electromagnetic wave of the same frequency propagating in the adjacent dielectric alone. Because the wave vector in the plane must be conserved—a condition equivalent to conservation of the in-plane component of linear momentum—it is impossible to excite an SPP at an interface by an electromagnetic wave propagating in the dielectric, and an SPP cannot radiate into the dielectric. Therefore, the SPPs are “dark waves.”

Fortunately, however, one can excite the SPPs using the so-called Kretschmann geometry, as sketched in figure 4a. The incident light with wave vector \mathbf{k} passes through a glass hemisphere with permittivity ϵ_1 and is incident on the lower interface of a metal nanofilm that has permittivity ϵ_m and whose thickness is comparable to the skin depth. The upper half-plane above the metal is filled with a medium of permittivity ϵ_2 . The evanescent field of the light wave at the upper interface of the metal is then able to excite an SPP wave if the angle of incidence θ is equal to the so-called Kretschmann angle θ_K , defined by the condition:

$$\sqrt{\epsilon_1} \sin \theta_K = \sqrt{\frac{\epsilon_m \epsilon_2}{\epsilon_m + \epsilon_2}}. \quad (1)$$

The equality is possible only if $\epsilon_1 > \epsilon_m \epsilon_2 / (\epsilon_m + \epsilon_2) > \epsilon_2$. Thus the SPPs are excited under total internal reflection conditions. For $\theta \approx \theta_K$, the reflection coefficient R of the incident wave experiences a sharp minimum, a signature that the incident light wave is efficiently transformed into the phase-matched SPP wave. The presence of even a monolayer of molecules on the metal's upper surface is enough to increase ϵ_2 and thus perceptibly shift θ_K . That is the foundation for one of the most common methods of plasmonic sensing.

A systematic and reproducible way to obtain a hot spot at a desired position over an extremely wide band of frequencies—from the near UV to THz—is to adiabatically concentrate optical energy using a plasmonic taper,⁸ as illustrated in figure 4b. As SPPs propagate toward the tip of the metal cone, they do not scatter, but slow down and deposit a significant fraction of their energy at the tip. The result is a hot spot with the local field intensity enhanced by orders of magnitude. The concentration of the energy has proved especially useful in nanoscopy-based applications sensitive enough to reveal chemical details of the surface at nanometer-scale resolution.⁹

Sensing

One of the most commonly exploited effects of SPs is the spectral shift in their plasmonic resonances, usually toward longer wavelengths, upon the aggregation of metal nanoparticles. Indeed, the effect is the foundation of what may be the most widely used sensor in nanoplasmonics: the home pregnancy test.

The test is an assay designed to detect human chorionic gonadotropin hormone (hCG) produced by the uterus from the beginnings of pregnancy. Primary antibodies immobilized on a strip of chromatography paper specifically target hCG, as sketched in figure 5a. If a drop of urine from a pregnant woman is placed on the sensing strip, hCG from the urine binds to the antibodies. Because the hCG molecules scatter little light, however, that binding is invisible. But when a suspension of gold nanospheres chemically linked to secondary antibodies is added, the secondary antibodies also bind to the hCG on the strip; the process causes the nanospheres to form a dense monolayer at the surface. Because the nanospheres have a high polarizability, they screen each other's plasmonic charges, which reduces the restoring force and the frequency of the SPs, redshifting their emission from a vaguely green color evident in the initial gold nanosphere suspension. Consequently, the test strip acquires a bright red color—confirmation of pregnancy.

The procedure is generalizable: Other widely used tests built on the same immunochromatographic assay principle can detect medical conditions such as prostate cancer, a heart attack, and HIV-AIDS.

Another class of sensing applications is based on the redshift of the localized SP resonances in response to covering a metal surface with analyte molecules. That method is also due to the dielectric screening of SP surface charges. The analyte molecules are detected if their permittivity differs from that of the surrounding dielectric host ϵ_d by some amount $\Delta\epsilon_a$.

Assume that the analyte molecules completely displace the host medium in the hot spots of the local plasmonic field. Then, from the

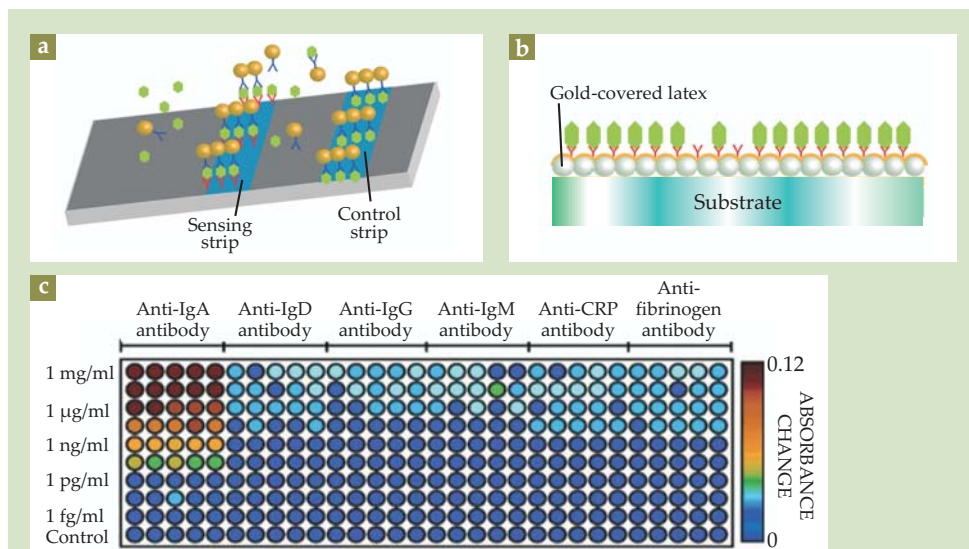


Figure 5. Sensing with localized surface plasmons. (a) A widely used test can detect the presence of human chorionic gonadotropin hormone (hCG) produced in a pregnant woman's uterus. When deposited on a sensing strip of antibody-laden chromatographic paper, the hCG analyte molecules (green) from a drop of her urine bind to the antibodies (red). To sense that reaction, a suspension of gold particles chemically linked to secondary antibodies (blue) is then added; when they bind to the analyte they strongly scatter light, producing a ruby-red color that can be compared with that from an adjacent control strip. (b) In a different test, analyte molecules can be sensed through the change in permittivity they induce in a dielectric medium, in this case gold-covered latex nanospheres. (c) The change in permittivity is manifest as a detectable change in absorbance. These results of an assay that tests for six different analyte proteins—immunoglobulins (IgA, IgD, IgG, IgM), C-reactive protein (CRP), and fibrinogen—prove that molecules are detectable at concentrations as low as 30 pg/ml. (Panel c adapted from ref. 11.)

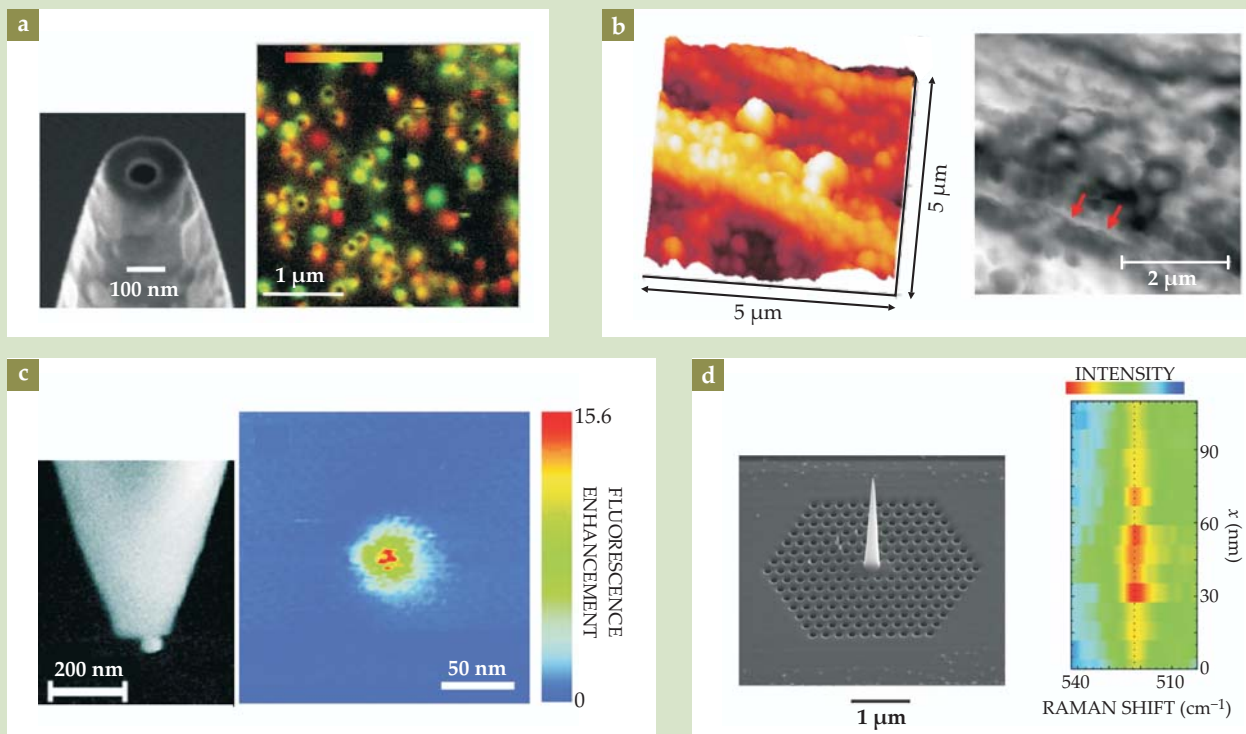


Figure 6. Plasmonic nanoscopy. (a) A metal-clad aperture tip (left) produces a fluorescence image of dye molecules at a resolution of tens of nanometers. (Adapted from ref. 17.) The false color indicates the local field's polarization: red in the plane and green normal to the plane. (b) The same area of an oligodendrocyte cell is imaged by atomic force microscopy (AFM; left) and by near-field reflection microscopy (right) using an aperture tip. The subwavelength cord marked by arrows in the reflection image shows features not visible in the AFM's map of cell topography. (Adapted from ref. 18.) (c) A nanosphere at the end of an apertureless dielectric tip enhances fluorescence from a single dye molecule with a resolution of about 10 nm. (Adapted from ref. 13.) (d) A silver cone with a 5-nm-radius tip mounted on a photonic crystal is used to obtain a surface-enhanced Raman scattering signal that yields chemical information—a sharp increase in the silicon 520 cm^{-1} Raman line—when scanned across a Si trench in the sample. (Adapted from ref. 9.)

ory that David Bergman, Sergey Faleev, and I worked out nearly a decade ago,^{2,10} the frequency shift $\Delta\omega_n$ of a plasmonic resonance relative to its spectral width γ_n can be expressed by a simple but precise and universal analytical formula:

$$\frac{\Delta\omega_n}{\gamma_n} = -Q \frac{\Delta\epsilon_d}{\epsilon_d}. \quad (2)$$

From that formula, one can estimate the minimum number of analyte molecules N_a that can be sensed as

$$N_a = \frac{|\Delta\omega_n|}{\gamma_n} \frac{\epsilon_d}{\alpha} \frac{V_m}{Q}, \quad (3)$$

where $|\Delta\omega_n|$ is a detectable frequency shift and α denotes the analyte's polarizability. The extremely small modal volume (roughly $10\text{--}10^3\text{ nm}^3$) of the nanoplasmonic hot spots accounts for the very high sensitivity of the nanoplasmonic sensing despite the relatively low Q (10–100) associated with plasmonic metals. Moreover, the large spectral width of the SP resonances compared to those in dielectric microcavities is advantageous because it makes the plasmonic sensing stable with respect to perturbations of the field environment, such as vibrations, temperature changes, and drifts in the laser frequency.

Figure 5b illustrates an immunoassay scheme based on that sensing principle. Imagine the upper surface of a corrugated gold layer that covers a dense assembly of latex nanospheres. That surface, which supports localized SPs, is

covered—or, more precisely, functionalized—with antibodies against targeted analyte molecules. When the analyte binds to the surface, the dielectric's permittivity ϵ_d increases, which redshifts the SP resonance in accord with equation 2 and reveals the presence of the analyte. Figure 5c exemplifies the utility and sensitivity of the technique: An immunoassay that simultaneously tests for six medically relevant proteins exhibits the shift in SP resonance as a change in absorbance of the immunoassay strip.¹¹

Localized SPs have many other existing and emerging applications; for a review, see reference 12. One that is especially promising is implantable robust sensors that can continuously monitor the glucose levels of diabetics. Given the 18 million people diagnosed with diabetes in the US alone (and more than 5 million estimated as yet undiagnosed ones), and that the ravages of the disease can lead to heart attacks, strokes, kidney failure, blindness, and amputations, the significance of such sensors cannot be overestimated. Moreover, the ability to quickly and robustly detect minute amounts of chemical substances and biological pathogens makes nanoplasmonic sensing important not only in science, engineering, and biomedicine but also in environmental monitoring, homeland security, and national defense.

Plasmonic nanoscopy

The technique known as near-field scanning optical microscopy (NSOM) is based on scanning nanometer-scale surface

features using a hot spot at the end of a pointed probe illuminated with light. The instruments come in two types: those with an aperture at the tip and those without it. Commonly used to image biological cell structures, aperture-based NSOM uses a tapered optical fiber whose tip is covered with a metal. Aluminum is often the metal of choice because, with three electrons per unit cell, it has a very small skin depth (about 13 nm), the parameter that ultimately limits the resolution the microscope can achieve. For examples, see figure 6a–b.

Apertureless NSOM, also widely used in medical imaging, may use a sharp metal tip that is directly excited by focused laser radiation. But in apertureless NSOM, a plasmonic metal nanosphere at the end of a tapered dielectric probe is also often used, as shown in figure 6c. The role of the nanotip or a nanosphere in NSOM can be likened to that of a nanoantenna that delivers optical energy to the nanoscale and enhances the light intensity scattered or emitted by an object, such as a single dye molecule, when the nanosphere is positioned directly above it.^{4,13}

Among newer nanoplasmonic applications is what might be termed “chemical vision” on the nanoscale: spectroscopic nanoscopy that allows researchers to identify the chemical structure of the object with nanometric resolution. One promising approach exploits the adiabatic nanofocusing of optical energy, discussed above.⁸ Consider, for example, mapping the chemical composition of a silica surface that contains an ultranarrow (30-nm-wide) trench of exposed silicon.⁹ The sensor consists of a silver cone mounted on a two-dimensional photonic crystal, as illustrated in figure 6d, that serves to efficiently couple incident light to the cone’s wider end, from which optical energy propagates to the tip as SPPs. The sensor is mounted on a cantilever and used both for atomic force microscopy and for NSOM measurements. The configuration has allowed researchers to map a silicon surface’s chemical fingerprints at exquisitely fine scales.

The sensing volume at the tip is roughly 25 nm^3 . Because the volume per Si atom in the solid is about 30 \AA^3 , no more than 1000 such atoms contribute to the optical signal. That sensitivity, which the technique can boast along with a roughly 5-nm spatial resolution, is unprecedented in Raman nanoscopy. Indeed, it is on par with the best existing specialized SERS sensors.

Cancer, solar energy, spasers, and beyond

Nanoplasmonics is a relatively young science, but as we’ve seen, it’s packed with applications that exploit the enhancement of local optical fields on tiny metal particles and the large number of electrons there that coherently contribute to SPPs. There are those well-established applications of practical significance, such as the biomedical tests and sensors and plasmonic nanoscopy surveyed in this article.

Yet there are also many nascent applications that have the potential to greatly benefit humankind. Most important among them may be the thermal phototherapy of tumors using nanoparticles composed of a dielectric core coated with a gold shell.¹⁴ As the metal nanoshell becomes progressively thinner, the peak in its optical absorption gradually shifts over a wide spectral range, from the visible to the near-IR. In the near-IR, biological tissues do not absorb light and are not damaged by the irradiation. The nanoshells tend to spontaneously accumulate in tumors when injected into the body, but they can also be targeted to cancer antigens. When irradiated by intense IR light, the nanoshells, with their high resonant oscillator strength, efficiently absorb radiation but scatter relatively little of it thanks to their small sizes. Thus they

generate heat that kills the tumor cells but leaves healthy tissue unharmed.

An advantage of such treatment over conventional chemotherapy is that the gold nanoshells are essentially completely nontoxic. Phototherapy based on the nanoshells is currently undergoing clinical trials on human patients, and promising results have also been obtained using nanorods.¹⁵

There are many other applications with great potential. In plasmon-assisted solar energy conversion,¹⁶ metal nanostructures are used to scatter solar radiation in a way that better couples it to semiconductor photovoltaic elements. The efficient extraction of light from light-emitting diodes exploits similar physics, in which the metal nanostructures play the roles of light scatterer and energy-transducing nanoantennas. And hydrogen sensing, a technology critically needed to prevent the potentially explosive mixing of hydrogen and air, exploits the change in the plasmonic response of palladium nanoparticles when leaking H_2 gas saturates the Pd lattice.

Applications and devices of other types are just emerging from the fundamental physics that inspired them. They include ultrafast nanoplasmonic modulators with a switching bandwidth on the order of 10 THz; nanoplasmonic circular polarizers and optical superlenses (see PHYSICS TODAY articles by Martin Wegener and Stefan Linden in October 2010, page 32, and by John Pendry and David Smith in June 2004, page 37); and optical components that concentrate or filter light using so-called extraordinary transmission through nanometer-scale holes engineered in metal substrates. There may even emerge applications based on a phenomenon that Bergman and I described in 2003: surface plasmon amplification by stimulated emission of radiation, or spaser, the nanoplasmonic analogue of a laser. In a spaser, a nanoparticle plays the role of resonant cavity, and SPPs play the role of photons. Spasers are thus quantum generators and nanoscale amplifiers of SPPs and are likely to find application in ultrafast information processing, lithography, nanoscopy, and optical loss compensation in nanocircuits and metamaterials.

Clearly, nanoplasmonics has come a long way since the stained glass of Roman times.

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