ADVANCED MATERIALS

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Plasmonic Materials**

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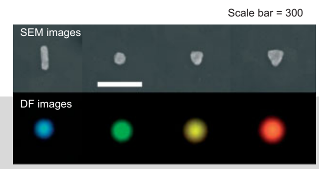

We provide an overview of the way in which different approaches to nanostructuring metals can lead to a wealth of interesting optical properties and functionality through manipulation of the plasmon modes that such structures support, a field known as plasmonics. The increasing interest in plasmonics derives in large measure from the interplay between better fabrication techniques and an awareness of the potential that controlled plasmon modes have to offer. The combination of nanometer-scale fabrication techniques and increasingly sophisticated numerical modeling capabilities thus enables a significant advance in our understanding of the science underlying plasmonics. Here, we survey some of the different structures that have been explored. We hope that this Review will spur others to continue the exploration of this fascinating topic.

1. Introduction

What is plasmonics? We typically think of metals as either conductors in electronics or reflectors in optics. In a scientific context, using metals as mirrors is not always desirable—their residual absorption and low damage threshold often make them second-rate in comparison to dielectric stack mirrors, for example in applications such as lasers and gyroscopes. However, there has been a recent surge of interest in optics based on metals that goes beyond their simple reflecting nature. From an electromagnetic point of view metals are plasmas, comprising fixed, positive ion cores and mobile conduction electrons. The recent interest exploits the collective oscillations of the conduction electrons of this plasma, and consequently the topic has become known as plasmonics. For a century or so, plasmons have been explored as an intriguing surface-wave phenomenon. Now they are coming into their own as a powerful way to incorporate optics into nanoscience and nanotechnology. Optics does not at first seem naturally suited to the nanometer world; the diffraction limit usually limits the length scales that can be probed to on the order of several hundred nanometers. However, part of the excitement of plasmonics is the realization that plasmons offer a way to beat this diffraction limit and thus enable a route to sub-wavelength optics.

In this Review we are concerned primarily with surveying the different types of metallic structures that have been explored in the context of plasmonics, the fabrication techniques that have been employed, and the properties of the plasmon modes that the different structures support. Because we wish to focus on the underlying science rather than on techniques, we have chosen to organize this Review around the different kinds of plasmon modes that have so far been investigated. First though, we provide a short section devoted to fabrication techniques, primarily to compare and contrast the different approaches adopted.

To exploit fully the properties of plasmon modes requires the use of a number of both well-established and novel fabrication techniques to generate structures over length scales ranging from a few nanometers up to a few centimeters. Broadly, these can be divided into two categories: top-down and bottom-up approaches. Top-down approaches are a powerful means to explore a wide range of structures with the advantage of excellent control. However, they are expensive, limited in the sample size that can be produced, and slow. Electron-beam lithography (EBL) offers high resolution, down to ten nanometers or so, with good reproducibility,[1,2] (an example is shown in Fig. 1). Focused ion-beam (FIB) milling allows the processing of existing planar films, for ex-

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ample by fabricating arrays of holes,[3] or by cutting trenches to enable guiding of plasmons[4] (an example is shown in Fig. 3). A technique that can be used over much larger areas is optical lithography, however, this approach is in general limited to simple periodic patterns. (In something of a reversal of the technique, confined plasmon fields can be used to expose sub-wavelength regions of photoresist via their near-field.[5]) For structures suitable for IR and THz frequencies contact printing is possible. In the microwave regime life is much simpler and computer-controlled milling machines and printed circuit board techniques can be used (an example is shown in Fig. 5). Less expensive and more parallel methods for producing lithographic masks utilize self-assembly techniques, in particular using polystyrene and silica nanospheres. Called nanosphere lithography (NSL), this has permitted the fabrication of periodic arrays of metallic[6] and magnetic nanoparticles[7] and arrays of holes in an otherwise continuous metallic film[8] (examples are shown in Figs. 2 and 4).

Bottom-up processes tend to involve the chemical deposition of material using electrolysis or the reduction of ionic compounds contained in solution, and a variety of shapes can be produced.[9] Anodic alumina masks that contain regular arrays of pores within an alumina film may be used as deposition masks. In this process an aluminum film is anodized and, under certain conditions, results in a hexagonal array of holes with dimensions as small as 25 nm.[10] Subsequent thermal evaporation or electrochemical deposition of gold results in the production of gold nanoparticles. Continuous gold films containing voids have also been formed using electrochemical deposition with close-packed arrays of nanospheres acting as a template.[11] Direct chemical synthesis of metallic particles is perhaps the dominant bottom-up technique. Core/shell particles,[12] rods,[13,14] and wires[15] are among the many shapes that can be fabricated in addition to spheres. These and other techniques allow a wide variety of metallic structures to be made with features on the nanometer scale. The resonant optical modes (plasmons) such structures support, and how those modes depend on the details of the structure concerned, are discussed below. First, we briefly review the concept of plasmons.

2. Plasmas and Plasmons

Plasmons are resonant modes that involve the interaction between free charges and light. The ionosphere and metals are both examples of plasmas: media that possess freely mobile charges. Bulk plasmas can sustain longitudinal plasma oscillations (plasmons), oscillations whose resonant frequency arises from the restoring force that the altered charge distribution exerts on the mobile charges when they are displaced from equilibrium, for example by the nearby passage of an electron.[16,17] For a bulk plasma this plasmon frequency, ω_p, is given by[18]

$$\omega_p^2 = \frac{ne^2}{\varepsilon_0 m} \quad (1)$$

where n is the number density of mobile charge carriers, e their charge, m their mass and ε_0 the relative permittivity of

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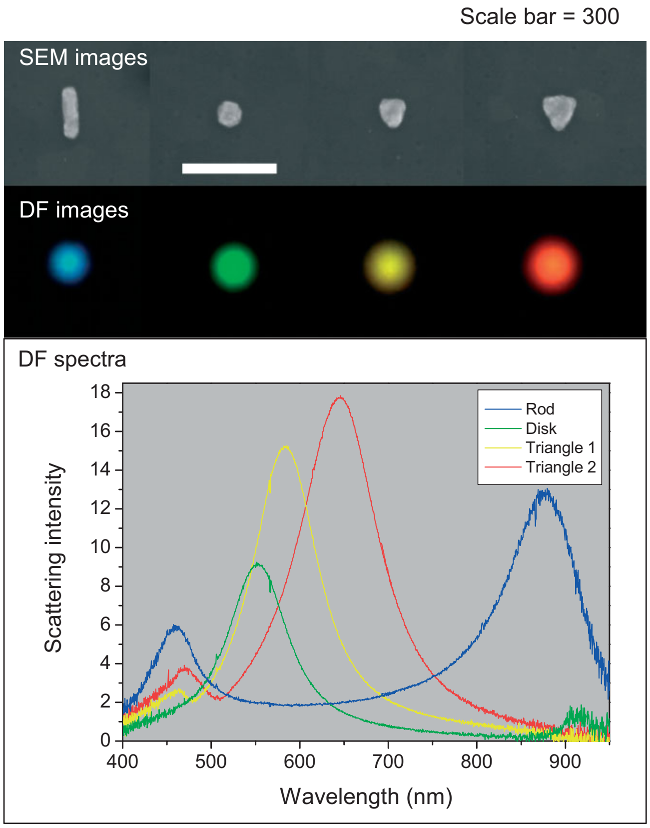

Figure 1. Scanning electron micrographs (top), dark-field images (middle), and dark-field spectra of several metallic nanoparticles made by e-beam lithography. From left to right the shapes are, a rod, a disc, and two triangles (the right hand one being the larger of the two). The thickness of these particles were 30 nm and the substrates were silica glass coated with 20 nm of ITO. (The scale bar in the top figure is 300 nm.)

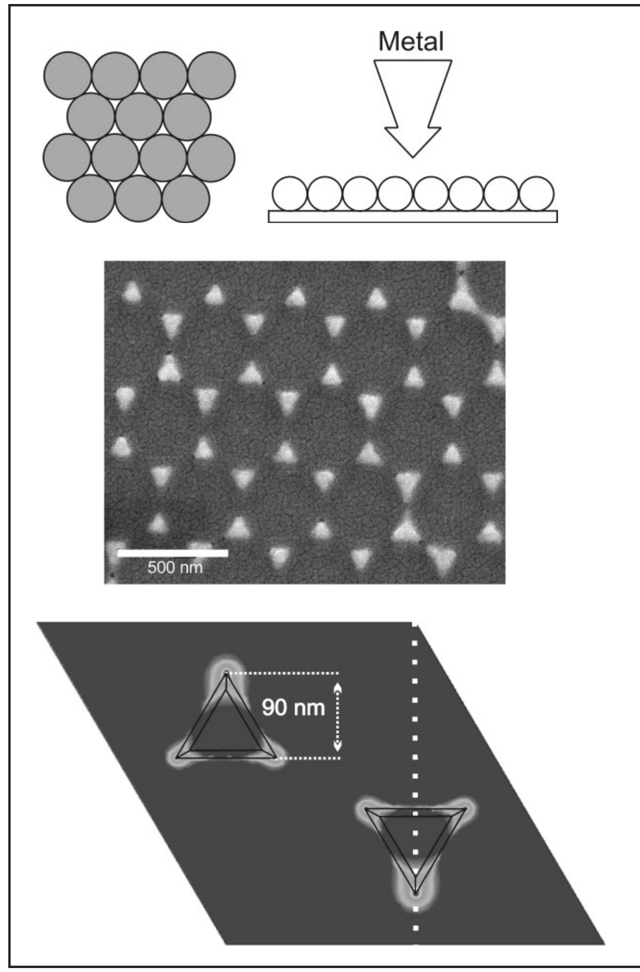

Figure 2. Arrays of triangular nanoparticles (middle figure shows SEM) can be made using nanosphere lithography (NSL). In the NSL process ordered arrays of submicrometer polystyrene spheres are formed on a substrate (top left) and metal deposited through the interstices via evaporation under vacuum (top right), the polystyrene spheres are then removed to leave the array of metallic particles. The lower figure shows the results of a finite element model of the optical field around the particles (a unit cell is shown) when illuminated on resonance—note the tight field confinement around the particle tips. Adapted with permission from [35]. Copyright 2006 American Chemical Society.

free space. Electromagnetic radiation (light) incident on the plasma at a frequency below the plasma frequency induces motion in the charge carriers that acts to screen out the incident field—incident waves are reflected; above the plasma frequency the charges are unable to respond quickly enough to screen out the incident field and the waves are instead transmitted. The ionosphere acts as a plasma, and inserting appropriate values into Equation 1 shows the plasma frequency to be in the MHz range—hence the importance of the ionosphere as a reflector for long wavelength radio communications. Carrying out the same calculation for the conduction electrons that form the plasma in silver yields a frequency in the UV; consequently, metals reflect light in the visible, thereby explaining their historical use as mirrors. Some forms of carbon also have high enough charge carrier densities to produce plasmons in the UV.[19] In general, the relative permittivity of a material is a complex quantity with an imaginary component that accounts for the dissipative processes the charge carriers suffer during their motion within the material. Thus far we have ignored this dissipation, but it is easily included within the concept of a plasma by introducing a damping term in addition to the plasma frequency. This results in the Drude model, where the frequency dependent relative permittivity of the metal, $\varepsilon_{\mathrm{m}}(\omega)$, is given by[20]

$$\varepsilon_m = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \tag{2}$$

where γ is the relaxation frequency associated with the metal (it is the inverse of the characteristic time interval between scattering events that dampen the motion of the conduction electrons). The frequency regime of interest occurs when the relative permittivity of the metal is negative because, as we will see below, this allows resonances to be set up. Bulk plasmons can not be excited by light owing to the longitudinal nature of the oscillating charges in the plasmon and the transverse nature of the electric field of light—an alternative tech-

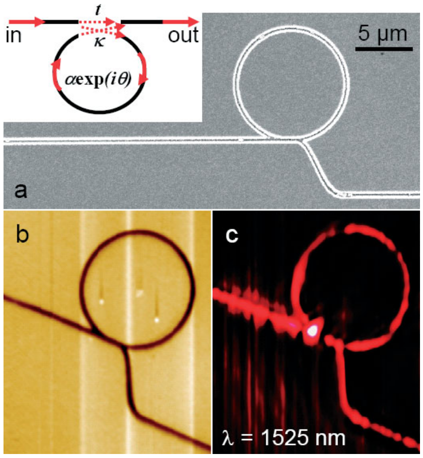

Figure 3. Grooves cut into metal using Focussed Ion Beam (FIB) milling (detail in inset lower left) can be used to make channel plasmon-polariton waveguides, here in the form of a ring resonator. a) Shows an SEM image, b) an AFM image, and c) a near-field scanning optical image of the ring resonator. The operating wavelength is ~1.5 µm. Reproduced with permission from [4] Copyright 2006 Macmillan Publishers Ltd.

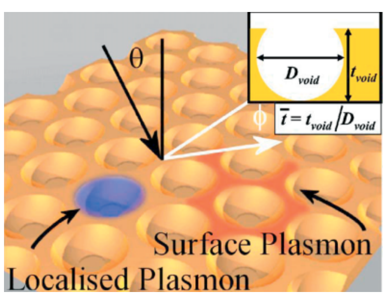

Figure 4. A variant of the Nanosphere lithography technique (Fig. 2) can be used to make structures that support void plasmons and propagating surface plasmon polaritons. Here metal is deposited by electro-deposition so as to fill the interstices in a 3D way. The inset shows a cross section of a void. Reproduced with permission from [130]. Copyright 2006 The American Physical Society.

nique is to excite plasmons by bombarding the metal with electrons,[16] a method that is enjoying a revival as a powerful way to probe the spatial distribution of the electromagnetic fields associated with plasmons.[17] As we will see, structuring the metal changes the nature of the plasmonic response of the metal and can allow light to couple to the associated plasmon mode; structured metals are thus the focus of this article. We begin by looking at perhaps the simplest structure: a metal sphere or particle.

2.1. Particle Plasmons

A particularly interesting optical effect has been known since antiquity, and was studied by Faraday—the strong colors of colloids of small metal particles.[21] The colors exhibited by such particles depend on the material they are made from,

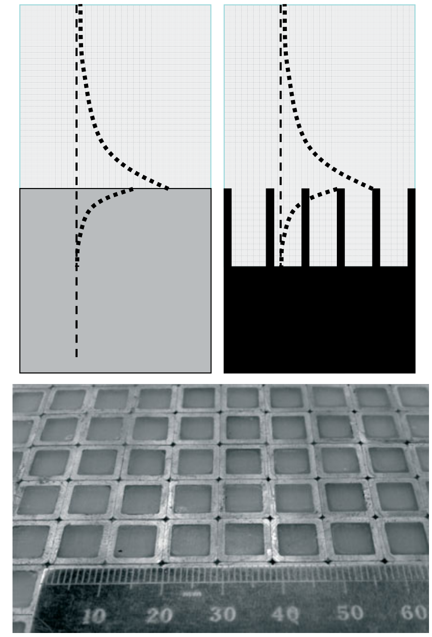

Figure 5. Spoof surface plasmon-polaritons. For real metals the optical field associated with the surface plasmon-polariton penetrates into the metal (top left). For the case of a perfect metal the field is perfectly screened and no surface mode is possible. However, sub-wavelength holes drilled into an otherwise perfect conductor allow the field to penetrate the effective surface, thus enabling a bound surface wave to exist (top right)—the so-called spoof surface plasmon polariton. The experimental demonstration [113] was based in a metal structure punctured by an array of sub-wavelength holes produced by assembling milled sections of square brass tube. The scale is mm.

their surroundings, their size, and their shape, see for example Figure 1. When light is incident on such a particle the oscillating electric field of the light produces a force on the mobile conduction electrons in the metal, the result of which is to induce a dipole moment in the particle. The redistribution of charge acts to provide a restoring force on the displaced electrons and, just as in the bulk plasma case discussed above, there is an associated resonant frequency. When the particle is small compared to the incident wavelength (radius $a \approx 5$ nm or less for visible light) one can use electrostatics to derive a simple analytical formula for the polarizability, α, of the particle[22]

$$\alpha = 4\pi a^3 \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \tag{3}$$

where ε_m is the relative permittivity of the metal and ε_d is the relative permittivity of the surrounding dielectric. The key to understanding the color of different metallic nanoparticles comes from recognizing that the relative permittivity (refractive index) of metals is not a fixed quantity but varies with frequency, or equivalently, with wavelength. The optical response of the particle is strongest when the denominator in Equation 3 is closest to zero. This means that the color of different metallic spheres is dictated by the frequency (wavelength) at which the relative permittivity of the metal satisfies

$\varepsilon_m = -2\varepsilon_d$. We can also see from this resonance condition that the plasmonic response of a metallic particle is sensitive to its local environment, a change in ε_d alters the value of ε_m at which resonance ($\varepsilon_m = -2\varepsilon_d$) occurs. For a typical glass in the visible the refractive index, n, is 1.5, so that the relative permittivity, ε_d, $\varepsilon_d = n^2$ is 2.25. The resonance condition is then satisfied when $\varepsilon_m' = -4.5$. For gold this occurs in the green part of the spectrum, at 520 nm, whilst for silver it occurs in the deep violet (420 nm). The electromagnetic fields associated with such resonances are confined to volumes much smaller than a cubic wavelength, and it is this small mode volume that is a key motivation behind work on particle plasmons, or localized surface plasmon resonances (LSPRs) as they are often known.[6]

For larger particles effects due to the variation in the amplitude and phase of the electromagnetic field across the particle become important (retardation effects). This results in a size dependence of the spectral position of the LSPR—as the particle size increases so the resonant wavelength also increases. Shape is also critical in determining the properties of the LSPR, the spectral position of the resonance again being influenced.[23,24]

2.2. Surface Plasmon-Polaritons

The planar surface of a metal may also support a plasmon mode, this time known as a surface plasmon-polariton (SPP). In contrast to the localized modes associated with particles, the SPP modes associated with a planar interface are extended in nature and may propagate, typically over a few tens of micrometers. This has encouraged research into using SPPs as a means of providing tighter integration of optical signals than is currently achieved using dielectric light-guides.[25] Because SPPs are in general propagating waves, it is instructive to look at their dispersion relation (the relationship between frequency and wavevector (inverse wavelength)) of the mode. This can be found by applying suitable boundary conditions to Maxwell's equations and looking for solutions that take the form of a surface wave.[26] The result is

$$k_{SPP} = k_0\sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} \tag{4}$$

where k_{SPP} is the wavevector of the surface plasmon ($k_{SPP} = 2\pi/\lambda_{SPP}$), k_0 is the free-space wavevector ($k_0 = 2\pi/\lambda_0$), with λ_0 being the wavelength of light in free space and λ_{SPP} being the wavelength of the SPP mode at the same frequency.

There are two points to note here. First, the square root term in Equation 4 is usually positive and greater than one. This means that the wavevector of the SPP mode is greater than that of light of the same frequency. In turn this means that freely propagating light is unable to couple to SPP modes—a wavevector (momentum) matching scheme is needed, such as prism coupling or Bragg scattering. Secondly, whilst the frequency (wavelength) of localized surface plasmon resonances are dictated by a resonance condition, for example Equation 3, surface plasmon-polaritons may exist over a wide frequency range.

In what follows we will look at both localized surface plasmon and surface plasmon-polariton resonances in more detail. Before doing so we mention two application areas by way of example, though there are many others. One potential application for particle plasmon resonances is in photovoltaic solar cells.[27] Here the inclusion of small metallic particles is intended to increase the absorption of incident solar light through excitation of particle plasmon resonances,[28] the spectral response being dominated by interparticle coupling. Another application of plasmon modes is that of biosensing. The SPP modes of planar metal films can be used[29–31] and have already achieved commercial success. LSPR modes may also be used; arrays of metallic nanoparticles produced by nanosphere lithography have been employed to demonstrate sensing of a biomarker for Alzheimer's disease.[32] It is the dependence of the position of the plasmon resonance on the surrounding material that is used.[33] Through the correct choice of chemical binding agents used to functionalize the particle surface, only the desired analyte will be bound to the particle, inducing a shift in the resonance position. Such applications bring into focus an important underlying question: how tightly can the field be concentrated around the particle? Reducing the sampling volume will lead to the ability to sense fewer molecules—there are indications that the field can be confined on length scales of order ca. 10 nm, that is, significantly into the sub-wavelength regime.[34–36]

Let us return now to the plasmon modes that different structures support.

3. Localized Surface Plasmon Resonances

Localized surface plasmon resonances can be supported by a wide variety of structures. Individual particles can take shapes ranging from the simple sphere to ellipsoids, rods,[37] stars,[38] and crescents.[39] New resonances can be achieved with interacting particle pairs,[1,40] whilst aggregation of colloidal particles takes this to an extreme and one can have localized modes associated with specific high-field regions of such random media.[41] One can also invert the geometry and consider the LSPR modes of holes[42] or voids[43] rather than particles. Further, there are also localized modes associated with particles with holes in them, such as toroidal structures.[44,45]

In this section we describe how the frequency at which the localized surface plasmon resonance of a metallic nanoparticle can be tuned from the ultraviolet, throughout the visible, and into the infrared regions of the electromagnetic spectrum, simply by adjusting the particle size and shape. We saw in the previous section that the material from which the particle is made is important in determining the spectral position of the resonance—here we will see that for particles much above 10 nm in size, particle size and shape are even more important in determining the position of the resonance.[23,24]

As the size of the particle increases there is an increase in the amount of absorption and scattering, both of which contribute to the optical extinction of a metallic nanoparticle. Also, as the size increases scattering takes over from absorption as the dominant contribution to the extinction,[46] and there is a change in the position and width of the LSPR. Increasing the size of a sphere from 10 to 90 nm results in a shift of the resonance peak from 400 nm to 800 nm. These changes, as discussed by Kreibig and Vollmer[20] and by Bohren and Huffman,[47] arise from the way in which the polarization field induced by the surface charges is affected by the amplitude and relative phase of the scattered and incident fields. In addition one must consider the dispersion of the optical properties of the constituent material of the nanoparticles—a shift in frequency of the LSPR means that the resonance will also experience a different degree of damping.[37]

Particle shape is important too, and the development of sophisticated methods for the fabrication of nanostructures has allowed optical studies of a wide variety of differently shaped particles to be undertaken. As noted in the Introduction, fabrication methods typically involve either growing the particles within solution or lithographic techniques whereby material is deposited through a patterned mask. The ultimate goal in many studies is to optimize the localization and enhancement of the field associated with the LSPR. Typically this is achieved by designing structures that have an inhomogeneous configuration, such as core/shell particles,[12] or that have sharp geometrical features such as nanoprisms,[6,48] nanocubes,[49] and star-shaped[38] particles. Mock et al.[23] collected spectra from individual particles with a variety of sizes and shapes using dark-field illumination. Shown in Figure 1 are similar data taken from particles fabricated using EBL, illustrating how the size and shape of particles influences the spectrum of the associated LSPR response.

The comparison of experiment and theory is vital in gaining a proper understanding of the optical response of metallic nanostructures. For very small particles that are ellipsoidal in shape, analytical methods predict a maximum of three dipolar resonances to exist, one associated with each of the three principal axes. In particular rod-shaped[50] and disc-shaped[51] particles have been extensively studied. In both theory and experiment the resonance associated with the major axis is red-shifted and that associated with the minor axis is blue-shifted relative to the resonance of a spherical particle. Within the small particle limit the position of the LSPR associated with a particular material depends mainly on the aspect ratio of the particle. For larger particles retardation-induced spectral shifts occur that can be accounted for by using a radiative damping correction.[52] An alternative method that allows the accurate modeling of the near-field properties of nanoscale objects is the Green dyadic approach.[53] This represents an object as a discretized perturbation of the surface upon which it is supported. Krenn et al. used this technique to successfully reproduce electromagnetic field profile characteristics obtained from photon scanning tunneling microscopy measurements on chains of particles.[54]

Theoretical predictions of the optical response of more complex shapes are complicated owing to the requirement that the geometry of the particle be represented within a convenient coordinate system. Therefore, numerical techniques are often needed to generate a suitable model of the particle response to an incident electromagnetic (EM) field, for example the discrete dipole approximation (DDA),[24] finite difference time domain (FDTD) and finite element simulations,[55,56] and modal expansion techniques.[57]

One can go beyond simply modifying the shape by modifying the topology of the particle. Ring-shaped (toroidal) structures may exhibit symmetric and antisymmetric modes akin to the coupled SPP modes that exist upon continuous thin metal films.[44,45] Further adjustment of the LSPR resonance may be achieved by fabricating particles that consist of a dielectric shell surrounded by a gold shell. These have been shown to produce tuneable resonances throughout the visible spectrum.[58] Other types of particle have been investigated including nonspherical core/shell structures,[59] nanocages,[60] and nanocrescents.[39] Some have been shown to exhibit very sharp resonances, for example the star-shaped[38] and cube-shaped[49] particles.

So far we have concentrated on the dipolar-type resonance, principally because this has been the focus of most of the research into the plasmonic properties of metallic nanoparticles. However, this is not the only resonance that can be excited since multipolar (e.g., quadrupole, octupole) resonances may also contribute significantly to the spectra obtained in optical measurements. Multipolar resonances have most commonly been observed with spherical particles,[20] however more recently other types of structure have been studied, such as rods[61] and spherical core–shell particles.[62,63] A particular motivation for the study of multipolar resonances are the differing field distributions compared to a dipolar resonance and the multiple frequencies at which the resonances occur.[64] Modes more akin to propagating surface plasmon-polariton modes may also be generated in nanowires with a length of few tens of micrometers.[65] Through a Fabry–Perot type effect, resonant modes with a wavelength considerably shorter than the free space wavelength are set up and, owing to their nonradiative nature, exhibit propagation lengths of ca. 10 μm. Interestingly, the quality of the crystalline structure of the wire was found to have a profound effect on the Q-factor of the resonance.[65] Single-crystal wires were observed to have sharper and more pronounced resonances compared to polycrystalline wires.

To further expand the range of available LSPR modes it is possible to allow an interaction between two or more particles separated by very small distances, typically within the decay length of the electromagnetic field associated with the mode. Coupling between LSPR modes can lead to a hybridization effect, producing high and low energy modes with differing

EM field distributions. For particle pairs these may be selected by altering the polarization state of the incident electric field between one oriented parallel to the interparticle axis and one oriented perpendicular to the interparticle axis.[40] The primary motivation for studying particle pairs is that strong EM field enhancements are expected to exist within the gap between the particles.[66] This has been shown theoretically for spherical particles with a view to explaining the surface enhanced Raman scattering (SERS) enhancement obtained in colloidal solutions. Aggregation of spheres is thought to generate "hot-spots" owing to the collective response,[41] indeed, the interaction between the plasmon modes of neighboring particles can lead to new hybridized plasmon modes.[12] In general, when aggregation occurs in colloidal solutions fractal structures are produced, consisting of random networks of connected nanoparticles. Such aggregates have been used in the pursuit of single-molecule SERS experiments.[67,68] Theoretical studies of closely packed aggregates of spheres have indicated the existence of electromagnetic resonances over a very broad spectral range, in contrast to the (typically) narrow range associated with colloidal metallic nanoparticles.[69] A related type of structure is that of nanometer-scale metallic islands that form as the result of interesting nucleation kinetics when one tries to fabricate thin (typically less than 10 nm) metal films by evaporation under vacuum.[70] Such island films tend to show broad plasmon resonances owing to the inhomogeneous distribution of island sizes and spacings.

We have seen how important particle interactions are when particles are separated by very small distances. Other effects may be observed when particles are arranged in a periodic lattice with a periodicity such that radiative (far-field) coupling can occur. In experimental studies the lattice spacing in arrays consisting of identical particles was found to influence the position of the LSPR.[71,72] Furthermore, the presence of diffracted orders has been predicted to cause a change in the extinction of nanoparticle arrays.[73–75] Other effects are observed when it is possible for coupling to occur between a LSPR and a propagating electromagnetic mode, this discussed in more detail in Section 5.

There are some fascinating materials questions here. By way of example: to what extent is the response of a particle plasmon dictated by the fabrication technique used to make the metal? How do different particle shapes alter the relative contributions of radiative and nonradiative decay and thus the Q-factor of the associated resonance.[37] An interesting materials question to ask is what is the smallest feature size that it makes sense to consider, for example, are atomic dimensions important. Very recently a wire of gold atoms only one atom thick has been investigated, and has been shown to support 1D plasmons.[76] This result implies that features at the atomic scale will be important in controlling plasmons, and that a full understanding of plasmonics will need to include the inherently quantum mechanical nature of electrons, such as electron correlation effects.

4. Propagating Plasmons

As we have seen above, surface plasmon modes may be localized in space by appropriately nanostructuring a metal, with fields localized down to nanometer length scales. In contrast, planar surfaces allow SPPs to propagate over distances determined by absorption in the metal and, perhaps surprisingly, by geometry. In the visible/near-IR regime this may lead to propagation over micrometer to centimeter length scales through appropriate choices of geometry and fabrication technique.[77]

Given the low loss at optical frequencies of silver, this is the metal predominantly used in surface plasmon waveguiding studies, though gold can also give good results towards the infra-red. The propagation length of a surface plasmon-polariton on a planar metal surface, δ_{SPP}, is given by[78]

$$\delta_{SPP} = \lambda_o \frac{(\varepsilon'_m)^2}{2\pi\varepsilon''_m}\left(\frac{\varepsilon'_m + \varepsilon_d}{\varepsilon'_m \varepsilon_d}\right)^{\frac{3}{2}} \quad (5)$$

where $\varepsilon_m' + i\varepsilon_m''$ is the complex relative permittivity of the metal, ε_d the relative permittivity of the overlying dielectric, and λ_0 the free-space wavelength. From Equation 5 we see that for a long propagation length we require a large (negative) real part of the relative permittivity of the metal, ε_m', and a small imaginary part, ε_m'', that is, we need a low loss metal, as one would expect.

4.1. Photonics Based on Surface Plasmons

For silver in the red part of the spectrum (630 nm) $\varepsilon_m = -18 + i$ and Equation 5 gives a propagation length of ca. 50 µm, in accord with experiment.[79] This is much shorter than the propagation length for dielectric waveguides, however, in plasmonics one is not trying to compete with dielectric waveguides. Rather we are interested in working on the nanoscale, and these propagation lengths indicate the viability of linking plasmonic elements together. It is natural to consider using metal stripes or wires as guides for surface plasmon-polaritons.[80] As the width of the stripe is reduced the propagation length falls, primarily owing to increased scattering at the lateral edges of the stripe.[79] An elegant way to increase propagation lengths is to make use of the coupled plasmon-polariton mode of symmetrically clad metal stripes. There are two such coupled modes, one of which has optical fields that are somewhat excluded from the metal in comparison to the single interface SPP. Using such structures Berini and coworkers have demonstrated propagation lengths of up to 1 cm at a wavelength of 1.5 µm.[77]

A number of alternative configurations have been explored for guiding SPPs. More recently the use of a channel in a metal surface to guide SPPs has been investigated,[81] an approach that has been demonstrated to allow integration of plasmonic components.[4] Rather than pattern the metal it is possible to add a patterned dielectric overlayer, the overlayer defining the guide.[82] An intriguing variant of the stripe guide is to confine the propagation of SPPs using a photonic bandgap approach. Here a planar surface has wavelength scale periodic texture imposed in the regions where propagation is to be blocked.[83] Finally we might also mention the use of particle chains as waveguides for plasmons. Although guiding using such structures has been demonstrated,[84,85] propagation lengths are currently low, of order 1 µm. However, if this is either sufficient, or can be extended, there are interesting prospects since numerical simulations show that coherent control of the incident light used to launch the plasmons may allow one to direct the flow of energy, switching for example between the different arms of a T junction.[86] Very recently this prospect has come much closer with the demonstration of control of plasmon excitation using adaptive shaping of the phase and amplitude of the femtosecond laser pulses used to excite resonances of particle-based structures.[87]

4.2. Surface Plasmon-Polaritons and Periodic Structures

Even though not recognized at the time, the first recorded observation of a phenomenon associated with surface plasmon-polaritons on an extended surface was made by Wood over a century ago[88] and concerned a periodically modulated metal surface, a diffraction grating. As noted in Section 2.2, surface plasmon-polaritons on a planar metal surface have more momentum than a photon of the same frequency. For this reason it is not possible for light to couple directly to surface plasmon-polaritons; some kind of momentum matching scheme is required, such as Bragg scattering from a periodically modulated surface—for example a diffraction grating. Periodic modulation of the surface can do more than simply allow coupling between SPPs and light, it can also modify the propagation of SPPs, even producing a bandgap for such modes.[89] A particularly fascinating phenomenon occurs when the grooves of the grating are deep enough to support localized surface plasmon resonances, this will be discussed in Section 5.2.

Ebbesen et al.[3] made spectacular use of another periodic structure, a metal film perforated by a periodic array of subwavelength holes. Such a film would normally be expected to show very weak transmission of light because i) it was 200 nm thick (a silver film this thick is optically opaque to visible light) and ii) the hole size used (150 nm) is below the diffraction limit of light. Remarkably, in 1998 they reported that under appropriate conditions such structures can transmit a significant amount of light—a phenomenon that has become known as the extraordinary transmission of light through metallic hole arrays. This work spurred much of the recent activity in plasmonics. The role of surface plasmons in this enhanced transmission is now well established,[90] and the importance of the surface modulation clear—holes are not essential, appropriate surface corrugations may also enhance the transmittance,[91] though holes are more effective. The use of hole arrays has been extended to other spectral regions, one example being their use in IR spectroscopy.[92] The holes may also support modes,[42,93] thereby making the exploitation of hole arrays and the interpretation of phenomena associated with them much richer, there being the possibility of having localized and extended plasmons present at the same time. A more extended discussion of such localized/propagating plasmon systems follows.

5. Localized/Propagating Systems

What about making structures that simultaneously support localized and propagating modes? We have seen that the electromagnetic field associated with the localized surface plasmon mode is strongly confined to a very small region near to the particle surface. However the interaction between light and the LSPR mode of a particle is in general only a weak function of the angle of the light with respect to the particle. In contrast the SPP mode of a planar film may have a very specific and sharp dependence on angle if some kind of appropriate wavelength-scale periodicity is built into the structure. One can therefore consider structures that support both types of modes simultaneously and thus allow high field enhancements and good directional control.

One example of such a mixed system is a structure consisting of voids within an otherwise continuous metallic film, the voids may support LSPR modes similar to those supported by isolated particles. In a recent study a periodic arrangement of voids was fabricated using a close-packed array of nanospheres as a template,[94] such structures are being explored as substrates for SERS, as are metal films that coat ordered monolayers of sub-micrometer polystyrene films.[95]

5.1. Particles and Films

Coupling between the LSPR mode of a particle or array of particles and the SPP mode of a planar metal film is another interesting mixed localized/propagating system.[96] Martin and colleagues have looked at the enhancement of the optical field associated with individual particles separated by 1–100 nm from a planar metal film and predict electric field enhancement factors as high as 5000 for a separation of 5 nm.[97] In an experimental study, multiple resonance peaks have been observed in reflectance spectra obtained from an array of gold nanoparticles spaced a small distance from a planar gold film. By modeling the optical response of the structure these resonances were identified as resulting from a coupling between the SPP and LSPR.[98] Interactions with waveguide modes within a dielectric cavity also offer some intriguing properties. A suppression of LSPR resonances associated with a square lattice of cylindrical gold particles has been shown to be due to the presence of diffractively coupled waveguide modes.[99] In another study, Maier et al. found that designing a periodic arrangement of nanoparticles upon an optically thin silicon waveguide allowed the transfer of power from an optical fiber into the waveguide with up to 75 % efficiency at telecom wavelengths.[100]

5.2. Slit-Groove Modes

Rather than adding particles to a planar film one can instead consider taking a weakly modulated film, for example one having a modestly corrugated surface (in the form of a diffraction grating), and making the modulation sufficiently deep enough that individual grooves may support localized modes. One way to view what happens is as follows. In a deep groove there are two metal surfaces that face each other. When these surfaces are close enough together the fields associated with the modes overlap and interact: a coupled mode is produced. If the depth of the groove is such as to sustain a standing wave for the coupled mode, then the mode may be localized to the groove. As the groove is made deeper still, higher-order localized modes may be supported.[101] Gaps as narrow as 3 nm have been investigated[102]—the modes supported by such structures are closely related to those associated with the gap between two closely spaced metallic particles,[66] and those associated with the gap between a particle and a plane.[97]

6. Plasmonic Metamaterials

Whilst the structures discussed above rely on there being an interface between a metal and a dielectric, the qualitative features (e.g., resonances) are in general determined by the properties of the metal alone, particularly its plasma frequency. However, a material made from two or more component materials may have properties that neither of the component materials have on their own, the properties depending fundamentally on the geometry of the chosen structure; such materials are known as metamaterials—a concept that seems ideally suited to plasmonics. Early work in this area showed how a network of metallic wires could be used to produce artificial materials with much lower plasma frequencies than those of the metals from which they were fabricated, the plasma frequency depending instead almost entirely on geometry.[103] One of the most surprising applications has been the prediction[104] and demonstration[105] of materials with negative permeability, materials that can turn Snell's law on its head. At visible and infrared frequencies most materials are not magnetically active. However, if structures can be introduced that exhibit a magnetic resonance at these frequencies, then a negative permeability is possible, provided the resonance is strong enough. If this negative permeability (μ) can be combined with a negative permittivity (ε) then a negative refractive index is possible—hence the reversal of the usual Snell's law for refraction. Just this combination of properties was achieved by Shelby et al.[105] who made arrays of split-ring resonators (to provide a magnetic resonance) and demonstrated negative refractive index in the microwave regime—the repeat unit being smaller than half the resonant wavelength so as to avoid diffraction.

How far towards the visible can this approach be pursued? It works well at microwave frequencies because of the low absorption of metals at such low frequencies. As the frequency is increased absorption becomes more important, so that generating artificial resonances with structures such as split-ring resonators becomes harder. Are there other shapes that might prove better than split-ring resonators? Recently Zhou et al. proposed and demonstrated H-shaped resonators in the microwave regime.[106] A pair of rods can also offer a resonance, the conducting path of the rods being completed into a circuit by the capacitance between the ends of the rods.[1,107] Chiral structures are another, as-yet untested possibility,[108] whilst metallic cavity structures can offer negative index properties for some types of plasmon.[109] Recently, using gold double posts[1] and cut-wire structures,[110,111] magnetic resonances as well as a negative refractive index have been found in the visible spectral range.

One of the most intriguing developments as far as plasmonics is concerned is that of designer or spoof plasmons. At microwave frequencies electromagnetic fields penetrate only a very small fraction of their associated wavelength into the metal. A consequence of this weak field penetration into the metal is the very poor confinement of the field by the interface—the mode is a grazing photon rather than a plasmon. However, by perforating the surface with an array of sub-wavelength holes it is possible to produce a layer on the surface that effectively allows the field to penetrate, via the evanescent fields associated with the *below cut-off* modes of the holes. This theoretical prediction[112] was recently confirmed experimentally by Hibbins et al., see Figure 5.[113] There are many other interesting developments, in what follows we briefly discuss two: first lensing, and second THz plasmonics

Resolution in optical imaging systems is limited by the diffraction limit, a limit that arises because the near-field/evanescent components of the optical field that are needed to resolve sub-wavelength spatial information are not collected by the usual lens/mirror systems of optics. Pendry[104] revived an idea due to Veselago[114] (and hinted at by Schuster more than a century ago[115]). The idea is to use the surface plasmons of a thin planar layer of metal to 'carry' the evanescent components from source to image, thereby allowing better than diffraction limited resolution. This has recently been demonstrated by Fang et al.[116] The limiting factor in such systems is the absorption in the metal film[117] so again, as with other topics discussed above, work on reducing these losses is much needed.

Interest in the field of plasmonics has recently been extended into the THz frequency regime. Due to a lack of efficient emitters and detectors, the THz frequency region (~ 0.1–30 THz, 1 THz is equivalent to a wavelength of 300 μm) has historically been the least explored region of the electromagnetic spectrum. However, recent advances in laser based THz sources[118] have lead to an explosion of interest in the THz frequency regime, as many important processes in nature occur at THz frequencies. For example, high frequency molecular rotations and low frequency vibrations can occur in the THz frequency region, making THz light a valuable tool for investigating biological processes and samples.[119] In the solid-state, phonon frequencies and charge scattering rates lie in the THz range, and THz spectroscopy has proven invaluable for investigating important processes such as charge transport.[120] The new field of THz plasmonics concentrates on the possibilities for confining THz light to surfaces for applications in sensing[121,122] and high frequency signal processing. From Equation 1 it can be seen that a plasma frequency of around 1 THz corresponds to a plasma density ~10^{21}–10^{22} m^{-3}. Such densities are easily achievable by chemically doping semiconductors, and propagation of THz plasmons on doped silicon surfaces has recently been demonstrated.[123] Furthermore, semiconductors offer the new and exciting possibility of optical plasmon control: photo-excitation with photons of energy larger than the semiconductor bandgap should modify the conductivity by orders of magnitude. In this way, the properties of plasmon modes on a semiconductor surface can be modified and switched by a visible light source such as a laser.[124] Ultra-short (sub-picosecond) laser pulses offer the exciting possibility of fast photo-switching, with switching times essentially determined by laser pulse width. Furthermore the existence of high quality materials and processing capabilities for semiconductors already exists; this is an area in which we can expect to see fascinating developments.

We have focused in this review on the plasmon modes of various metallic structures. We would also like to mention that one can obtain an even richer range of optical behavior by considering metallic nanostructures that exploit the properties of adjacent molecules. As examples we mention that SPP modes can be hybridized with excitons,[125,126] that the LSPR modes of particle plasmons can be manipulated through excitation of nearby molecule resonances[127] and optical switching demonstrated.[128] These new developments point towards the much greater degree of functionality that we can expect to see as we understand the interaction between the plasmon modes of metallic nanostructures and adjacent molecules

7. Conclusions and Perspective

Plasmonics has taken off as a research topic in recent years, despite having an already lengthy history. Developments in materials have played an important part in this renewed interest, as we have tried to describe above. We expect that there will be many further developments as we are able to control better and understand more about the materials involved. Material length scales of interest range from the atomic up to many centimeters, and it is only through a full exploration over this entire range that the true potential of plasmonics will emerge.

For many outside the field there was, and perhaps to some extent remains, considerable skepticism over the value of plasmonics: metals exhibit absorption—so why should they be appealing for photonics when many low-loss alternatives are well established? The two key features that plasmonics brings to photonics are a way to concentrate light into sub-wavelength volumes and a means by which to achieve significant optical field enhancements. The latter enables the enhancement of many surface phenomena, e.g., nonlinear effects (something we have not covered here, but see for example[129]), biosensing,[32,33] plasmon-molecule coupling, whilst the former offer the prospect of controlling light on the sub-wavelength scale. As we have tried to show through the examples we have discussed, despite the loss, there is more than sufficient potential to control and manipulate light using surface plasmons. Thus plasmonics seeks not to compete with other photonics technologies, but rather to provide a complementary approach, one that offers new potential. As we develop a deeper understanding and are able to exert greater control over fabrication that potential can only be extended.

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[1] A. N. Grigorenko, A. K. Geim, H. F. Gleeson, Y. Zhang, A. A. Firsov, I. Y. Khrushchev, J. Petrovic, *Nature* **2005**, *438*, 335.
[2] H. Ditlbacher, J. R. Krenn, G. Schider, A. Leitner, F. R. Aussenegg, *Appl. Phys. Lett.* **2002**, *81*, 1762.
[3] T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio, P. A. Wolff, *Nature* **1998**, *391*, 667.
[4] S. I. Bozhevolnyi, V. S. Volkov, E. Devaux, J.-Y. Laluet, T. W. Ebbesen, *Nature* **2006**, *440*, 508.
[5] A. Sundaramurthy, P. J. Schuck, N. R. Conley, D. P. Fromm, G. S. Kino, W. E. Moerner, *Nano Lett.* **2006**, *6*, 355.
[6] T. R. Jensen, M. D. Malinsky, C. L. Haynes, R. P. Van Duyne, *J. Phys. Chem. B* **2000**, *104*, 10 549.
[7] S. M. Weekes, F. Y. Ogrin, W. A. Murray, P. S. Keatley, *Langmuir* **2007**, *23*, 1057.
[8] A. W. Murray, S. Astilean, W. L. Barnes, *Phys. Rev. B* **2004**, *69*, 165 407.
[9] Y. Xiong, J. M. McLellan, J. Chen, Y. Yin, Z.-Y. Li, Y. Xia, *J. Am. Chem. Soc.* **2005**, *127*, 17 118.
[10] M. S. Sander, L.-S. Tan, *Adv. Funct. Mater.* **2003**, *13*, 393.
[11] P. N. Bartlett, J. J. Baumberg, P. R. Birkin, M. A. Ghanem, M. C. Netti, *Chem. Mater.* **2002**, *14*, 2199.
[12] E. Prodan, C. Radloff, N. J. Halas, P. Nordlander, *Science* **2003**, *302*, 419.
[13] S. Link, M. A. El-Sayed, *Int. Rev. Phys. Chem.* **2000**, *19*, 409.
[14] J. Boleininger, A. Kurz, V. Reuss, C. Sönnichsen, *Phys. Chem. Chem. Phys.* **2006**, *8*, 3824.
[15] A. Graff, D. Wagner, H. Ditlbacher, U. Kreibig, *Eur. Phys. J. D* **2005**, *34*, 263.
[16] C. J. Powell, J. B. Swan, *Phys. Rev.* **1959**, *115*, 869.
[17] N. Yamamoto, K. Araya, F. J. García de Abajo, *Phys. Rev. B* **2001**, *64*, 205 419.
[18] C. Kittel, *Introduction to Solid State Physics*, Wiley, New York **1986**.
[19] L. A. Bursill, P. A. Stadelmann, J. L. Peng, S. Prawer, *Phys. Rev. B* **1994**, *49*, 2882.
[20] U. Kreibig, M. Vollmer, *Optical Properties of Metal Clusters*, Vol. 25, Springer, Berlin **1995**.
[21] M. Faraday, *Philos. Trans. R. Soc. London* **1857**, *147*, 145.
[22] C. F. Bohren, D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, Wiley, New York **1983**.

[23] J. J. Mock, M. Barbic, D. A. Schultz, S. Schultz, *J. Chem. Phys.* **2002**, *116*, 6755.
[24] K. L. Kelly, E. Coronado, L. L. Zhao, G. C. Schatz, *J. Phys. Chem. B* **2003**, *107*, 668.
[25] R. Charbonneau, N. Lahoud, G. Mattiussi, P. Berini, *Opt. Express* **2005**, *13*, 977.
[26] H. Raether, *Surface Plasmons*, Vol. 111, Springer, Berlin **1988**.
[27] M. Westphalen, U. Kreibig, J. Rostalski, H. Luth, D. Meissner, *Sol. Energy Mater. Sol. Cells* **2000**, *61*, 97.
[28] B. P. Rand, P. Peumans, S. R. Forrest, *J. Appl. Phys.* **2004**, *96*, 7519.
[29] I. Lundstrom, *Biosens. Bioelectron.* **1994**, *9*, 725.
[30] I. R. Hooper, J. R. Sambles, *J. Appl. Phys.* **2004**, *96*, 3004.
[31] D. G. Myszka, R. L. Rich, *PSTT* **2000**, *3*, 310.
[32] A. J. Haes, L. Chang, W. L. Klein, R. P. Van Duyne, *J. Am. Chem. Soc.* **2005**, *127*, 2264.
[33] G. Raschke, S. Kowarik, T. Franzl, C. Sonnichsen, T. A. Klar, J. Feldmann, *Nano Lett.* **2003**, *3*, 935.
[34] J. P. Kottmann, O. J. F. Martin, D. R. Smith, S. Schultz, *Phys. Rev. B* **2001**, *64*, 235 402.
[35] A. W. Murray, J. R. Suckling, W. L. Barnes, *Nano Lett.* **2006**, *6*, 1772.
[36] H. Liao, C. L. Nehl, J. H. Hafner, *Nanomedicine* **2006**, *1*, 201.
[37] C. Sönnichsen, T. Franzl, T. Wilk, G. von Plessen, J. Feldmann, *Phys. Rev. Lett.* **2002**, *88*, 077 402.
[38] C. L. Nehl, H. Liao, J. H. Hafner, *Nano Lett.* **2006**, *6*, 683.
[39] J. S. Shumaker-Parry, H. Rochholz, M. Kreiter, *Adv. Mater.* **2005**, *17*, 2131.
[40] W. Rechberger, A. Hohenau, A. Leitner, J. R. Krenn, B. Lamprecht, F. R. Aussenegg, *Opt. Commun.* **2003**, *220*, 137.
[41] V. M. Shalaev, R. Botet, R. Jullien, *Phys. Rev. B* **1991**, *44*, 12 216.
[42] A. Degiron, T. W. Ebbesen, *J. Opt. A* **2005**, *7*, S90.
[43] S. Coyle, M. C. Netti, J. J. Baumberg, M. A. Ghanem, P. R. Birkin, P. N. Bartlett, D. M. Whittaker, *Phys. Rev. Lett.* **2001**, *87*, 176 801.
[44] J. Aizpurua, P. Hanarp, D. S. Sutherland, M. Käll, G. W. Bryant, F. J. García de Abajo, *Phys. Rev. Lett.* **2003**, *90*, 057 941.
[45] A. Mary, A. Dereux, T. L. Ferrell, *Phys. Rev. B* **2005**, *72*, 155 426.
[46] V. Jacobsen, P. Stoller, C. Brunner, V. Vogel, V. Sandoghdar, *Opt. Express* **2006**, *14*, 405.
[47] C. Bohren, D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, Wiley, Hoboken, NJ **1998**.
[48] J. C. Hulteen, R. P. Van Duyne, *J. Vac. Sci. Technol. A* **1995**, *13*, 1553.
[49] L. J. Sherry, S.-H. Chang, G. C. Schatz, R. P. Van Duyne, *Nano Lett.* **2005**, *5*, 2034.
[50] S. Link, M. A. El-Sayed, *J. Phys. Chem. B* **1999**, *103*, 8410.
[51] L. Gunnarson, T. Rindzevicius, J. Prikulis, B. Kasemo, M. Käll, S. Zou, G. C. Schatz, *J. Phys. Chem. B* **2005**, *109*.
[52] A. Wokaun, J. P. Gordon, P. F. Liao, *Phys. Rev. Lett.* **1982**, *48*, 957.
[53] C. Girard, A. Dereux, *Rep. Prog. Phys.* **1996**, *59*, 657.
[54] J. R. Krenn, A. Dereux, J. C. Weeber, E. Bourillot, Y. Lacroute, J. P. Goudonnet, G. Schider, W. Gotschy, A. Leitner, F. R. Aussenegg, G. Girard, *Phys. Rev. Lett.* **1999**, *82*, 2590.
[55] M. Futamata, Y. Maruyama, M. Ishikawa, *J. Phys. Chem. B* **2003**, *107*, 7607.
[56] T. Grosges, A. Vial, D. Barchiesi, *Opt. Express* **2005**, *13*, 8483.
[57] J. Bravo-Abad, F. J. García-Vidal, L. Martín-Moreno, *Phys. Rev. Lett.* **2004**, *93*, 227 401.
[58] S. J. Oldenberg, R. D. Averitt, S. L. Westcott, N. J. Halas, *Chem. Phys. Lett.* **1998**, *288*, 243.
[59] H. Wang, D. W. Brandl, F. Le, P. Nordlander, N. J. Halas, *Nano Lett.* **2006**, *6*, 827.
[60] J. Chen, B. Wiley, Z. Y. Li, D. Campbell, F. Saeki, H. Cang, L. Au, J. Lee, X. Li, Y. Xia, *Adv. Mater.* **2005**, *17*, 2255.
[61] J. R. Krenn, G. Schider, W. Rechberger, B. Lamprecht, A. Leitner, F. R. Aussenegg, *Appl. Phys. Lett.* **2000**, *77*, 3379.
[62] S. J. Oldenburg, J. B. Jackson, S. L. Westcott, N. J. Halas, *Appl. Phys. Lett.* **1999**, *75*, 2897.
[63] S. J. Oldenburg, G. D. Hale, J. B. Jackson, N. J. Halas, *Appl. Phys. Lett.* **1999**, *75*, 1063.
[64] A. Hohenau, J. R. Krenn, G. Schider, H. Ditlbacher, A. Leitner, F. R. Aussenegg, W. L. Schaich, *Europhys. Lett.* **2005**, *69*, 538.
[65] H. Ditlbacher, A. Hohenau, D. Wagner, U. Kreibig, M. Rogers, F. Hofer, F. R. Aussenegg, J. R. Krenn, *Phys. Rev. Lett.* **2005**, *95*, 257 403.
[66] F. J. García-Vidal, J. B. Pendry, *Phys. Rev. Lett.* **1996**, *77*, 1163.
[67] K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. Dasari, M. S. Feld, *Phys. Rev. Lett.* **1997**, *78*, 1667.
[68] S. M. Nie, S. R. Emery, *Science* **1997**, *275*, 1102.
[69] V. A. Markel, V. M. Shalaev, E. B. Stechel, W. Kim, R. L. Armstrong, *Phys. Rev. B* **1996**, *53*, 2425.
[70] R. Doremus, *Thin Solid Films* **1998**, *326*, 205.
[71] C. L. Haynes, A. D. McFarland, L. Zhao, R. P. Van Duyne, G. C. Schatz, L. Gunnarson, J. Prikulis, M. Kall, *J. Phys. Chem. B* **2003**, *107*, 7337.
[72] B. Lamprecht, G. Schider, R. T. Lechner, H. Ditbacher, J. R. Krenn, A. Leitner, F. R. Aussenegg, *Phys. Rev. Lett.* **2000**, *84*, 4721.
[73] K. T. Carron, W. Fluhr, M. Meier, A. Wokaun, H. W. Lehmann, *J. Opt. Soc. Am. B* **1986**, *3*, 430.
[74] E. M. Hicks, S. Zou, G. C. Schatz, K. G. Spears, R. P. Van Duyne, L. Gunnarson, T. Rindzevicius, B. Kasemo, M. Kall, *Nano Lett.* **2005**, *5*, 1065.
[75] S. Zou, N. Janel, G. C. Schatz, *J. Chem. Phys.* **2004**, *120*, 10 871.
[76] T. Nagao, S. Yaginuma, T. Inaoka, T. Sakurai, *Phys. Rev. Lett.* **2006**, *97*, 116 802.
[77] P. Berini, R. Charbonneau, N. Lahoud, G. Mattiussi, *J. Appl. Phys.* **2005**, *98*, 043 109.
[78] W. L. Barnes, *J. Opt. A* **2006**, *8*, S87.
[79] B. Lamprecht, J. R. Krenn, G. Schider, H. Ditlbacher, M. Salerno, N. Félidj, A. Leitner, F. R. Aussenegg, J. C. Weeber, *Appl. Phys. Lett.* **2001**, *79*, 51.
[80] J. R. Krenn, J.-C. Weeber, *Philos. Trans. R. Soc. London Ser. A* **2004**, *326*, 739.
[81] S. I. Bozhevolnyi, V. S. Volkov, E. Devaux, T. W. Ebbesen, *Phys. Rev. Lett.* **2005**, *95*, 046 802.
[82] B. Steinberger, A. Hohenau, H. Ditlbacher, A. L. Stepanov, A. Drezet, F. R. Aussenegg, A. Leitner, J. R. Krenn, *Appl. Phys. Lett.* **2006**, *88*, 094 104.
[83] S. I. Bozhevolnyi, J. Erland, K. Leosson, P. M. W. Skovgaard, J. M. Hvam, *Phys. Rev. Lett.* **2001**, *86*, 3008.
[84] M. Quinten, A. Leitner, J. R. Krenn, F. R. Aussenegg, *Opt. Lett.* **1998**, *23*, 1331.
[85] S. A. Maier, P. G. Kik, H. A. Atwater, S. Meltzer, E. Harel, B. E. Koel, A. A. G. Requicha, *Nat. Mater.* **2003**, *2*, 229.
[86] M. Sukharev, T. Seideman, *Nano Lett.* **2006**, *6*, 715.
[87] M. Aeschlimann, M. Bauer, D. Bayer, T. Brixner, F. J. Garcia de Abajo, W. Pfeiffer, M. Rohmer, C. Spindler, F. Steeb, *Nature* **2007**, *446*, 301.
[88] R. W. Wood, *Philos. Mag.* **1902**, *4*, 396.
[89] S. C. Kitson, W. L. Barnes, J. R. Sambles, *Phys. Rev. Lett.* **1996**, *77*, 2670.
[90] W. L. Barnes, A. W. Murray, J. Dintinger, E. Devaux, H. J. Lezec, T. W. Ebbesen, *Phys. Rev. Lett.* **2004**, *92*, 107 401.
[91] N. Bonod, S. Enoch, L. Li, E. Popov, M. Nevière, *Opt. Express* **2003**, *11*, 482.
[92] K. R. Rodriguez, S. Shah, S. M. Williams, S. Teeters-Kennedy, J. V. Coe, *J. Chem. Phys.* **2004**, *121*, 8671.
[93] C. Genet, T. W. Ebbesen, *Nature* **2007**, *445*, 39.
[94] S. Cintra, M. E. Abdelsalam, P. N. Bartlett, J. J. Baumberg, T. A. Kelf, Y. Sugawara, A. E. Russell, *Faraday Discuss.* **2006**, *132*, 191.

[95] X. Zhang, J. Zhao, A. V. Whitney, J. W. Elam, R. P. Van Duyne, *J. Am. Chem. Soc.* **2006**, *128*, 10 304.
[96] F. Le, N. Z. Lwin, J. M. Steele, M. Käll, N. J. Halas, P. Nordlander, *Nano Lett.* **2005**, *5*, 2009.
[97] G. Lévêque, O. J. F. Martin, *Opt. Express* **2006**, *14*, 9971.
[98] J. Cesario, R. Quidant, G. Badenes, S. Enoch, *Opt. Lett.* **2005**, *30*, 3404.
[99] S. Linden, J. Kuhl, H. Giessen, *Phys. Rev. Lett.* **2001**, *86*, 4688.
[100] S. A. Maier, M. D. Friedman, P. E. Barclay, O. Painter, *Appl. Phys. Lett.* **2005**, *86*, 071 103.
[101] I. R. Hooper, J. R. Sambles, *Phys. Rev. B* **2002**, *66*, 205 408.
[102] H. T. Miyazaki, Y. Kurokawa, *Phys. Rev. Lett.* **2006**, *96*, 097 401.
[103] J. B. Pendry, A. J. Holden, D. J. Robbins, W. J. Stewart, *J. Phys. Condens. Matter* **1998**, *10*, 4785.
[104] J. B. Pendry, *Phys. Rev. Lett.* **2000**, *85*, 3966.
[105] R. A. Shelby, D. R. Smith, S. Schultz, *Science* **2001**, *292*, 77.
[106] J. Zhou, T. Koschny, L. Zhang, G. Tuttle, C. M. Soukoulis, *Appl. Phys. Lett.* **2006**, *88*, 221 103.
[107] V. A. Podolskiy, A. K. Sarychev, V. M. Shalaev, *Opt. Express* **2003**, *11*, 735.
[108] J. B. Pendry, *Science* **2004**, *306*, 1353.
[109] H. Shin, S. Fan, *Phys. Rev. Lett.* **2006**, *96*, 073 907.
[110] G. Dolling, C. Enkrich, M. Wegener, J. F. Zhou, C. M. Soukoulis, *Opt. Lett.* **2005**, *30*, 3198.
[111] V. M. Shalaev, W. S. Cai, U. K. Chettiar, H. K. Yuan, A. K. Sarychev, V. P. Drachev, A. V. Kildishev, *Opt. Lett.* **2005**, *30*, 3356.
[112] J. B. Pendry, L. Martín-Moreno, F. J. García-Vidal, *Science* **2004**, *305*, 847.
[113] A. P. Hibbins, B. R. Evans, J. R. Sambles, *Science* **2005**, *308*, 670.
[114] V. G. Veselago, *Soviet Physics Uspekhi-USSR* **1968**, *10*, 509.
[115] A. Schuster, *An Introduction to the Theory of Optics*, Edward Arnold, London **1904**.
[116] N. Fang, H. Lee, C. Sun, X. Zhang, *Science* **2005**, *308*, 534.
[117] D. R. Smith, D. Schurig, M. Rosenbluth, S. Schultz, S. A. Ramakrishna, J. B. Pendry, *Appl. Phys. Lett.* **2003**, *82*, 1506.
[118] M. C. Beard, G. M. Turner, C. A. Schmuttenmaer, *J. Phys. Chem. B* **2002**, *106*, 7146.
[119] A. G. Markelz, A. Roitberg, E. J. Heilweil, *Chem. Phys. Lett.* **2000**, *320*, 42.
[120] E. Hendry, F. Wang, J. Shan, T. F. Heinz, M. Bonn, *Phys. Rev. B* **2004**, *69*, 081 101.
[121] J. Saxler, J. G. Rivas, C. Janke, H. P. M. Pellemans, P. H. Bolivar, H. Kurz, *Phys. Rev. B* **2004**, *69*, 155 427.
[122] F. Miyamaru, S. Hayashi, C. Otani, K. Kawase, Y. Ogawa, H. Yoshida, E. Kato, *Opt. Lett.* **2006**, *31*, 1118.
[123] J. G. Rivas, M. Kuttge, P. H. Bolivar, H. Kurz, J. A. Sanchez-Gil, *Phys. Rev. Lett.* **2004**, *93*, 256 804.
[124] J. G. Rivas, J. A. Sanchez-Gil, M. Kuttge, P. H. Bolivar, H. Kurz, *Phys. Rev. B* **2006**, *74*, 245 324.
[125] J. Bellessa, C. Bonnand, J. C. Plenet, J. Mugnier, *Phys. Rev. Lett.* **2004**, *93*, 036 404.
[126] J. Dintinger, S. Klein, F. Bustos, W. L. Barnes, T. W. Ebbesen, *Phys. Rev. B* **2005**, *71*, 035 424.
[127] A. J. Haes, S. Zou, C. Zhang, G. C. Schatz, R. P. Van Duyne, *J. Am. Chem. Soc.* **2006**, *128*, 10 905.
[128] J. Dintinger, S. Klein, T. W. Ebbesen, *Adv. Mater.* **2006**, *18*, 1267.
[129] J. A. H. van Nieuwstadt, M. Sandtke, R. H. Harmsen, F. B. Segerink, J. C. Prangsma, S. Enoch, L. Kuipers, *Phys. Rev. Lett.* **2006**, *97*.
[130] T. A. Kelf, Y. Sugawara, R. M. Cole, J. J. Baumberg, M. E. Abdelsalam, S. Cintra, S. Mahajan, A. E. Russell, P. N. Bartlett, *Phys. Rev. B* **2006**, *74*, 245 415.