Reaching the Limits of Enhancement in (sub)Nanometer Metals Structures

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Abstract

Plasmonic enhancement has had remarkable success in optical coupling to the nanometer scale, enabling feats such as Raman spectroscopy with single molecule sensitivity. Here it is argued that much greater enhancements are possible in the near future by combining the gains of plasmonic resonances, directivity, sub-nanometer gaps and permittivity near zero materials. The pursuit of such extraordinary enhancements promises to bring new physics such as peering into the world of quantum optomechanics. It also promises new applications such as quantitative single molecule Raman spectroscopy and low photon number nonlinear optical switching. In addition, by pushing the limits of plasmonic enhancement, it is expected that the community will gain a greater appreciation of how physical phenomena such as non-locality, surface scattering and quantum tunneling each play a role in determining the ultimate performance.

Keywords

Plasmonics, Raman, Nonlinear Optics, Near-field

1 Introduction

It is well known that metal nanostructures can enhance the local electric field, and this phenomenon has been exploited in: surface-enhanced Raman scattering,[1–5] surface enhanced IR absorption,[6] nonlinear wavelength conversion,[7] multi-photon fluorescence,[8,9] optical tweezers[10] and quantum coupling.[11] While the basic theoretical understanding of plasmonic resonances in nanostructured metals has been present for more than a century[12] (see Figure 1), there are still several conflicting reports in the literature about the ultimate limits of plasmonic enhancement. For example, some works suggested that non-local effects would reduce the plasmonic enhancement and effectively increase the gap distances, whereas theoretical works have suggested that the gap distance is narrowed once again by the electron wavefunction entering the gap region.[13,14] Many works have considered field enhancements from singularities from sharp tapers and nearly touching metals in the absence of quantum or non-local effects.[15] As dimensions of fabrication enter the sub-nanometer regime, possibilities are emerging for greater field enhancements than previously thought possible with classical models.

Field enhancement in metal nanostructures arises from three main sources: local geometry of the permittivity (gaps, lightening rod effects), resonant field build up (plasmonic resonances), and efficient coupling (directivity, adiabatic enhancement). Affecting this field enhancement are material losses, surface scattering, the single channel limit, the non-local material response, quantum effects (confinement and tunneling of electrons) and material damage (such as melting). Here we aim to provide a perspective on field enhancements, considering existing achievements and what is ultimately possible. The overall finding is that significantly greater enhancement is within reach, and even greater enhancements than

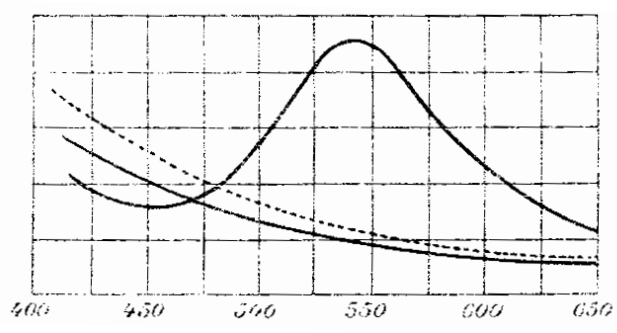

Figure 1: Scattering of a gold nanoparticle showing plasmon resonance peak at around 540 nm, as compared with perfect conductor nanoparticles (dashed line includes higher order contribution). Horizontal axis is wavelength in nanometers. From Ref.[12]

we originally thought possible.

2 Enhancement Factors

The spheroid is a canonical example in the analysis of plasmonic effects.[16–19] Many other field enhancing geometries exist, and these may perform better in different wavelength regions.[20–22] The goal here, however, is to understand the different enhancement factors that come from nanostructuring and the material response. The local field enhancement with respect to the incident plane wave field from a small prolate spheroid at the end of the long axis can be expressed analytically as:

$$f = \frac{\epsilon_m}{A(\epsilon_m - \epsilon_d) + \epsilon_d - \frac{i4\pi^2 V}{3\lambda^3}\epsilon_d^{3/2}(\epsilon_m - \epsilon_d)} \tag{1}$$

where $\epsilon_{m,d}$ is the relative permittivity of the metal, surrounding dielectric, V is the volume of the spheroid, λ is the free-space wavelength, and A is a geometric factor.

$$A = (\xi^2 - 1)(\xi/2)\ln\left[\frac{\xi + 1}{\xi - 1} - 1\right] \tag{2}$$

where $\xi = a/\sqrt{a^2 - b^2}$ and a and b are the long and short axes of the spheroid. From Eq. 1 it appears shrinking the particle will give higher field enhancement, up to the point where the permittivity is still valid. This will be discussed in more detail below.

2.1 Plasmonic Enhancement and Local Geometry

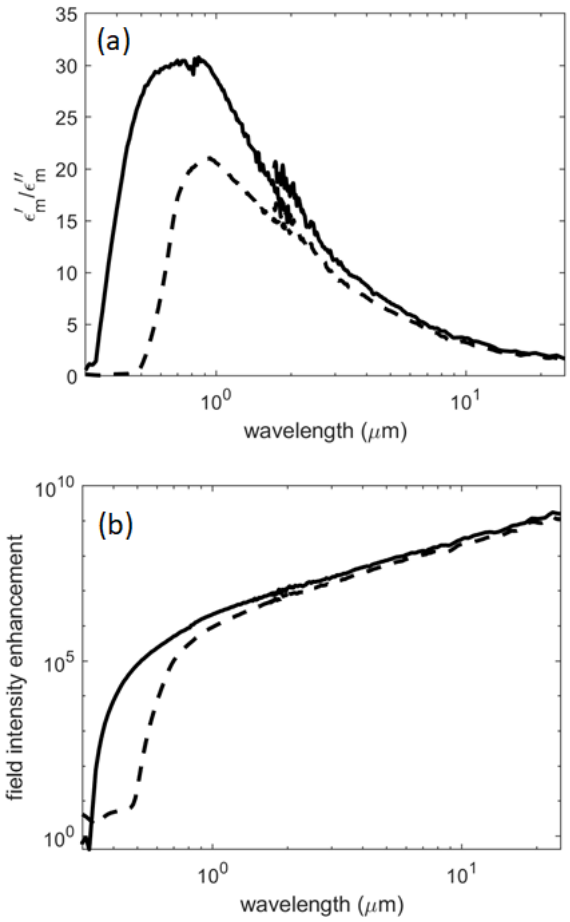

Figure 2: (a) Ratio of real and imaginary part of permittivity for silver (solid) and gold (dashed). (b) Maximum field intensity enhancement for a spheroid for silver (solid) and gold (dashed). Data from set C of previous work.[23]

The plasmonic resonance is defined as the wavelength where the real part of the denominator in Equation 1 is approaches zero. For a very small volume and $\epsilon_d = 1$, the field

intensity enhancement may be found as:

$$|f|^2 = \frac{\left(\frac{\epsilon'_m}{\epsilon''_m}\right)^2 + 1}{A^2} \tag{3}$$

where ϵ'_m and ϵ''_m are the real and imaginary parts of the metal's relative permittivity. This shows two important features: first that the magnitude of the ratio between the real and imaginary parts of the relative permittivity should be large (a common figure of merit), and second that A should be small (the lightning rod effect). Typical values of $\frac{\epsilon'_m}{\epsilon''_m}$ and $1/A$ are around 3–30 in the visible and near-IR, so that 100–10^5 is the range for field intensity enhancement expected. Figure 2a shows the ratio of the real and imaginary of the relative permittivity for gold and silver. We show an example calculation with 10^4 enhancement for a gold spheroid operating near the optimal permittivity condition in the Supporting Information.

We may also consider operating at longer wavelengths by elongating the spheroid. The resonance condition (neglecting retardation) is given when the real part of the denominator in Eq. 1 is zero, or $A = \epsilon_d / (\epsilon_d - \Re(\epsilon_m))$, where $\Re$ is the real part. Figure 2b shows the field intensity enhancement at the tip of a spheroid for resonances set at different wavelengths. It is clear from this figure that working at longer wavelengths increases the field intensity enhancement for this geometry, which results from the high permittivity contrast and sharp features.

2.2 Increased Confinement via Gaps

Of course, A is specific to the spheroid geometry chosen here, and other structures, such as gaps, can achieve similar geometric field enhancement at shorter wavelengths. For a capacitor, the stored charge varies inversely with the gap distance, which means that the field in the gap has the same scaling. Figure 3 shows this scaling for a numerical simulation of a prolate spheroid dimer with varying separation. Reducing the gap size leads to

a red-shift of the resonance, so to maintain the resonance frequency at least one degree of freedom should be altered as well to provide a compensating blue shift. For example, one may reduce the major axis of the spheroid (see Supporting Information for examples). Techniques such as atomic layer deposition,[24] self-assembled monolayers,[13] molecular spacers,[25,26] break-junctions[27] and shadow lithography[28] allow for creating gaps in the nanometer and subnanometer range. This is approximately an order of magnitude smaller than achieved with focussed ion beam lithography[29] and electron beam lithography[30] and so an enhancement of two orders of magnitude in the local field intensity is expected.

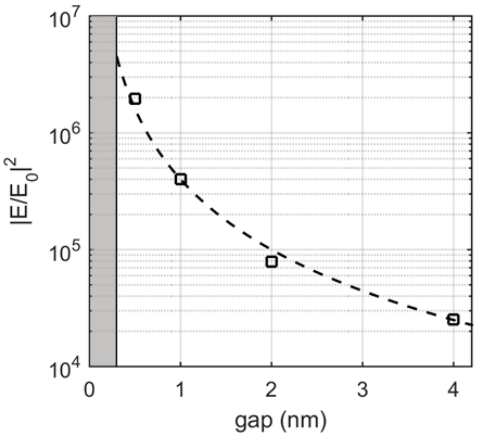

Figure 3: Scaling in the field intensity in a prolate spheroid dimer as a function of gap size (see Supporting Information for the numerical calculation approach). The fit is an inverse squared dependence, since the field alone should scale as the inverse of the gap size. The vertical line shows the onset of significant tunneling in vacuum at 0.3 nm.[31]

2.3 Efficient Coupling

Often efficient coupling to the metal structure is overlooked, and the result is suboptimal field enhancement. For an isolated subwavelength structure operating in the dipole regime, the single channel limit sets the ultimate coupling possible. Considering only the quasi-static response without retardation can lead to over-estimates of the field enhancement. For example, a self-similar chain of nanoparticles can operate as a nanolens, where the nanopar-

ticles get smaller and each nanoparticle enhances the field of the larger nanoparticle,[32] which provides in the quasi-static regime 10^{12} enhancements when considering the fourth power dependence of surface enhanced Raman. Comprehensive calculations of the same cascaded structures, however, produced two orders of magnitude enhancement,[33] which would allow for 10^8–10^9 Raman enhancement. This emphasizes the importance of including retardation to first order, allowing for radiative losses.

The retardation term in Equation 1 is $\frac{i4\pi^2 V}{3\lambda^3}\epsilon_d^{3/2}(\epsilon_m - \epsilon_d)$. The same term appears in the denominator of the polarizability of a spheroid. This ensures that, in the absence of material losses, the maximum scattering cross section is $\frac{3\lambda^2}{2\pi}$. This is actually a general result, not specific to plasmonics, often referred to as the "single channel limit" and also occurs for the cross section of a molecule.[34] If we consider the electromagnetic energy contained within this scattering cross section for one optical cycle, it amounts to the energy in a volume of $\frac{3\lambda^3}{4\pi}$ (the factor of a half comes from the average square of the field intensity over a cycle). In other words, the ratio in the retardation term is the ratio of the plasmonic focusing volume to the volume of energy captured in one cycle by the dipole. It is possible to add channels in a subwavelength structure by introducing multipole resonances ,[35,36] but this is quite challenging to achieve and so far scattering demonstrations remain well within the single channel limit.[37] The spheroid considered here is electric-dipole in nature, however, magnetic dipole and higher multipoles (magnetic and electric) can all contribution to field enhancement, and each is restricted by the single channel limit. It is interesting to note that narrow-band excitation of single molecules at low temperatures allows for the resonant scattering (reflection) of 85% of the incident beam; so diffraction limited focusing can couple efficiently to a single channel.[38] Of the resonance channels, the dipole with a gap has the advantage of having a single hotspot so that the energy is not shared between multiple hotspots.

If the constraint of having the entire structure be substantially subwavelength is removed, then antenna theory can more easily aid in achieving better coupling. It is possible

to suppress spurious radiation and thereby improve the coupling efficiency to the plasmonic volume. In antenna theory, this is referred to as directivity gain. Various antenna designs exist that achieve this goal, and many of these have been implemented in the visible to near-IR regime, including the Yagi-Uda,[39–41] the horn antenna,[42,43] and the waveguide antenna (cantenna).[29,44,45] Directivity gain provides typically an additional factor of 10 improvement in the local field intensity enhancement in antenna design. For Raman, where this is applied to the incident and the emitted photon, the overall enhancement is 100, allowing for reliable single molecule sensitivity[29,45] with overall enhancements approaching 10^{12}. Adiabatic focusing is another way to achieve efficient coupling to the nanometer scale.[46,47]

There is an optimal coupling condition for maximum field enhancement in structures that have finite absorption: the radiation quality factor should equal absorption quality factor.[48] This is analogous to the maximum power transfer theorem. If the radiative coupling is less, the energy will be absorbed before it has a chance to build up; if it is more, then the energy will radiate out faster. Directivity is a way to suppress spurious radiative channels; one may also consider using resonances with intrinsically less radiation, like magnetic dipoles.[49]

The single channel limit also provides another limit for consideration for dense plasmonic substrates that deserves further attention. If there are several plasmonic resonators in an area smaller than half the wavelength squared, then they will be forced to share the energy from the source beam and each receive lower overall enhancement. Therefore, it may be better to have a lower density of hotspots to maximize the total enhancement. In general though, plasmonic resonances do not achieve the single channel limit,[37] and so the areal density should be comparable to the extinction of each resonance. In many applications (such as surface enhanced Raman scattering), it is common to attempt to maximize the density of hotspots[50] since they are known to contribute most to the signal; here we caution that this may reduce the maximum enhancement of any individual hotspot as they compete with one another for the available photon energy. An optimal spacing in closely spaced arrays of split-ring resonators has been shown for second harmonic generation.[51]

2.4 Permittivity Near Zero and Quantum Tunneling

If the permittivity is near zero in the dielectric region, continuity of the normal component of the displacement vector means that the field is enhanced in that region. It is possible to achieve even greater field intensities in this situation, and this has been exploited to achieve enhanced Raman for J-aggregates, where the permittivity passes through zero.[52]

Quantum tunneling provides an intriguing possibility for artificially creating a permittivity near zero environment. In the gap region, the electron wavefunction decays and so the effective electron density is also reduced. By selecting the gap width appropriately, an electron density where the permittivity is zero can be achieved.[53] An order of magnitude increase in the local field intensity is anticipated for these cases. Within the quasi-static regime, it is possible to formulate this more concretely by noting that:[54]

$$\int_{\text{dielectric}} \epsilon_d \overline{E^2}\, dV = -\int_{\text{metal}} \epsilon'_m \overline{E^2}\, dV \tag{4}$$

where ϵ_d is the permittivity of the dielectric, ϵ'_m is the real permittivity of the metal and $\overline{E^2}$ is the time averaged field intensity. From this equation we see that if the permittivity of dielectric is near zero, the finite field in the metal forces the field in the dielectric to be large.

2.5 Combining Enhancement Factors

Combining simply the effects of plasmonic resonances, directivity enhancements, subnanometer gap enhancements and weak tunneling to give permittivity near zero, an astounding $\sim 10^9$–10^{10} field intensity enhancement is found. This amounts to a 10^{18}–10^{20} enhancement for processes like Raman spectroscopy where the enhancement is felt twice, first for the incident photon and then for the scattered one. It is interesting to consider the new physics that may be allowed in this regime. Already researchers have claimed to have observed strong coupling regime for single emitters at room temperature in subnanometer plasmonic

gaps.[25] Recent observations show nonlinear power dependence of parametric Raman processes in ultra-small gap cavities.[55] Interesting predictions exist about new physical features in the Raman spectrum that arise from quantum coupling of the optomechanical system.[56] These features go beyond back-action enhancements already predicted for single molecule Raman.[57]

3 Limiting Processes

Many physical processes have been explored in terms of their limits on the plasmonic response. Some of the limitations are reviewed critically here.

3.1 Material Losses

From Equation 1, we see that material loss from the imaginary part of the permittivity is one such limitation. To reduce material loss, operation at a low loss wavelength for high quality metals can be used. Ultraflat materials created by templates stripping can provide lower losses due to reduced surface roughness scattering.[58] One may also attempt crystalline metals. Crystalline materials can be nanofabricated more reliably, and this removes surface roughness to allow for more predictable enhancements (although the ultimate enhancement may be lower).[59] In addition, cooling down the metal can provide some benefit, but it is most often impractical. For example, in cooling from room temperature to 80 K, the imaginary permittivity is reduced by a factor of 3.[60] At 5 K, ultraflat and crystalline Ag films showed similar improvements.[61]

3.2 Atomic Spacing and Diffusion

Creating arbitrarily small structures in metal is limited by the atomic spacing. It is not possible to make features sharper than the actual atoms. At the same time, it has been theorized that the discontinuous atomic structure can lead to field enhancements by providing

locally sharp features.[62] This provides a local sharpness that can result in greater field enhancement.[63] The diffusion of atoms can assist in creating such sharp features (where a single atom juts out of the lattice), but can also lead to blunting of tips.[64]

3.3 Non-local effects, Surface Scattering, Landau Damping

A number of effects are expected to arise for small features. For example, the nonlocal response has been observed in the infrared with graphene-Au structures;[65] however, it was not observed for experiments at visible and near-IR frequencies.[66,67] Based on this, the validity of applying the Fermi pressure theory for frequencies higher than the electron collision rate should be explored further.

Surface scattering has also been proposed to increase the losses of metals, particularly in small structures where the mean free path is comparable to the structure size.[68,69] The exact magnitude of this effect has been debated in the literature with typical scaling parameters varying over an order of magnitude.[70] Chemical interface damping can play a significant role in scattering and can be modified by changing the surface properties.[71,72] Attempts to measure plasmon resonance widths of single nanoparticles in controlled matrices using nearfield spectroscopy have agreed well with Mie theory (neglecting any surface effects).[73] There seems to be some discrepancy between this work and another far-field single particle approach.[74] Again, further investigation is warranted.

Landau damping is a related phenomena that allows absorption of the field due to electron excitation with momentum matching coming from high spatial frequency in the interaction;[75] hence the connection to rough surfaces and small features that have high spatial frequency and can provide the required large wavevector to the electron absorption process. This effect has been suggested to limit the field enhancement in 0.5 nm gaps for 2.5 nm particles.[76] The degree to which this loss mechanism plays a significant role should be investigated further.

3.4 Melting

A practical issue with plasmonic enhancement, particularly for high field intensities, is material damage (e.g., melting). To remove heat effectively from the area of excitation, connected metal films and apertures have been used.[77–79] Also, refractory plasmonic materials have been investigated to achieve enhancements without melting.[80]

4 Conclusions and Outlook

While there has been impressive progress in the local field intensity enhancement seen for various nanoplasmonic systems, here it was argued that 3-4 orders of magnitude greater enhancement is possible by combining in a single platform all the features of: (a) a single subnanometer gap, (b) directivity gain, (c) epsilon near zero materials in the gaps, and (d) operating at high real-to-imaginary permittivity ratios. While each of these features has been seen individually at least, the combination is expected to reveal new physics and applications unique to plasmonics. By directing efforts to platforms that incorporate all of these features, we believe the community will better understand the impact of Landau damping, surface scattering and non-local effects are on the actual achievable enhancement.

4.1 New physics

Strong coupling in sub-nanometer plasmonic gaps has already been claimed.[25,81] This provides a remarkable platform for studying quantum interactions and non-classical phenomena. For example, it is possible to look for a single-photon nonlinear response.[82] While such phenomena have been observed in other quantum electrodynamic systems, plasmonics uniquely provides the possibility for quantum interactions at ultra-fast timescales (sub-100 fs); and therefore, there exists the potential for quantum information processing at room temperature before decoherence can set in. Non-resonant phenomena, like Raman, also benefit from this broadband response and it is anticipated that careful design will allow the community

to explore further the regimes of quantum optomechanics.

4.2 Applications

Ultra-fast single photon sources may be enabled by stronger light-matter interaction at the sub-nanometer scale. This promises single photon communication at data rates commensurate with existing optical networks.[83]

A strong optical nonlinearity at the single or few photon level may enable ultra-fast all-optical switching that is comparable to electronic platforms, but with much faster data rates. Some of the best demonstrations for all-optical switching are still several orders of magnitude less efficient than conventional electronics (at a similar speed) making them impractical from a scaling point of view.[84] Nanoplasmonics also naturally provides dense integration capability for such platforms.

Widescale adoption of single molecule spectroscopy, through Raman and IR excitation, will require robust plasmonic substrates with reproducible signal. One of the common challenges of SERS is the large variation in the response intrinsic to having a fourth power intensity scaling combined sub-nanometer gaps.[85] Even slight variations provide huge variability; whereas reliable spacers and directional coupling promise more stable enhancements that advance this field towards widescale adoption. Digital detection of SERS and IR spectra events may also allow for quantitative analysis in these fields that are not as susceptible to the magnitude of each event.

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Supporting Information Available

Contains details of numerical simulation and calculations for isolated nanoparticles, dimers, addition of a ground reflector and addition of an ENZ material. This material is available free of charge via the Internet at `http://pubs.acs.org/`.

References

(1) Fleischmann, M.; Hendra, P. J.; McQuillan, A. J. Raman spectra of pyridine adsorbed at a silver electrode. *Chemical Physics Letters* **1974**, *26*, 163–166.

(2) Jeanmaire, D. L.; Van Duyne, R. P. Surface Raman spectroelectrochemistry: Part I. Heterocyclic, aromatic, and aliphatic amines adsorbed on the anodized silver electrode. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1977**, *84*, 1–20.

(3) Moskovits, M. Surface roughness and the enhanced intensity of Raman scattering by molecules adsorbed on metals. *The Journal of Chemical Physics* **1978**, *69*, 4159–4161.

(4) Nie, S.; Emory, S. R. Probing single molecules and single nanoparticles by surface-enhanced Raman scattering. *Science* **1997**, *275*, 1102–1106.

(5) Kneipp, K.; Wang, Y.; Kneipp, H.; Perelman, L. T.; Itzkan, I.; Dasari, R. R.; Feld, M. S. Single molecule detection using surface-enhanced Raman scattering (SERS). *Physical Review Letters* **1997**, *78*, 1667.

(6) Hartstein, A.; Kirtley, J.; Tsang, J. Enhancement of the infrared absorption from molecular monolayers with thin metal overlayers. *Physical Review Letters* **1980**, *45*, 201.

(7) Kauranen, M.; Zayats, A. V. Nonlinear plasmonics. *Nature Photonics* **2012**, *6*, 737.

(8) Schuck, P.; Fromm, D.; Sundaramurthy, A.; Kino, G.; Moerner, W. Improving the mismatch between light and nanoscale objects with gold bowtie nanoantennas. *Physical Review Letters* **2005**, *94*, 017402.

(9) Muehlschlegel, P.; Eisler, H.-J.; Martin, O. J.; Hecht, B.; Pohl, D. Resonant optical antennas. *Science* **2005**, *308*, 1607–1609.

(10) Juan, M. L.; Righini, M.; Quidant, R. Plasmon nano-optical tweezers. *Nature Photonics* **2011**, *5*, 349.

(11) Tame, M. S.; McEnery, K.; Özdemir, Ş.; Lee, J.; Maier, S.; Kim, M. Quantum plasmonics. *Nature Physics* **2013**, *9*, 329.

(12) Mie, G. Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen. *Annalen der Physik* **1908**, *330*, 377–445.

(13) Ciracì, C.; Hill, R.; Mock, J.; Urzhumov, Y.; Fernández-Domínguez, A.; Maier, S.; Pendry, J.; Chilkoti, A.; Smith, D. Probing the ultimate limits of plasmonic enhancement. *Science* **2012**, *337*, 1072–1074.

(14) Teperik, T. V.; Nordlander, P.; Aizpurua, J.; Borisov, A. G. Robust subnanometric plasmon ruler by rescaling of the nonlocal optical response. *Physical Review Letters* **2013**, *110*, 263901.

(15) Gramotnev, D. K.; Bozhevolnyi, S. I. Nanofocusing of electromagnetic radiation. *Nature Photonics* **2014**, *8*, 13.

(16) Wokaun, A.; Gordon, J.; Liao, P. Radiation damping in surface-enhanced Raman scattering. *Physical Review Letters* **1982**, *48*, 957.

(17) Boyd, G.; Rasing, T.; Leite, J.; Shen, Y. Local-field enhancement on rough surfaces of metals, semimetals, and semiconductors with the use of optical second-harmonic generation. *Physical Review B* **1984**, *30*, 519.

(18) Raether, H. *Surface Plasmons on Smooth and Rough Surfaces and on Gratings*; Springer, 1988.

(19) Calander, N.; Willander, M. Theory of surface-plasmon resonance optical-field enhancement at prolate spheroids. *Journal of Applied Physics* **2002**, *92*, 4878–4884.

(20) Biagioni, P.; Huang, J.-S.; Hecht, B. Nanoantennas for visible and infrared radiation. *Reports on Progress in Physics* **2012**, *75*, 024402.

(21) Amendola, V.; Pilot, R.; Frasconi, M.; Marago, O. M.; Iati, M. A. Surface plasmon resonance in gold nanoparticles: a review. *Journal of Physics: Condensed Matter* **2017**, *29*, 203002.

(22) Lu, X.; Rycenga, M.; Skrabalak, S. E.; Wiley, B.; Xia, Y. Chemical synthesis of novel plasmonic nanoparticles. *Annual Review of Physical Chemistry* **2009**, *60*, 167–192.

(23) Yang, H. U.; D'Archangel, J.; Sundheimer, M. L.; Tucker, E.; Boreman, G. D.; Raschke, M. B. Optical dielectric function of silver. *Physical Review B* **2015**, *91*, 235137.

(24) Im, H.; Bantz, K. C.; Lindquist, N. C.; Haynes, C. L.; Oh, S.-H. Vertically oriented sub-10-nm plasmonic nanogap arrays. *Nano Letters* **2010**, *10*, 2231–2236.

(25) Chikkaraddy, R.; de Nijs, B.; Benz, F.; Barrow, S. J.; Scherman, O. A.; Rosta, E.; Demetriadou, A.; Fox, P.; Hess, O.; Baumberg, J. J. Single-molecule strong coupling at room temperature in plasmonic nanocavities. *Nature* **2016**, *535*, 127.

(26) Lim, D.-K.; Jeon, K.-S.; Hwang, J.-H.; Kim, H.; Kwon, S.; Suh, Y. D.; Nam, J.-M. Highly uniform and reproducible surface-enhanced Raman scattering from DNA-tailorable nanoparticles with 1-nm interior gap. *Nature Nanotechnology* **2011**, *6*, 452.

(27) Ward, D. R.; Halas, N. J.; Ciszek, J. W.; Tour, J. M.; Wu, Y.; Nordlander, P.; Natelson, D. Simultaneous measurements of electronic conduction and Raman response in molecular junctions. *Nano Letters* **2008**, *8*, 919–924.

(28) Zhu, W.; Banaee, M. G.; Wang, D.; Chu, Y.; Crozier, K. B. Lithographically fabricated optical antennas with gaps well below 10 nm. *Small* **2011**, *7*, 1761–1766.

(29) Ahmed, A.; Gordon, R. Single molecule directivity enhanced Raman scattering using nanoantennas. *Nano Letters* **2012**, *12*, 2625–2630.

(30) Fromm, D. P.; Sundaramurthy, A.; Schuck, P. J.; Kino, G.; Moerner, W. Gap-dependent optical coupling of single bowtie nanoantennas resonant in the visible. *Nano Letters* **2004**, *4*, 957–961.

(31) Savage, K. J.; Hawkeye, M. M.; Esteban, R.; Borisov, A. G.; Aizpurua, J.; Baumberg, J. J. Revealing the quantum regime in tunnelling plasmonics. *Nature* **2012**, *491*, 574.

(32) Li, K.; Stockman, M. I.; Bergman, D. J. Self-similar chain of metal nanospheres as an efficient nanolens. *Physical Review Letters* **2003**, *91*, 227402.

(33) Boriskina, S. V.; Reinhard, B. M. Molding the flow of light on the nanoscale: from vortex nanogears to phase-operated plasmonic machinery. *Nanoscale* **2012**, *4*, 76–90.

(34) Jackson, J. D. *Classical electrodynamics*; Wiley, 1999; pp 766–768.

(35) Ruan, Z.; Fan, S. Superscattering of light from subwavelength nanostructures. *Physical Review Letters* **2010**, *105*, 013901.

(36) Chen, S.; Jin, S.; Gordon, R. Super-transmission from a finite subwavelength arrangement of slits in a metal film. *Optics Express* **2014**, *22*, 13418–13426.

(37) Husnik, M.; Linden, S.; Diehl, R.; Niegemann, J.; Busch, K.; Wegener, M. Quantitative experimental determination of scattering and absorption cross-section spectra of individual optical metallic nanoantennas. *Physical Review Letters* **2012**, *109*, 233902.

(38) Zumofen, G.; Mojarad, N.; Sandoghdar, V.; Agio, M. Perfect reflection of light by an oscillating dipole. *Physical Review Letters* **2008**, *101*, 180404.

(39) Taminiau, T. H.; Stefani, F. D.; van Hulst, N. F. Enhanced directional excitation and emission of single emitters by a nano-optical Yagi-Uda antenna. *Optics Express* **2008**, *16*, 10858–10866.

(40) Kosako, T.; Kadoya, Y.; Hofmann, H. F. Directional control of light by a nano-optical Yagi–Uda antenna. *Nature Photonics* **2010**, *4*, 312.

(41) Curto, A. G.; Volpe, G.; Taminiau, T. H.; Kreuzer, M. P.; Quidant, R.; van Hulst, N. F. Unidirectional emission of a quantum dot coupled to a nanoantenna. *Science* **2010**, *329*, 930–933.

(42) Bao, W. et al. Mapping local charge recombination heterogeneity by multidimensional nanospectroscopic imaging. *Science* **2012**, *338*, 1317–1321.

(43) Choo, H.; Kim, M.-K.; Staffaroni, M.; Seok, T. J.; Bokor, J.; Cabrini, S.; Schuck, P. J.; Wu, M. C.; Yablonovitch, E. Nanofocusing in a metal–insulator–metal gap plasmon waveguide with a three-dimensional linear taper. *Nature Photonics* **2012**, *6*, 838.

(44) Ahmed, A.; Gordon, R. Directivity enhanced Raman spectroscopy using nanoantennas. *Nano Letters* **2011**, *11*, 1800–1803.

(45) Wang, D.; Zhu, W.; Best, M. D.; Camden, J. P.; Crozier, K. B. Directional Raman scattering from single molecules in the feed gaps of optical antennas. *Nano Letters* **2013**, *13*, 2194–2198.

(46) Stockman, M. I. Nanofocusing of optical energy in tapered plasmonic waveguides. *Physical Review Letters* **2004**, *93*, 137404.

(47) Ropers, C.; Neacsu, C.; Elsaesser, T.; Albrecht, M.; Raschke, M.; Lienau, C. Grating-coupling of surface plasmons onto metallic tips: a nanoconfined light source. *Nano Letters* **2007**, *7*, 2784–2788.

(48) Seok, T. J.; Jamshidi, A.; Kim, M.; Dhuey, S.; Lakhani, A.; Choo, H.; Schuck, P. J.; Cabrini, S.; Schwartzberg, A. M.; Bokor, J.; Yablonovitch, E.; Wu, M. C. Radiation engineering of optical antennas for maximum field enhancement. *Nano Letters* **2011**, *11*, 2606–2610.

(49) Bozhevolnyi, S. I.; Søndergaard, T. General properties of slow-plasmon resonant nanostructures: nano-antennas and resonators. *Optics express* **2007**, *15*, 10869–10877.

(50) Asiala, S. M.; Schultz, Z. D. Characterization of hotspots in a highly enhancing SERS substrate. *Analyst* **2011**, *136*, 4472–4479.

(51) Linden, S.; Niesler, F.; Förstner, J.; Grynko, Y.; Meier, T.; Wegener, M. Collective effects in second-harmonic generation from split-ring-resonator arrays. *Physical Review Letters* **2012**, *109*, 015502.

(52) Zamecnik, C. R.; Ahmed, A.; Walters, C. M.; Gordon, R.; Walker, G. C. Surface-enhanced Raman spectroscopy using lipid encapsulated plasmonic nanoparticles and J-aggregates to create locally enhanced electric fields. *The Journal of Physical Chemistry C* **2013**, *117*, 1879–1886.

(53) Khademi, A.; Dewolf, T.; Gordon, R. Quantum plasmonic epsilon near zero: field enhancement and cloaking. *Optics Express* **2018**, *26*, 15656–15664.

(54) Wang, F.; Shen, Y. R. General properties of local plasmons in metal nanostructures. *Physical Review Letters* **2006**, *97*, 206806.

(55) Lombardi, A.; Schmidt, M. K.; Weller, L.; Deacon, W. M.; Benz, F.; de Nijs, B.; Aizpurua, J.; Baumberg, J. J. Pulsed Molecular Optomechanics in Plasmonic Nanocavities: From Nonlinear Vibrational Instabilities to Bond-Breaking. *Physical Review X* **2018**, *8*, 011016.

(56) Dezfouli, M. K.; Gordon, R.; Hughes, S. Molecular optomechanics in the nonlinear cavity-QED regime. *arXiv preprint arXiv:1805.10153* **2018**,

(57) Roelli, P.; Galland, C.; Piro, N.; Kippenberg, T. J. Molecular cavity optomechanics as a theory of plasmon-enhanced Raman scattering. *Nature Nanotechnology* **2016**, *11*, 164–169.

(58) Nagpal, P.; Lindquist, N. C.; Oh, S.-H.; Norris, D. J. Ultrasmooth patterned metals for plasmonics and metamaterials. *Science* **2009**, *325*, 594–597.

(59) Huang, J.-S.; Callegari, V.; Geisler, P.; Brüning, C.; Kern, J.; Prangsma, J. C.; Wu, X.; Feichtner, T.; Ziegler, J.; Weinmann, P.; Kamp, M.; Forchel, A.; Biagioni, P. B.; Sennhauser, U.; Hecht, B. Atomically flat single-crystalline gold nanostructures for plasmonic nanocircuitry. *Nature Communications* **2010**, *1*, 150.

(60) Bouillard, J.-S. G.; Dickson, W.; OConnor, D. P.; Wurtz, G. A.; Zayats, A. V. Low-temperature plasmonics of metallic nanostructures. *Nano Letters* **2012**, *12*, 1561–1565.

(61) Jayanti, S. V.; Park, J. H.; Dejneka, A.; Chvostova, D.; McPeak, K. M.; Chen, X.; Oh, S.-H.; Norris, D. J. Low-temperature enhancement of plasmonic performance in silver films. *Optical Materials Express* **2015**, *5*, 1147–1155.

(62) Barbry, M.; Koval, P.; Marchesin, F.; Esteban, R.; Borisov, A. G.; Aizpurua, J.; Sánchez-Portal, D. Atomistic near-field nanoplasmonics: reaching atomic-scale resolution in nanooptics. *Nano Letters* **2015**, *15*, 3410–3419.

(63) Benz, F.; Schmidt, M. K.; Dreismann, A.; Chikkaraddy, R.; Zhang, Y.; Demetriadou, A.; Carnegie, C.; Ohadi, H.; de Nijs, B.; Esteban, R.; Aizpurua, J.; Baumberg, J. J. Single-molecule optomechanics in picocavities. *Science* **2016**, *354*, 726–729.

(64) Sun, J.; He, L.; Lo, Y.-C.; Xu, T.; Bi, H.; Sun, L.; Zhang, Z.; Mao, S. X.; Li, J. Liquid-

like pseudoelasticity of sub-10-nm crystalline silver particles. *Nature Materials* **2014**, *13*, 1007.

(65) Lundeberg, M. B.; Gao, Y.; Asgari, R.; Tan, C.; Van Duppen, B.; Autore, M.; Alonso-González, P.; Woessner, A.; Watanabe, K.; Taniguchi, T.; Hillenbrand, R.; Hone, J. H.; Polini, M.; Koppens, F. H. L. Tuning quantum nonlocal effects in graphene plasmonics. *Science* **2017**, *357*, 187–191.

(66) Hajisalem, G.; Min, Q.; Gelfand, R.; Gordon, R. Effect of surface roughness on self-assembled monolayer plasmonic ruler in nonlocal regime. *Optics Express* **2014**, *22*, 9604–9610.

(67) Doyle, D.; Charipar, N.; Argyropoulos, C.; Trammell, S. A.; Nita, R.; Naciri, J.; Pique, A.; Herzog, J. B.; Fontana, J. Tunable subnanometer gap plasmonic metasurfaces. *ACS Photonics* **2017**, *5*, 1012–1018.

(68) Genzel, L.; Martin, T.; Kreibig, U. Dielectric function and plasma resonances of small metal particles. *Zeitschrift für Physik B Condensed Matter* **1975**, *21*, 339–346.

(69) Kreibig, U.; Genzel, L. Optical absorption of small metallic particles. *Surface Science* **1985**, *156*, 678–700.

(70) Scholl, J. A.; Koh, A. L.; Dionne, J. A. Quantum plasmon resonances of individual metallic nanoparticles. *Nature* **2012**, *483*, 421.

(71) Hövel, H.; Fritz, S.; Hilger, A.; Kreibig, U.; Vollmer, M. Width of cluster plasmon resonances: Bulk dielectric functions and chemical interface damping. *Physical Review B* **1993**, *48*, 18178.

(72) Foerster, B.; Joplin, A.; Kaefer, K.; Celiksoy, S.; Link, S.; Sönnichsen, C. Chemical interface damping depends on electrons reaching the surface. *ACS Nano* **2017**, *11*, 2886–2893.

(73) Klar, T.; Perner, M.; Grosse, S.; Von Plessen, G.; Spirkl, W.; Feldmann, J. Surface-plasmon resonances in single metallic nanoparticles. *Physical Review Letters* **1998**, *80*, 4249.

(74) Baida, H.; Billaud, P.; Marhaba, S.; Christofilos, D.; Cottancin, E.; Crut, A.; Lermé, J.; Maioli, P.; Pellarin, M.; Broyer, M.; Del Fatti, N.; Vallée, F.; Sánchez-Iglesias, A.; Pastoriza-Santos, I.; M, L.-M. L. Quantitative determination of the size dependence of surface plasmon resonance damping in single Ag SiO2 nanoparticles. *Nano Letters* **2009**, *9*, 3463–3469.

(75) Shahbazyan, T. V. Landau damping of surface plasmons in metal nanostructures. *Physical Review B* **2016**, *94*, 235431.

(76) Khurgin, J.; Tsai, W.-Y.; Tsai, D. P.; Sun, G. Landau damping and limit to field confinement and enhancement in plasmonic dimers. *ACS Photonics* **2017**, *4*, 2871–2880.

(77) Wang, K.; Schonbrun, E.; Steinvurzel, P.; Crozier, K. B. Trapping and rotating nanoparticles using a plasmonic nano-tweezer with an integrated heat sink. *Nature Communications* **2011**, *2*, 469.

(78) Melentiev, P. N.; Afanasiev, A. E.; Kuzin, A. A.; Baturin, A. S.; Balykin, V. I. Giant optical nonlinearity of a single plasmonic nanostructure. *Optics Express* **2013**, *21*, 13896–13905.

(79) Nezami, M. S.; Yoo, D.; Hajisalem, G.; Oh, S.-H.; Gordon, R. Gap plasmon enhanced metasurface third-harmonic generation in transmission geometry. *ACS Photonics* **2016**, *3*, 1461–1467.

(80) Guler, U.; Boltasseva, A.; Shalaev, V. M. Refractory plasmonics. *Science* **2014**, *344*, 263–264.

(81) Hugall, J. T.; Singh, A.; van Hulst, N. F. Plasmonic Cavity Coupling. *ACS Photonics* **2018**, *5*, 43–53.

(82) Rousseaux, B.; Baranov, D. G.; Käll, M.; Shegai, T.; Johansson, G. Quantum description and emergence of nonlinearities in strongly coupled single-emitter nanoantenna systems. *Physical Review B* **2018**, *98*, 045435.

(83) Hoang, T. B.; Akselrod, G. M.; Mikkelsen, M. H. Ultrafast room-temperature single photon emission from quantum dots coupled to plasmonic nanocavities. *Nano Letters* **2015**, *16*, 270–275.

(84) Nozaki, K.; Tanabe, T.; Shinya, A.; Matsuo, S.; Sato, T.; Taniyama, H.; Notomi, M. Sub-femtojoule all-optical switching using a photonic-crystal nanocavity. *Nature Photonics* **2010**, *4*, 477.

(85) Zhu, W.; Crozier, K. B. Quantum mechanical limit to plasmonic enhancement as observed by surface-enhanced Raman scattering. *Nature Communications* **2014**, *5*, 5228.

Graphical TOC Entry

Perspective piece on the achieving the ultimate field intensity enhancement with (sub)nanometer metal structures. Directivity, sub-nanometer structures, epsilon-near-zero materials, maximum power transfer and optimizing material properties all contribute to achieving orders of magnitude larger enhancement than plasmonics has seen so far, promising new physics and applications.