

How to deal with the loss in plasmonics and metamaterials

Jacob B. Khurgin

Metal losses affect the performance of every plasmonic or metamaterial structure; dealing with them will determine the degree to which these structures will find practical applications.

The past decade and a half has seen a steady rise of interest in plasmonics and metamaterials (P&M), a duo of closely related fields. The inspiration driving P&M research is the enticing prospect of concentrating and manipulating the electromagnetic field on the subwavelength scale to achieve unprecedented enhancement of linear and nonlinear optical processes, and to develop nanoscale optical interconnects, optical cloaking and super-resolution imaging^{1–3}. Inspired by a few visionaries, P&M research has been enabled by the determined work of an army of engineers and scientists in microelectronics research who have been making steady advances in nanofabrication. However, when it comes to the materials palette used in P&M, it has remained sparse and unchanged, consisting mostly of the metals used in reflection optics, predominantly silver and gold. The reason for the choice of these two noble metals is the low rate of scattering of free electrons in them, which leads to high conductivity in the radiofrequency range and high reflectivity in the optical range. And yet, after a decade-long effort, which did produce attention-grabbing results, the P&M community is beginning to face the unpleasant fact that, even in the noblest of metals, losses in the optical range (and here we include near- and mid-infrared (IR) regions) are still too high to make most, if not all, practical P&M devices. At this time, the one and only widespread practical application of plasmonics is surface-enhanced Raman scattering (SERS)⁴, which predates the term ‘plasmonics’ itself, whereas the best results in the areas of nanoantennas and metamaterials have been attained in the microwave range, where these structures have been known, albeit under a different *nom de guerre* of artificial dielectrics⁵, since the early 1950s.

If one is to summarize the current state of efforts to enhance performance of various optical devices using P&M, it can be done by noticing that although inefficient devices can indeed be improved, the performance of any

relatively efficient device will only deteriorate, as loss in the metal will exceed whatever improvement the field concentration achieves. That is why for fluorescence sensors, for which the absolute efficiency (light out versus light in) is typically quite low, P&M does offer some promise. (Raman scattering can be thought of as fluorescence with efficiency approaching zero — hence the aforementioned spectacular success of SERS.) But when it comes to the devices where the efficiency must be high, such as light sources and detectors, solar cells, interconnects, switches and modulators, the community is gradually beginning to realize that unless metal loss is reduced significantly the promise of P&M will remain unfulfilled^{6,7}.

A number of strategies for loss mitigation (or avoidance) are being pursued. These involve using advances in fabrication aimed at reduction of surface roughness and effects⁸, using highly doped semiconductors in place of metals⁹, using polar dielectrics in the Reststrahlen region (phononics)¹⁰, and using media with optical gain. Furthermore, a number of groups have realized that if absorption in the metal cannot be avoided, it may as well be used for productive purposes, for example in applications ranging from photodetection¹¹ to solar photocatalysis¹². In this Commentary I will try to reflect on the prospects of each of these directions, in the process making a few observations of fundamental nature.

Why does plasmonics always mean loss?

First of all, it is important to emphasize that metal (or any material with negative permittivity ϵ) is essential for field concentration beyond the diffraction limit. Let us consider an optical resonator with characteristic dimension a larger than the wavelength λ in the dielectric (Fig. 1a). When the electromagnetic mode oscillates inside the resonator, every half period the energy is transferred from the electric field energy $u_E \sim \frac{1}{2}\epsilon E^2$ to the magnetic field energy $u_H \sim \frac{1}{2}\mu H^2$ and back, where μ is the permeability. This is similar to the mechanical

analogue of an oscillating mass on a spring, where potential energy is transferred into kinetic energy and then back. Both E and H have harmonic dependence on the spatial coordinate z , as $\sin(2\pi z/\lambda)$. From the Maxwell equation $\nabla \times \mathbf{H} = \epsilon \partial \mathbf{E} / \partial t$ (where t is time), it follows that $H = \sqrt{\epsilon/\mu} E$, and hence $u_H = u_E$, which means that energy is conserved while transferred from one form to another. In this configuration self-sustaining oscillations are possible. Unsurprisingly, the second Maxwell equation $\nabla \times \mathbf{E} = -\mu \partial \mathbf{H} / \partial t$ is also automatically satisfied when $H = \sqrt{\epsilon/\mu} E$. Now, if the characteristic size is less than $\lambda/2n$, where n is the refractive index (Fig. 1b), the field spatial dependence becomes $\sin(\pi z/a)$, and from the first Maxwell equation it follows that for truly sub- λ mode, the magnetic energy is much smaller than the electric energy, which makes self-sustaining oscillations impossible, as expected from the diffraction limit. If, however, one introduces free carriers into the mode (Fig. 1c), the energy can also be stored in the form of kinetic energy $u_K \sim \frac{1}{2}\epsilon_0(\omega_p^2/\omega^2)E^2$ (here ϵ_0 is the vacuum permittivity, ω is frequency, and ω_p is the plasma frequency that for noble metals lies in the ultraviolet). Thus, depending on the exact geometry, the energy balance $u_H + u_K = u_E$ can be restored at certain frequencies ω_{sp} (typically on the scale of a fraction of ω_p), precisely the frequencies of sub- λ surface plasmon polaritons (SPP). Surface plasmon polaritons can be either localized or propagating along the metal/dielectric interface with effective wavelength that is much shorter than $\lambda/2n$. Note that since the magnetic field is small, the second Maxwell equation $\nabla \times \mathbf{E} = -\mu \partial \mathbf{H} / \partial t$ dictates that the electric field must be nearly irrotational, resembling an electrostatic field; hence the term ‘quasistatic’ that is often used to describe the sub- λ regime.

Note that, in principle, one could have also approached the sub-wavelength confinement from the opposite angle, by considering the situation where E is small, $E \ll \sqrt{\mu/\epsilon} H$, while H is quasistatic and irrotational, and $u_E \ll u_H$.

Then to restore energy balance one would have to find a way to store additional potential energy, which cannot be done without increasing the dielectric constant and thus going back to the diffraction limit. Whereas free carriers naturally have large kinetic but no potential energy, finding an entity with the opposite characteristics at optical frequencies is not easy. In other words, an electric dipole is perfectly capable of oscillating without a substantial magnetic field, but a magnetic dipole always requires an electric field somewhere in its vicinity to support self-sustaining oscillations.

Based on this reasoning, one can also choose to combine two separate regions — one storing electrical energy and the other storing magnetic energy — into a single cell of metamaterial, essentially creating inductor–capacitor resonance circuits on a microscopic level (a split ring resonator¹³ is one example). But as dimensions of subwavelength inductors become comparable to the plasma wavelength $\lambda_p = 2\pi c/\omega_p \approx 200$ nm (where c is the speed of light in vacuum), corresponding to an operational wavelength of a few micrometres or less, most of the energy will be stored in the form of kinetic energy of electrons rather than as magnetic energy⁶, which brings us back to the situation similar to that in Fig. 1c. Or, in other words, in structures that are comparable to the plasma wavelength in at least one dimension the kinetic inductance exceeds the magnetic inductance. Only at wavelengths longer than a few micrometres, a smaller proportion of energy gets stored in the kinetic motion of electrons leading to lower losses. That is why nanoantennas and metamaterials in the mid-IR and longer-wavelength range operate with much smaller loss than in the optical and near-IR range.

So, the diffraction limit can be beaten with help from free carriers, but this success comes at a price — almost half of the time the energy is stored in the form of kinetic energy, and therefore it is lost at the rate that is commensurate with the rate of scattering of electrons in metal, γ , which is on the scale of 10 fs (this value will be discussed later). Thus, once the optical mode becomes sub- λ in all three dimensions, independent of its shape, the SPP energy will be lost on the 10-fs scale⁶.

It is instructive to relate losses and the Purcell effect, which is used extensively to enhance fluorescence and Raman scattering in P&M structures. The Purcell effect follows from Fermi's golden rule and states that the rate of spontaneous decay of excited atoms and molecules is proportional to the density of states into which emission takes place. The density of photons in free space is low because of the large speed of the light term, but in the P&M structures, the density of photons is much higher and the rate of spontaneous

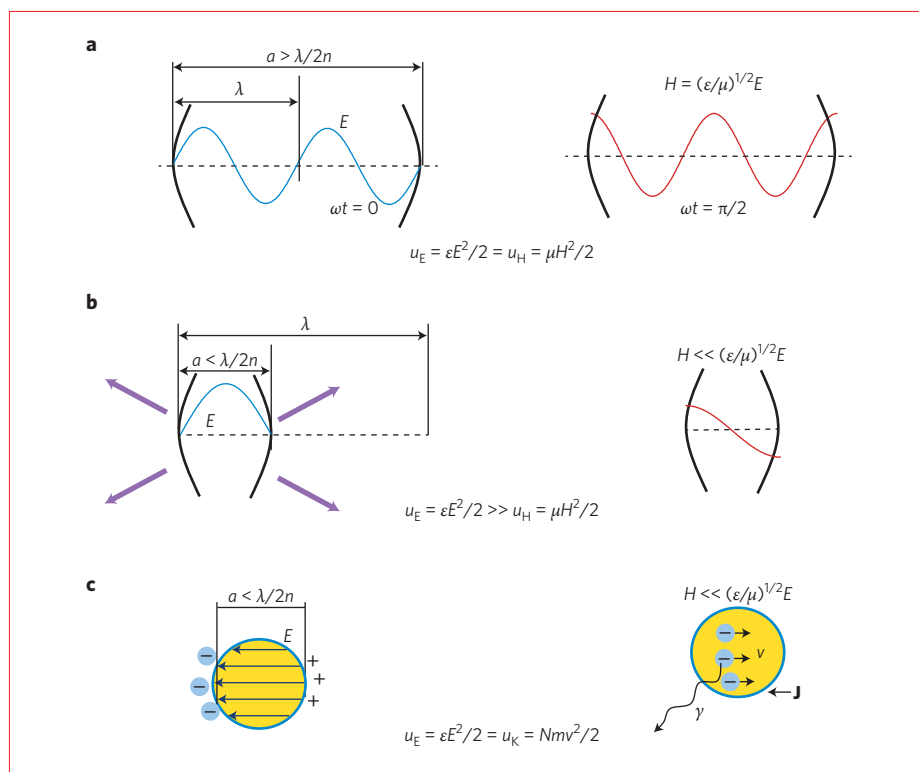


Figure 1 | Energy balance in photonic and plasmonic structures. **a**, In an optical cavity with dimensions larger than half wavelength $\lambda/2n$ energy alternates between u_E (left), the energy of electric field \mathbf{E} , and u_H (right), energy of magnetic field \mathbf{H} , analogous to energy alternating between potential and kinetic forms for a mass oscillating on a spring. **b**, In a subwavelength cavity with characteristic size a the magnetic energy is too small, hence the cavity radiates energy out (purple arrows) in agreement with the diffraction limit. **c**, When free carriers are introduced a current \mathbf{J} flows and the energy alternates between u_E and kinetic energy of carriers u_K , where N , m and v are respectively the carrier density, mass and velocity. The diffraction limit is beaten, but the motion of carriers is strongly damped with the damping rate γ , and the SPP mode is lossy.

emission can be increased manifold. One must recognize though, that the ‘new’ states into which the emission takes place cannot magically appear out of nowhere: essentially they are the states (degrees of freedom) of the motion of free electrons that couple into the original photon states. Their density is very high (because the electron velocity is much less than c), but they also dissipate energy on the femtosecond scale. Hence, Purcell enhancement in P&M structures is obtained by coupling energy into lossy electronic states, and once there, the energy has a much higher chance to be dissipated rather than radiated into space. That is why, as mentioned above, plasmonic enhancement works well only for originally weak and inefficient optical processes, such as Raman.

Basics of absorption in metals

Let us now see what makes absorption in the metal so strong in the first place. Although most of the aspects of it was investigated thoroughly half a century ago¹⁴, the P&M community has not paid enough attention to

the physics of absorption in metals. Consider the simplified band structure of a metal in Fig. 2 showing two states with wavevectors (momenta) \mathbf{k}_1 and \mathbf{k}_2 , and energies E_1 and $E_2 = E_1 + \hbar\omega$, respectively, below and above the Fermi level (E_F). The magnitude difference between these two momenta is $\Delta k_{1,2} > \Delta k_0 \sim \omega v_F$ (where $v_F \sim 10^8$ cm s⁻¹ is the Fermi velocity), typically more than 3 nm⁻¹, way too large to be supplied by a photon, or a SPP. Therefore, the absorption process requires a phonon or an imperfection (Fig. 2a) and it results in two ‘hot’ carriers — electron and hole — whose energy can be harvested if and when they reach the surface of the metal. The probability of absorption assisted by phonons and defects is proportional to $\gamma_{ph}(\omega)\omega_p^2/\omega^2$ and weakly dependent on frequency (typically, $\gamma_{ph}(\omega) \sim 10^{14}$ s⁻¹). The reason for this large value, as follows from Fermi's golden rule, is a huge density of states above the Fermi level available for the transition.

The other momentum-conserving process that can lead to absorption is electron–electron (e–e) scattering in which

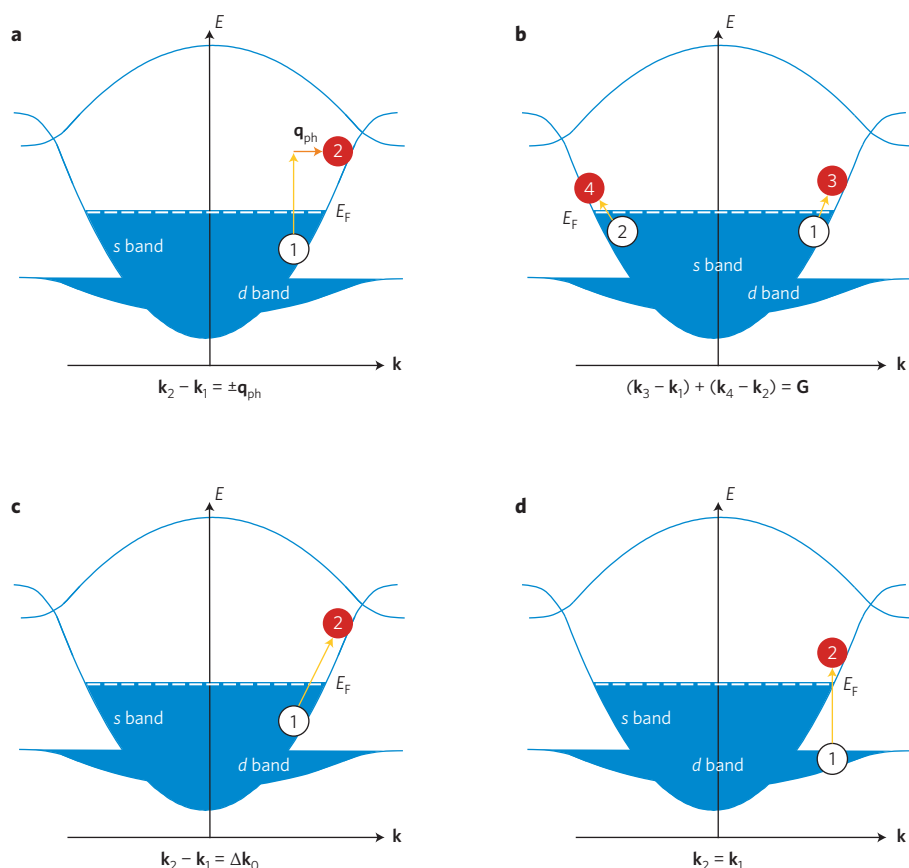


Figure 2 | Absorption of a quantum of electromagnetic energy $\hbar\omega$ in a metal. **a**, Absorption assisted by a phonon with wavevector \mathbf{q}_{ph} creates hot hole (1) with wavevector \mathbf{k}_1 and hot electron (2) with wavevector \mathbf{k}_2 , with energy E_2 above the Fermi level, E_F . **b**, Electron–electron scattering assisted absorption, an Umklapp process involving reciprocal lattice vector \mathbf{G} creates four lukewarm carriers — two holes (1,2) and two electrons (3,4). **c**, Direct absorption (Landau damping) assisted by the SPP momentum $\Delta\mathbf{k}_0$ creates hot hole (1) and hot electron (2). **d**, Interband absorption from the d to s shell does not create hot carriers because hole (1) in the d band has low velocity and excited electron (2) is too close to the Fermi level.

two electrons make the transition from the states \mathbf{k}_1 and \mathbf{k}_2 below the Fermi level to the states \mathbf{k}_3 and \mathbf{k}_4 (Fig. 2b). The momentum conservation in this so-called Umklapp process is $\mathbf{k}_3 + \mathbf{k}_4 = \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{G}$, where \mathbf{G} is the reciprocal lattice vector. The energy conservation relation $E_3 + E_4 = E_1 + E_2 + \hbar\omega$ indicates that rather than two ‘hot’ carriers sharing energy $\hbar\omega$, one ends up with four ‘lukewarm’ carriers having kinetic energies on the order of $\hbar\omega/4$ each — and this is the fact with the gravest of consequences for applications such as photodetection and energy harvesting in which hot carriers must eventually surpass some energy barrier. The e–e scattering is strongly frequency dependent since high photon energy means more electrons and holes are involved in the process, and one can roughly say that $\gamma_{ee}(\omega) \sim \gamma_0(\hbar\omega/E_F)^2$ (ref. 14), where $\gamma_0 \sim 10^{15} \text{ s}^{-1}$ (ref. 15) becomes comparable to γ_{ph} in the visible range. Note that neither $\gamma_{ee}(\omega)$ nor $\gamma_{ph}(\omega)$ vanishes at low

temperatures, because in the first case, no phonons participate in the e–e process, while in the second case, phonons can always get spontaneously emitted. Unlike the case of radiofrequency, any attempt to reduce the loss in the optical range by cooling is therefore not advisable.

Another, often overlooked, mechanism that may lead to the absorption is associated with the finite size of SPP modes. If the effective size of the SPP mode inside the metal $a_m \ll \lambda/2$, it will include spatial frequencies larger than $\Delta\mathbf{k}_0$, and therefore will introduce absorption by the ‘diagonal’ process shown in Fig. 2c. This process, known as Landau damping, leads to an additional ‘confinement’ contribution to the absorption $\gamma_c \sim v_F/a_m$, which becomes comparable to the other ‘bulk’ contributions γ_{ph} and γ_{ee} when $a_m \sim 10 \text{ nm}$. This result has two important consequences for sub- λ SPP modes. First, the bulk contribution plays a progressively less important role; even if

an ‘ideal’ metal with no bulk losses existed, confinement-induced absorption would still make losses enormous. Because there are plenty of available states, electrons will still make the transition; the only way to avoid it is to have a structure with a bandgap. Second, the confinement-dependent loss actually prevents a tight nanofocusing of light and limits the maximum attainable Purcell factor — an effect phenomenologically described as ‘diffusion’ in the hydrodynamic model used in ref. 16.

Finally, in all metals, there is band-to-band absorption (Fig. 2d), which becomes significant around 600 nm for Au, 400 nm for Ag, and in the ultraviolet for Ga. Note that when band-to-band absorption takes place, no hot carriers are formed, because the hot electron is created in the vicinity of the Fermi level, and while the hole in the d band does have high energy, its velocity is low because the effective mass in the d band is much higher than in the s band.

Out of four mechanisms causing absorption in metals only two (Fig. 2a,c) actually generate hot carriers. Ironically, it is at higher photon energies, where one would want to have them that hot carriers are generated with relative low probability, as mechanisms in Fig. 2b,d become the dominant ones.

Once the hot carriers have been generated, they lose their energy in two steps. First is e–e scattering in which a hot electron with energy E_0 above the Fermi level ‘collides’ with one with energy below the Fermi level and as a result three carriers (one hole and two electrons) are generated with average energy of $E_0/3$. This process quickly leads to thermalization of hot carriers where they all have thermal energy $k_B T_e$ only slightly above the Fermi level. Just like e–e-assisted absorption, the thermalization rate has quadratic energy dependence $\gamma_{th}(E) \sim ((E - E_F)/E_F)^2$ (ref. 15), but since it does not involve the optical field, thermalization does not have to be an Umklapp process. Hence, the rate γ_{th} is typically faster than γ_{ee} , and is on the scale of $(10 \text{ fs})^{-1}$ for $E > 1 \text{ eV}$, as measured in ref. 17. A longer thermalization time (up to 1 ps), as assumed by many in the P&M community, is therefore rather unjustified. Following thermalization, the electron temperature T_e gets equalized with the lattice temperature T_L via emission of acoustic phonons in the 100-fs timescale. For prospective applications in energy harvesting and detection, which require a certain threshold energy on the 0.5–1 eV scale, one can safely say that hot carriers disappear after a few tens of femtoseconds, that is, the time comparable to the scattering times, γ^{-1} , in the Drude theory.

What can and cannot be done?

Let us now briefly survey the methods proposed for the reduction of loss in P&M. One approach is to use highly doped semiconductors in place of metal⁹. The rate of scattering in highly doped semiconductors is on the scale of 10^{13} s^{-1} , simply because the Fermi level is much lower than in metals, and therefore the density of states into which the photoexcited carriers can end up is an order of magnitude lower than in metals. But ω_p in semiconductors is also an order of magnitude lower, making these materials most useful at mid-IR and longer wavelengths, where, for the most part, losses are also not that large. Indeed, in this wavelength range, highly doped semiconductors have not shown performance superior to metals. Similarly one could consider superconducting P&M devices, but they would have to operate at energies less than the superconductive gap, that is, in the THz or far-IR, where, as we have already mentioned, metals can perform adequately.

If we now return to the argument made earlier about the necessity of having kinetic motion to achieve energy balance in sub- λ modes, note that the charged particles undergoing this motion do not have to be free electrons and therefore may include ions in polar crystals, such as SiC, BN and others¹⁰. The permittivity (Fig. 3) of the polar crystal can be written as $\epsilon(\omega) = \epsilon_\infty(1 + (\omega_{LO}^2 - \omega_{TO}^2)/(\omega_{TO}^2 - \omega^2 - i\omega\gamma))$, where ϵ_∞ is the permittivity at high frequencies, and ω_{TO} and ω_{LO} are the frequencies of transverse and longitudinal optical phonons, respectively, lying in the mid-IR between 8 and 15 μm . In the so-called Reststrahlen region $\omega_{TO} < \omega < \omega_{LO}$, the real part of ϵ is negative. Hence, one can achieve sub- λ confinement of mid-IR radiation with relatively low loss, since the damping rate $\gamma \sim 10^{12} \text{ s}^{-1}$ — two orders of magnitude less than in metals. This fact makes ‘phononics’ — the use of surface phonon polaritons (SPP) — an attractive alternative to plasmonics. However, relying on phonons does have a significant drawback. As shown in Fig. 3, in addition to kinetic energy $u_k(t)$, the oscillating ions also carry potential energy $u_p(t)$, which in the Reststrahlen region is only slightly less than $u_k(t)$. Therefore, energy is transferred back and forth between u_k and u_p with only a small fraction of energy actually being that of the electric field. Formally this follows from the much stronger dispersion of $\epsilon(\omega)$ in polar dielectrics than in metals, since the total energy is proportional to $\partial(\omega\epsilon)/\partial\omega$. In other words, in the vicinity of resonance, the energy is stored in the ion vibrations and not in the electric field. The net result is that one

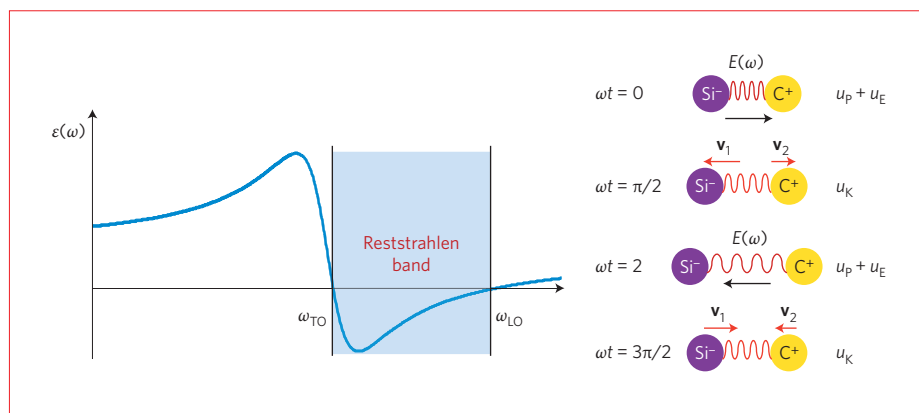


Figure 3 | Dispersion of the real part of the dielectric permittivity ϵ of a polar crystal and the alternation of energy in it using SiC as an example. \mathbf{v}_1 and \mathbf{v}_2 are the velocities of ions in the presence of an optical field $E(\omega)$.

can attain a high degree of concentration of energy in phononic materials and a narrow resonance linewidth, but when it comes to the electric field, the field concentration and Purcell factor are not much better than in metals. When it comes to propagating SPPs, their lifetime is orders of magnitude longer than of SPPs, but the propagation length of SPPs is not much longer than that of SPPs, since the group velocity of SPPs is very low due to high dispersion. To summarize this part, phononic materials are an attractive, relatively low loss sub- λ energy-storage media, but they do not couple well with electromagnetic waves, whereas plasmonic materials do couple well with electromagnetic waves, but lose energy very fast. In my view, combining phononic structures with plasmonic nanoantennas may offer an attractive solution in the mid-IR region of the spectrum.

We finally turn our attention to the often discussed idea of compensating metal losses in P&M structures with optical gain¹. Although gain can be achieved, in principle, by optical pumping, practical devices usually require electrical pumping. Even though the loss coefficient in SPPs approaches thousands of cm^{-1} , gain in semiconductor media can be just as high and transparency achieved when the carrier concentration is on the order of $N_{tr} \sim 10^{19} \text{ cm}^{-3}$. This has led to extensive efforts to develop such loss-mitigated structures. Conceivably, what has been overlooked is that from the practical point of view what matters is the pump current density at which transparency is achieved, $J_{tr} \sim eN_{tr}d/\tau_{sp}$, where e is electron charge, d is the active layer thickness ($\sim 100 \text{ nm}$) and τ_{sp} is the Purcell-shortened spontaneous recombination time. For tightly confined SPPs, the Purcell factor easily surpasses 100; as a result, the transparency density exceeds

1 MA cm^{-2} (ref. 18), which is at least 1,000 times higher than threshold current densities in conventional injection lasers. Such high pumping densities have been achieved by short-pulse optical pumping, which always creates exciting news, but does not, in my opinion, lead to remotely practical devices.

Parting thoughts

In summary, I want to stress that the goal of this Commentary is not to offer a broad ‘vision’ of the future P&M developments as many competing (and compelling) visions have already propagated in the literature by the scientists who have mastered this art much better than I can ever hope. My modest objective was to present a few hard facts, substantiated by numbers, and then let the readers decide which of the visions can actually become a reality in the not-so-distant future. Yet, in my opinion, one would be well justified to focus activities in the mid-IR region of the spectrum, where the losses, be it in metals, semiconductors or polar dielectrics, become manageable, and where one can find numerous applications in thermal management and vibrational spectroscopy. When it comes to near-IR and visible spectral regions, with the materials available today, I simply do not see any application where a decent absolute efficiency is required, be it in light emission, transmission, manipulation, detection, or harvesting, that could benefit from incorporating P&M structures. On the other hand, sensing, where there is no need for high absolute efficiency, can be enhanced with P&M, although one needs to be very careful and not to forget about numerous competing methods of enhancing sensitivity, such as micro-resonators¹⁹, which, while perhaps not being as trendy as P&M, may offer equal if not better performance. And of course,

one can always use high absorption in P&M to generate highly localized heat. The most exciting and paradigm-changing direction of P&M research, and I hope not just in my view, is the search for novel materials with lower loss. This search, however, should not follow today's pattern of rapid-fire testing of all the well-known conductors, doped semiconductors, or popular materials *du jour* (graphene, MoS₂, and whatever comes next), in hope of a miracle, but instead should be a well thought-out and concerted effort by condensed-matter theorists, chemists and growth specialists to synthesize man-made negative permittivity materials with reduced loss²⁰. With that, I believe, P&M science will live up to its promise. □

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The case for plasmon-derived hot carrier devices

Martin Moskovits

Plasmons' progeny are invading the territory currently commanded by semiconductors.

Arguably the most important photochemical process on the Earth is photosynthesis. Its overall outcome is a simple reaction that converts water and CO₂ to sugar and oxygen (the reverse reaction of sugar combustion). Photosynthesis is a highly thermodynamically unfavourable process whose mechanism involves multiple photons and many light and dark steps. The term 'artificial photosynthesis' normally refers to simpler light-induced redox chemistry such as the production of gaseous H₂ and O₂ from water^{1,2}, or formate ion from CO₂ and H₂O (refs 3,4). An artificial photosynthesis device is a variant of a photovoltaic device in which the positive and negative poles are replaced by appropriate catalysts that use the electrons and holes to carry out redox chemistry instead of generating power in a load. Commercially, however, the two devices differ enormously. Photovoltaics is a highly evolved field of science and engineering, and a mature industry, whereas artificial photosynthesis has no major commercial impact, and its science still faces great challenges such as the rapid photodegradability of most (narrow-bandgap) semiconductors in aqueous electrolytes⁵ and the large overpotentials that need to be overcome for many important reactions to become photo-electrochemically accessible. These lacunae open up

opportunities for alternative solar conversion strategies such as generating energetic charge carriers plasmonically⁶.

Because most of the current work on plasmon-mediated photochemistry is carried out on nanostructures, only processes involving localized surface plasmons (LSPs) will be discussed here, although photocurrents resulting from surface plasmon polariton decay have also been reported⁷. The LSP is a normal mode of oscillation of a bounded ensemble of electrons, as would approximately be the case for the conduction electrons in a small particle composed of a good conductor such as gold. Its frequency is strongly influenced by the shape of the ensemble. This high spectroscopic sensitivity to shape can potentially be exploited to construct plasmonic nanostructures that absorb across the full solar spectrum. The plasmon (and its connection with the dielectric function) has been rather well understood both classically and quantum dynamically since the 1950s. For example, in 1953 Bohm and Pines published a quantum mechanical treatment of a dense electron gas embedded in a uniform positively charged background⁸. Expanding on a one-dimensional analysis by Tomonaga⁹, they described the long-range part of the collective electronic Coulomb interactions in terms of fields, which represent "organized plasma

oscillation of the system as a whole." Although we have a rather good quantum mechanical description of the LSP, an advanced quantum description of the transient hot electrons and hot holes surviving briefly following the plasmon's decay would be highly desirable (Box 1).

Plasmon-mediated redox chemistry is predicated on the premise that as LSPs dephase there will exist, transiently, an ensemble of energetic electrons that can be accessed either directly or through the intermediacy of other phases, some acting as catalysts, which might also discourage the electrons, once transferred, from returning to the plasmonic material (Fig. 1). Excess positive charges in the plasmonic medium would act as holes that can carry out oxidation reactions. The overall power conversion efficiency would depend on the product of the individual efficiencies of the extraction of the hot electrons from the plasmonic nanostructure, and of the rates of the subsequent reduction and oxidation reactions (Fig. 1), limited by the slowest of these rates. For example, the loss of electrons would result in a positively charged particle that would progressively impede further electron loss, achieving a steady state that is governed by the rate at which the lost electrons are restored to the nanoparticle.