Plasmonic Nanocavity Coupling

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[Abstract]

The large losses of plasmonic nanocavities, orders of magnitude beyond those of photonic dielectric cavities, places them, perhaps surprisingly, as exceptional enhancers of single emitter light-matter interactions. The ultra-confined, sub-diffraction limited, mode volumes of plasmonic systems offer huge coupling strengths (in the 1-100 meV range) to single quantum emitters. Such strengths far outshine the lower coupling strengths of dielectric microcavities, which nonetheless easily achieve single emitter 'strong coupling' due to the low loss rates of dielectric cavities. In fact, it is the much higher loss rate of plasmonic cavities that make them desirable for applications requiring bright, fast-emitting photon sources. Here we provide a simple method to reformulate lifetime measurements of single emitters in terms of coupling strengths to allow a useful comparison of the literature of plasmonic cavities with that of cavity-QED, typically more closely associated with dielectric cavities. Using this approach, we observe that the theoretical limit of coupling strength in plasmonic structures has almost been experimentally achieved with even single molecule strong coupling now observed in plasmonic systems. However, key problems remain to maximise the potential of plasmonic cavities, including precise and deterministic nanopositioning of the emitter in the nanosized plasmonic mode volumes, understanding the best geometry for the plasmonic cavity, separating useful photons from background photons and dealing with the fluorescence quenching problems of metals. Here we attempt to raise awareness of the benefits of plasmonic nanocavities for cavity-QED and tackle some of the potential pitfalls. We observe that there is increasing evidence, that using correct geometries, and improving emitter placement abilities, significant quenching can be avoided and photon output maximised towards the extraordinary limit provided by the high radiative rates of plasmonic nanocavities.

Keywords: Plasmonics, strong coupling, weak coupling, nanocavity, coupling strength, cavity-QED, quenching

[Main Text]

The wavelength of visible light is far larger than the size of the single atoms and molecules that create it (Figure 1a). At room temperature, the absorption cross-section of atoms and molecules is equally small.[1] This fundamental size difference, or impedance mismatch, is responsible for two key features of the interaction of light and matter: (1) The probability of absorbing light using an atom or molecule is very small, and (2) an excited atom or molecule finds it hard to emit light and therefore has a considerable lifetime before emitting a photon from its excited state (if the energy is not dissipated by other non-radiative means).

How easy it is for a single emitter to produce a photon, however, depends not just on the intrinsic properties of that emitter, but also on the photonic environment. Fermi's golden rule dictates this transition probability and crucially depends on the number of final states available to the transition. Changing the photonic environment of an emitter alters the lifetime of the excited state by making it easier or harder for the emitter to relax via emitting a photon.

The density of optical states (DOS) quantifies the number of states available to an emitter and in a homogeneous medium depends on the refractive index and frequency of the light to be emitted. Introducing inhomogeneity changes the photonic environment and leads to an altered local density of optical states (LDOS) (Figure 1b and c). Specifically, by creating a resonant environment for a certain frequency, the LDOS at that frequency dramatically increases; much like a guitar string picks out certain frequencies or notes when it is struck. A photonic emitter experiences the increased LDOS and emits photons more efficiently; its excited state lifetime decreases. (N.B. It is also possible to reduce the LDOS at a certain frequency, with off-resonant cavities, therefore suppressing emission.)

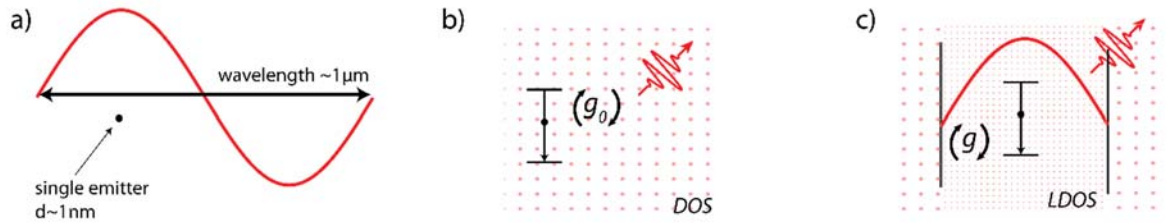

Figure 1 (a) At room temperature there is a fundamental mismatch between the absorption cross-section of an emitter and the wavelength of light. The mismatch prevents easy excitation of emitters with light and simultaneously inhibits their spontaneous emission. (b) The emission of a single emitter depends on the density of optical states available for it to emit into: the more states available, the faster the emission can occur. (c) A cavity provides a frequency-specific way to locally increase the density of states. By placing an emitter in a cavity resonant to its emission, the rate with which it emits can be considerably enhanced.

Purcell[2] was the first to realise that an optical cavity tuned to the emission frequency of an emitter creates the resonant environment necessary to enhance an emitter's spontaneous emission rate. The enhancement in spontaneous emission due to an increased LDOS is frequently referred to as the Purcell effect or Purcell enhancement. The coupling of a quantum emitter to a resonant cavity is a powerful concept which allows us to tune the interaction of light and matter down to the single photon level. This notion has led to intense research allowing the study and testing of fundamental concepts of quantum mechanics in the area of cavity-QED.[3] The ability to enhance a quantum emitter's emission rate while maintaining its pure quantum characteristics, as well as the ability to create strongly coupled mixed light and matter states is of direct interest to the development of quantum information technologies.[4,5]

Cavity Emitter Interaction

The frequency-dependent coupling of an emitter to the DOS or LDOS depends on the projection of the emitter's transition dipole moment ($\boldsymbol{\mu}$) onto the corresponding local electric field ($\boldsymbol{E}$). The coupling strength (in units of energy), in the dipole approximation, is defined as:

$$g(\boldsymbol{r}, \hat{\boldsymbol{e}}, \omega) = \boldsymbol{\mu} \cdot \boldsymbol{E}(\boldsymbol{r}, \hat{\boldsymbol{e}}, \omega) \quad , \tag{1}$$

where $\boldsymbol{r}$ is the vectorial displacement between the emitter and the cavity, $\hat{\boldsymbol{e}}$ the relative orientation between the emitter dipole and the electric field at $\boldsymbol{r}$ and ω the resonant frequency of the emitter and cavity. Twice this quantity (divided by $\hbar$) is known as the Rabi frequency, while in free-space, this quantity is the vacuum Rabi oscillation frequency ($2g_0$). When a cavity is introduced, we can define g as the coupling of the emitter to the cavity modes (N.B. elsewhere, it is sometimes defined as the coupling to all electromagnetic modes from both free-space and the cavity). In the case of a single emitter in a cavity, the coupling strength g quantifies the rate of energy interchange between the emitter in the ground state and a single photon in the cavity, where the single photon electric field is given by $E = \sqrt{\frac{\hbar\omega}{2\epsilon_r\epsilon_0 V_m}}$, where $\hbar\omega$ is the energy of the photon, ϵ_0 the vacuum permittivity, ϵ_r the relative permittivity ($\epsilon_r = 1$ for air, with $\epsilon_r = n^2$ for dielectric materials with a real refractive index n) and V_m is the effective mode volume of the cavity. The mode volume is the crucial variable which encodes the change in LDOS. Smaller mode volumes, lead to higher LDOS and stronger cavity-emitter coupling strengths.

The coupling strength is a useful quantity as it can be compared to the other energy transfer rates in the system, most importantly, the excited state lifetime of the emitter (Γ_0) and the cavity loss rate (κ). This comparison yields two key coupling regimes to explore. *Strong coupling* (where $g > \kappa, \Gamma_0$) and *weak coupling* ($g < \kappa \; or \; g < \Gamma_0$).

Strong Coupling

In the *strong coupling* regime, the coupling between the emitter and cavity is so large that the emitter and the cavity become a new single quantum object with energy shared coherently and reversibly between them. The energy levels of the emitter and cavity hybridize to form new states that vary in energy according to the strength of the coupling. Tuning the coupling strength shifts the energy levels of the system, providing a very powerful tool. Strongly coupled systems are useful for many applications that use light-matter interactions down to the single atom level. Potential applications include fine tuning chemical reactions[6], creating low- or no-threshold lasers[7,8] and enhancing non-linear effects[9] at low light intensities down to single photons. We are just beginning to explore the potential of this regime but probably their most promising use is in quantum information technologies. Here, strong coupling allows the preservation of quantum states between light and matter that is essential for qubit creation and exchange in quantum optical circuitry and quantum computation.[10–12]

Weak Coupling

In the *weak coupling* regime, the coupling strength is such that energy exchange from the emitter to the cavity occurs but is non-reversible and incoherent. Typically, this regime has been used to increase the spontaneous emission of emitters, which is the case when $\kappa > g \gg \Gamma_0$, i.e. the coupling strength is strong relative to the emitter decay rate, but not strong enough to surpass the cavity decay rate and reach strong coupling. When $\kappa \gg g \gg \Gamma_0$, this regime is sometimes referred to as the bad-cavity regime,[13,14] to emphasise that the emitter couples with great strength to the cavity, with nearly all of its emission happening through the cavity mode (rather than free-space), but that the cavity has losses much greater than the coupling. The cavity losses prevent coupling back to the emitter and the energy has a highly fast and one-directional flow. In the weak coupling regime, the emitter and the cavity remain separate quantum entities and so enhancement of emission occurs without changing the photon energy of the emission and the energy levels of the emitter remain unchanged. Increasing the emission rate of single emitters is useful to study the properties of certain emitters which normally have very low light output[15] and to maximise the brightness of quantum emitters. While strong coupling is sought after in many quantum applications, certain quantum technologies, such as all-optical quantum optic circuitry[16,17], require fast and pure single photon light sources, which efficient weak or strong coupling can both provide.

Minimise mode volume to maximise coupling strength

To achieve strong coupling or efficient weak coupling, we need to maximise the coupling strength. We see from Eq. 1 that the electromagnetic mode volume must be minimised. The first optical cavities

used air or dielectric material to embed an emitter surrounded by mirrors (either metallic or dielectric) and had relatively large mode volumes. To further decrease the mode volume, dielectric microcavities were developed using carefully fabricated Bragg stack microstructures[18], photonic crystals[19], microresonators[20] etc. Such cavities, designed on the micro and nanoscale, squeeze the mode volume down to the diffraction limit[21] (Figure 2). Pushing beyond this limit is difficult with pure dielectric structures, which limits coupling strengths to around $100\ \mu eV$ for visible light when coupling to emitters with dipole strengths of $\mu \sim 1$ Debye. The typical dipole moment of fluorescent molecules is ~ 1 Debye, although it can be roughly 10 x higher for stronger dipole moment emitters such as quantum dots. As a result, to enter the strong coupling limit for such quantum emitters, a cavity with low losses κ is needed, with $Q = \omega/\kappa >$ 10,000 for such a 1 Debye emitter at visible wavelengths. Since dielectric materials do have low intrinsic losses strong coupling is relatively easily achievable under the right conditions.

Strong coupling with a single emitter and a cavity was first experimentally demonstrated using a trapped cold caesium atom[22] and later this achievement was transferred to the solid-state using quantum dots trapped in micropillar cavities and other elegant microcavity geometries.[18] Despite the achievement of strong coupling in dielectric cavities, there are a couple of drawbacks for their use in enhancing single photon emission and creating strong coupling. Firstly, the coupling strengths have reached their maximum values since the mode volumes cannot be easily pushed beyond the diffraction limit. As a consequence, the absolute photon output or brightness that can be achieved with such cavities cannot be greatly increased beyond what has already been achieved. The second problem of dielectric cavities is that to obtain strong coupling they need to be made low-loss and high-Q such that their limited coupling strength can overcome the cavity losses; as a result, they have very narrow bandwidths. Although in some applications this is desirable, with highly selectivity, for good coupling the linewidth of the emitter should overlap well with that of cavity. As a result, such cavities generally have to be operated at low temperatures[21] (around 10K) to allow for line-narrowing of the emitter and precise tuning of the emitter to overlap the cavity resonance. A third problem of all-dielectric cavities is that they are hard to make with complex fabrication techniques with the emitter in general placed inside the cavity as it is constructed, further complicating fabrication and limiting adaptability. These problems restrict the use of dielectric cavities in many technological applications.

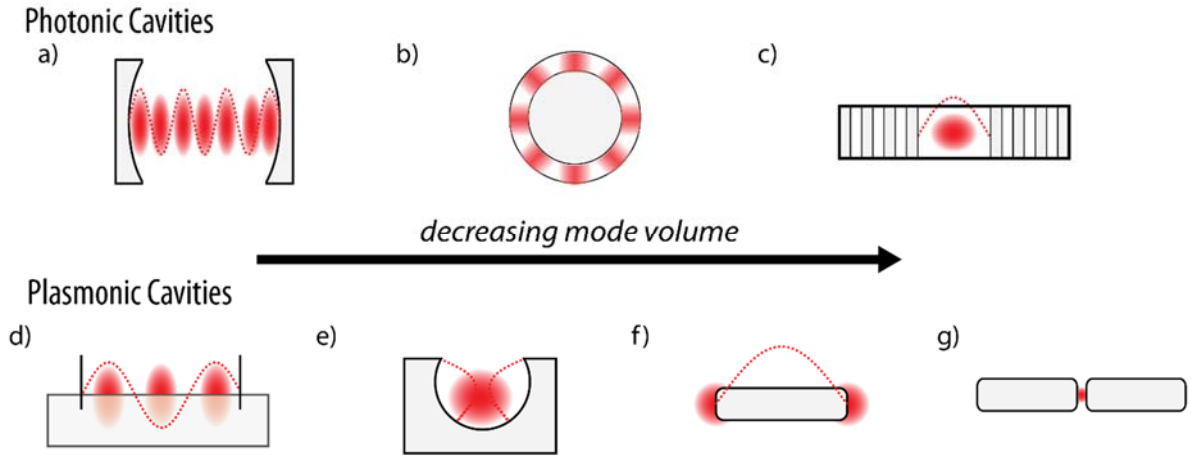

Figure 2 Photonic cavities have a wide-range of forms that have resonant modes depending on their size and confinement ability. They have developed from the simple concept of (a) light trapped between two mirrors, to more sophisticated dielectric only options (to reduce metal losses), such as (b) micro-resonators and (c) micro-Bragg stacks or photonic crystals with defects. Precise micro or nano-engineering is necessary to create these high-quality pure-dielectric structures. Equivalently, plasmonic cavities (which trap light as plasmons) are available in many different forms analogous to their pure photonic counterparts. From (d) trapped standing wave-type surface plasmon polariton cavities, to similar collapsed structures (e) with localised modes, to true nanoantenna systems such as (f) the dipole antenna, and even coupled systems for ultimate EM-field confinement in (g) gap plasmon systems.

Plasmonic Cavities

To shrink resonant mode volumes beyond the diffraction limit and increase coupling strength, a solution beyond conventional optics must be sought. Surface plasmon polaritons (SPPs) couple light to the collective movement of free electrons in a material. This coupled mode can be excited at the interface between metals (with a negative real part of their dielectric coefficient) and a dielectric.[23] SPPs couple to electrons bound in a material and therefore are tightly confined to the interface of that material with the electric field decaying exponentially away from the interface. SPPs preserve their bosonic photonic character acting as confined photons. Plasmons can either propagate along a surface or be further confined by geometry in the remaining dimensions to create localised surface plasmons analogous to standing waves on a water surface. Various plasmon cavities can be constructed (Figure 2) by reflecting SPPs from defects or gratings on a metal wire,[24] or ridge.[25] A flat surface with an indented structure can also confine a plasmon inside it,[26,27] where the indented structure can be imagined as the inverse structure of a nanoparticle, which supports such localised plasmon modes in a highly confined manner. When the nanoparticle is sized and shaped correctly, the localised plasmon becomes resonant with the so-called $\lambda/2$ fundamental resonance[28] (Figure 2f). In this particular limiting case, the plasmonic cavity is referred to as a dipole nanoantenna, since it acts like a dipole emitter. The electromagnetic field in such nanoantennas becomes tightly confined to the two nodal

points at each end of the dipolar rod, creating two optical hotspots with diameters of tens of nanometres. By coupling two such system together the light can be squeezed into even tighter volumes in the gap between the two nanoantennas, representing the ultimate limit (so far) of light confinement, orders of magnitude below the traditional diffraction limit, with hotspot diameters below 10 nm easily achievable.[29]

In the literature, these plasmonic systems are variously referred to by a plethora of names including: nanoparticles, nanoantennas, nanocavities, nanoresonators etc., depending on the purpose for which they were imagined. Although in the purest sense an optical cavity is an air-gap between two reflecting surfaces, such definition is extremely rigid. Since the physics of coupling an emitter to these plasmonic based system remains almost the same as that for standard optical cavities, here we choose to refer to them as nanocavities and we elaborate the measurement of their coupling strength analogous to an emitter in a dielectric optical cavity.

Compared to dielectric cavities, plasmonic cavities are far lossier. Indeed, the heavy ohmic loss of surface plasmons has plagued the field of plasmonics and is seen as a scrooge preventing the most useful applications of plasmonics.[30,31] Typical plasmonic cavities have low quality factors of between Q = 5 to 20 (far below that of dielectric cavities), they are indeed very bad cavities in terms of storing photon energy. The high loss rate, has meant that the long sought-after strong coupling[32] has been very hard to achieve and mode volumes have had to be squeezed to the limit to get close. Despite such losses, however, when the plasmonic structures support just the fundamental radiative plasmon mode, as in the case of dipole nanoantennas, most of their loss (over 50%)[33] is radiative in nature: this antenna efficiency we can exploit. The high radiation efficiency provides a great opportunity to provide high photon rate systems, far superior to those with dielectric cavities, which in fact are *limited* by their low losses. As well as their high radiative rate, plasmonic nanocavities have some other advantages over microcavities: (1) They are easier to fabricate, with colloidal synthesis possible for many implementations;[34] (2) They take up less space than dielectric cavities as true nanosized objects; (3) The mode volume is generally more easily accessible to an emitter as it is situated at the metal interface; (4) Their low Q means they respond very fast to changes in the system, good for switching; and (5) they are broadband, and so do not need fine tuning to the emitter. One of the main challenges is the accurate positioning of the photon emitter within the nanometric volume of the optical hotspot and reproducibility from structure to structure. Despite the multiple benefits and pioneering work,[35] use of metal plasmonic systems in cavity-QED experiments has so far been limited and is rarely taken seriously in the context of cavity-QED work.

Most of the discussion in the literature of plasmonic structures with single emitters refers to Purcell enhancement factors. While the "Purcell factor" provides an intelligent way to look at the enhancement of single photon emission and compare between different works, we believe reformulating the rate enhancement in terms of coupling strength provides an intuitive number to compare different systems. Specifically, it provides a number which can easily be compared with the cavity loss rate in systems and thus determine how far from strong coupling a particular system might be, or how bright a source it could make. It also links together the regimes of strong and weak coupling, and as such, provides a quantity for the weak coupling regime which in strong coupling is measured directly through spectral splitting or anti-crossing in photoluminescence, scattering or extinction experiments. Importantly, our approach places plasmonic systems in the established language of cavity-QED providing a bridge between these two communities, especially important for the comparison of plasmonic cavity-QED systems and their dielectric counterparts.

Measuring the coupling rate

In the strong coupling regime, the coupling strength can be measured directly from Rabi-oscillations in time, or the spectral splitting caused by the coupling of the two modes, yet in the weak coupling regime such oscillations or splitting are not visible. To determine the coupling rate of an emitter to a plasmonic structure in the weak coupling regime, we need to reformulate the coupling strength in terms of measurable quantities.

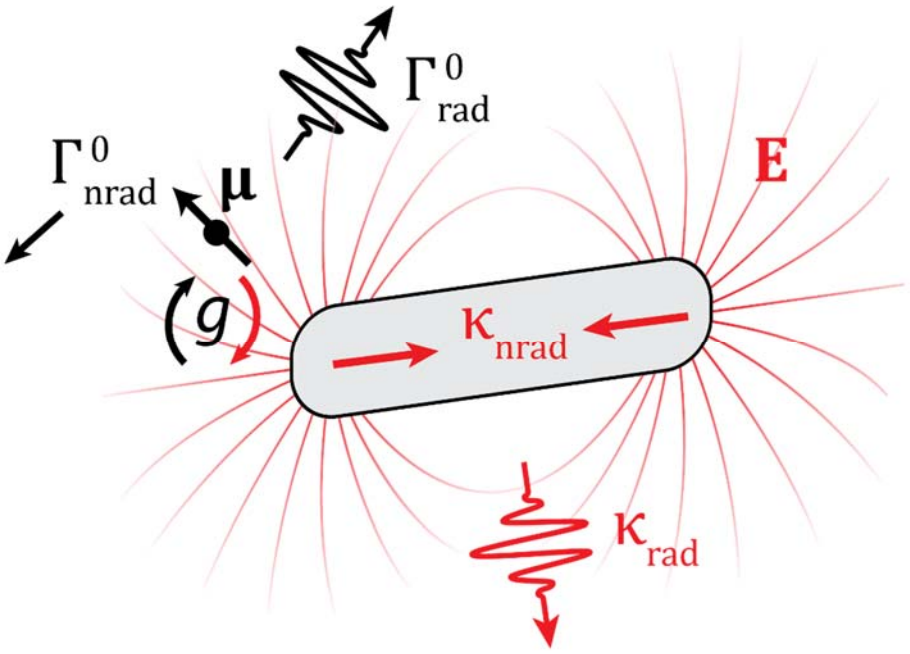

Figure 3 Schematic indicating the various energy dissipation mechanisms for an excited emitter with dipole moment ($\boldsymbol{\mu}$) in a plasmonic cavity mode ($\boldsymbol{E}$). The emitter can either directly emit into free-space radiatively (Γ_{rad}^{0}) or lose its energy non-

radiatively (Γ_{nrad}^{0}) through internal process or other environmental coupling mechanisms. It also couples to the cavity with strength g, where the energy is emitted through the plasmon mode (κ_{rad}), or lost ohmically to the metal (κ_{nrad}).

An emitter in free-space has a total decay rate (inversely proportional to the emitter's excited state lifetime τ_0) equal to the sum of its radiative and non-radiative decay pathways (see Figure 3a), i.e.:

$$\Gamma_0 = {}^{1}/_{\tau_0} = \Gamma_{rad}^{0} + \Gamma_{nrad}^{0} \tag{2}$$

This total decay rate is the rate that is measured in fluorescence lifetime experiments such as time-correlate single photon counting. When the emitter is placed inside a cavity, new decay paths become available through the modes of the cavity:

$$\Gamma_{tot} = \Gamma_0 + \Gamma_{cav} \tag{3}$$

In the weak-coupling[13] regime the contribution of the nanoantenna to the total decay rate can be expressed as:

$$\Gamma_{cav} = \left(\frac{4g^2}{\kappa}\right)\frac{1}{1+(2\delta/\kappa)^2} \tag{4}$$

where $\delta = \omega_{cav} - \omega_{em}$ is the detuning between the central frequencies of the emitter ω_{em} and that of the resonator ω_{cav}. The coupling strength to the antenna is g (where the total coupling to electromagnetic modes would be $g_{tot} = g + g_0$) and the total loss rate of the cavity is given by $\kappa = \kappa_{rad} + \kappa_{nrad}$. Limiting ourselves to the case when the emitter is on resonance with the cavity, $\delta = 0$, which is frequently the case in an optimised system, we obtain the simple relation:

$$\Gamma_{cav} = \left(\frac{4g^2}{\kappa}\right) \tag{5}$$

Assuming we do not introduce significant changes to the non-radiative rate of the emitter through other non-radiative quenching routes, an assumption most valid for high quantum efficiency emitters not too close to the metal surface, then we can combine Eq. 3 and Eq. 5:

$$\Gamma_{tot} = \Gamma_0 + \frac{4g^2}{\kappa} \tag{6}$$

Eq. 6 can easily be re-arranged to give the coupling strength g:

$$2g = \sqrt{(\Gamma_{tot} - \Gamma_0)\kappa} \tag{7}$$

The coupling strength can now be obtained simply by measuring the fluorescence lifetime when coupled and not coupled to the cavity, and with knowledge of the total loss in the plasmonic cavity (κ), which can be experimentally obtained, for example, from the linewidth of scattering spectra of

the cavity. Thus we present a simple formula from which to approximate the coupling strength from easily observable experimental quantities.

Coupling strengths in plasmonic cavities

Plasmonic cavity systems have evolved from isolated nanoparticles providing modest coupling strengths, including spheres, nanoantennas, nanorods and nanoshells, to more elaborate gap systems, where highly confined modes are formed in nanometre-sized gaps between pairs of nanoparticles such as in bowtie nanoantennas or nanorod dimers. Alternatively, such a gap mode can be formed between a real nanoparticle and a virtual nanoparticle formed from its image dipole on a flat metal surface.[36] In the literature, there are a huge number of works showing coupling of emitters to such systems and the enhancement of photoluminescence or fluorescence which occurs. Here we focus specifically on examples involving a single quantum emitter interacting with a plasmonic nanocavity as is the focus of this article. In Figure 4, we plot the coupling strengths directly extracted from the literature for the case of strong coupling or in the case of weak coupling, we calculate based on the experimental lifetime changes observed in the papers using equation (7) and approximate Q-factors of the cavity system from corresponding extinction/scattering spectra. We make no correction for changes in quantum efficiency of the emitter, since most of the papers use high quantum efficiency emitters to start with. We plot the obtained coupling strengths against $\sqrt{\frac{1}{V_m}}$ where we estimate the mode volume V_m, based on the geometry of the structures and electromagnetic simulations contained within the papers (where the exact calculated value was not provided). These values are compared to the theoretical maximal coupling values for a given mode volume calculated based on Eq. 1, i.e.: $g_{max} = \mu\sqrt{\frac{\hbar\omega}{2\epsilon_0 n^2}}\sqrt{\frac{1}{V_m}}$ for a single quantum emitter with transition dipole moments μ = 1 Debye and 10 Debye (representative of fluorescent emitters) at a photon energy of $\hbar\omega = 1.9$ eV, inside a polymer of refractive index n = 1.3, similar conditions to most of the experiments.

Figure 4 starts at volumes around the diffraction limit of light (the limits of typical photonic microcavities) and reduces to extremely small mode volumes approaching the maximal coupling strengths we can expect from plasmonic cavities, which for visible quantum emitters will be in the 100-1000 meV range if the mode volume is reduced to an optimistic 1 nm^3. Even smaller volumes reach into the realm of direct quantum size effects which appear at such sub-nm distances, such as tunnelling due to the overlap of the molecular orbitals with those of the metal. These are strong couplings indeed, with coupling strengths nearly reaching the energy of a single photon (1.9 eV), i.e. approaching the ultrastrong coupling regime,[32] and highlights the potential of plasmonic cavities.

Of course, Eq. 1 is vectorial in nature and the actual coupling achieved depends on the emitter's precise position and orientation within the cavity mode volume. The emitter orientation is increasingly important as the mode volume decreases towards dimensions of only a few nanometres (beyond attolitre and towards zeptolitre volumes) and the field takes on a full, and rapidly varying, vectorial nature.[37]

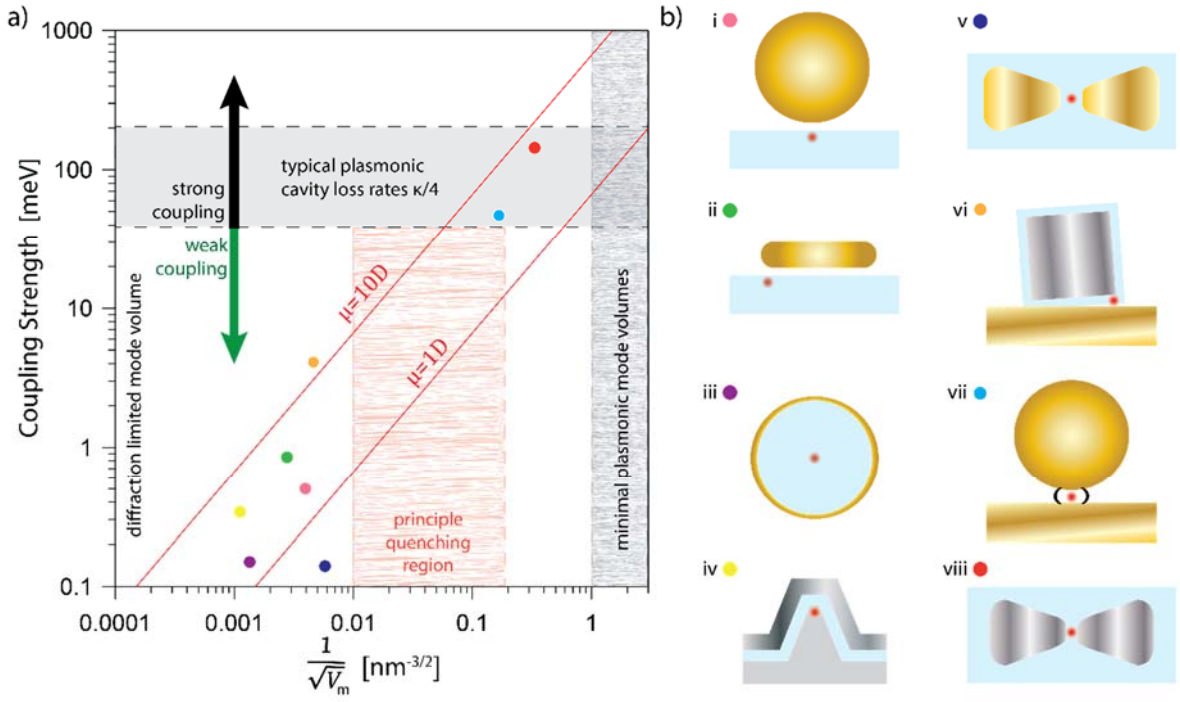

Figure 4 – (a) Coupling strength vs inverse root(effective mode volume) for different plasmonic cavities reported in the literature, with colour of dots indicating the geometry in (b). The typical plasmonic cavity loss zone has been calculated based on antennas of Q = 5 to Q = 10, and scaled by 4, since the conditon for strong coupling is roughly $g > \kappa/4$ for $\kappa \gg \Gamma_0$. This signifies the approximate boundary between weak and strong coupling as indicated. The volume axis runs from a diffraction limited volume on the left to a minimal plasmonic mode volumes on the right ducking just below a cubic nanometre, beyond which quantum size effects prohibit further confinement of the mode volume. (b) Corresponding cavity schematics indicating intended emitter location in the cavity: (i) A gold nanoparticle positioned using near-field microscopy on top of a terrylene molecule,[38](ii) a dipole resonant aluminium nanoantenna positioned on top of a TDI molecule,[39] (iii) a colloidally grown quantum dot coated in a silica shell surrounded by a gold plasmonic resonator shell,[40] (iv) a sandwich plasmonic structure with a epitaxially grown quantum dot coated in a dielectric and silver layer,[41] (v) a bowtie gold nanostructure encased in PMMA containing TPQDI molecules,[42] (vi) a quantum dot randomly positioned underneath a resonant plasmonic silver nanocube coated with a thin silica layer,[43] (vii) a methylvilogen dye molecule capured in the gap of a nanoparticle on mirror system using a cage-like macromolecule,[44] and (viii) a bowtie silver structure with a quantum dot placed in between using lithography and capillary forces.[45] Lines showing the theoretical coupling strengths for a dipole-approximated quantum emitter of strength $\mu = 1$ and $\mu = 10$ Debye assuming single photon occupation of the cavity with a photon energy of $\hbar\omega = 1.9$ eV in a medium of refractive index n = 1.3.

As can been seen in Figure 4, a variety of plasmonic cavity types have been used in the literature for single emitter coupling. In general, single nanoparticle structures such as (i)-(iv) in Figure 4 provide modest couplings up to around 1 meV. Such coupling already compares favourably to high-refractive index dielectric microcavities which typically display coupling strengths < 0.1 meV, despite being in the strong coupling regime.[18,19] Although basic single plasmonic structures already sustain coupling strengths stronger than advanced microcavities systems, the far stronger coupling is shown by coupled plasmonic dimer systems with ultra-confined gap plasmon modes. This advantage is evidenced in the large strengths achieved by structures (vi)-(viii) with coupling strengths in the 10-100 meV range, with the latter two of sufficient strength to even achieve strong coupling ($g > \kappa/4$ for $\kappa \gg \Gamma_0$) in these lossy plasmonic systems both with single molecules[44] and single quantum dots.[45] This coupling is around 3 orders of magnitude greater than the strength achieved in photonic dielectric microcavities.

It should be noted that our analysis does not differentiate between the different emitters used in the experiments. Different quantum emitters have different dipole moment strengths, with fluorescent molecules typically having moments around 1 Debye, whereas quantum dots can have higher moments up to around 30 Debye. To compare the efficiency of different plasmonic structures for creating high coupling strengths, it might also be useful to normalise to the dipole moment of the emitters used.

An interesting observation from Figure 4 is a region which we labelled as the 'principle quenching region'. Here we notice a lack of experimental works published in this region. The quenching range corresponds to mode volumes between 100 and 10,000 nm^3. A plausible explanation for the lack of published works is that for these small mode volumes, an emitter must be placed extremely close to the plasmonic surface < 5 nm to be efficiently coupled, leading to extreme quenching of the fluorescence and inability to observe the coupling. Indeed, it is only when the mode volume is reduced below 100 nm^3 that we start to enter the strong coupling regime and coupling is observed again. Here the coupling is observed as a split (anti-crossing) in the scattering or extinction spectra of the plasmonic cavity (not occurring in the weak coupling regime), without the need to observe fluorescence. Moreover, quenching in the strong coupling regime may even be suppressed in volumes below the principle quenching region, as discussed later on.

Interestingly, most of the structures perform close or above the predicted values for a 1 Debye emitter. This high performance is both testament to the achievements in the field and also likely enhanced by an overestimation of the mode volumes we used here, the use of stronger dipole emitters and the experimental bias to select the best cases observed in stochastic experiments.

One potential limitation of the above analysis and definition of the coupling strength is that it assumes the dipole approximation is valid. While in general this probably is still a valid approximation, as mode volumes are reduced to ultra-small volumes, it might be necessary to re-evaluate the assumption.

Reproducibility and emitter placement

Some of the largest couplings of single molecules to plasmonic cavities has been achieved using self-assembly chemistry techniques. This approach allows the smallest gaps to be produced (below the standard resolution of lithographically created structures) but, being indeterministic, does not always provide reliable enhancement. The variability is clearly evident in the work by the group of M. Mikkelsen,[43] where dielectric coated silver cubes are scattered on top of emitters on a gold surface. Despite achieving very large couplings, the approach is intrinsically random, clearly visible in the data, with the coupling different for each cube, and no guarantee that an emitter and cube will even be located at the same position. The work by the group of Baumberg,[44] create a similar system, although using a molecular cage-like molecule to trap a dye molecule in a far smaller gap between a metal nanoparticle and metal surface. Here the geometry restraints should mean that the molecule orientation is better controlled and they indeed see higher reproducibility from particle to particle. However, whether or not there is 1,2,3 or more molecules in the gap varies from particle to particle, and there is no real control over whether it really is single molecule cavity coupling from cavity to cavity. Other work requiring emitters to flow into the gap structure are even less reliable[42], and evidenced in the poor coupling strengths achieved, despite the small expected mode volumes as is shown in structure (v) in Figure 4. Some of the highest coupling strengths achieved with quantum dots in the group of Haran, use an elaborate technique to place quantum dots in gaps using a combination of lithography and capillary forces. The process remains semi-stochastic however, with no guarantee of one and only one emitter in any one hotspot, let alone placement at the maximal position of coupling strength.[45] Such variability limits the use from a technological point of view (until such processing is improved) but also dampens reproducibility and prevents standard proofs of single molecule coupling to the cavity.

More convincing proof of true single molecule coupling to nanoantennas comes from deterministic approaches, using some form of nanoplacement technique such as near-field microscopy,[46] or scanning tunnelling microscopy.[47] The benefit of these techniques is that the distance between the plasmonic cavity and the emitter is controlled down to sub-nm level. An important consequence of deterministic scanning is that the single emitter nature can first be robustly verified in the absence of the nanoantenna using second order photon correlation to verify the purity of the quantum emission on one and the same single emitter.

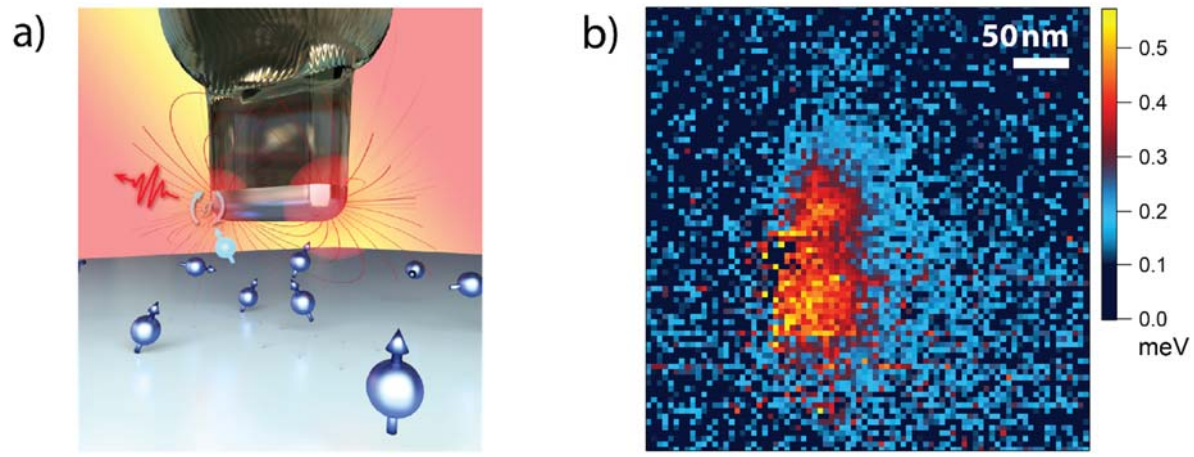

Figure 5- (a) Using a plasmonic nanoantenna attached to a near-field scanning probe, we deterministically scan a single emitter through the cavity mode and record the fluorescence lifetime to map the coupling strength of the emitter to the nanoantenna. (b) Map showing coupling strength as the nanoantenna is scanned over an excited single fluorescent molecule at a particular height separation extracted using Eq. (7) from the lifetime values recorded at each point using time-correlated single photon counting as per in (a).[39]

In our group's recent work,[39] for example, we have shown that such deterministic technique can be applied using scanning nano-antenna microscopy (see Figure 5b and c). We use a single fluorescent dye molecule in a polymer matrix held within the focus of a pulsed excitation laser. Using shear-force feedback we position a nanoantenna cavity resonant with the molecule's emission in the close vicinity (< 10 nm) of the emitter so as to couple it to the nanocavity mode but avoid quenching to the metal. We continuously record every photon arrival time on our detectors using time-correlated single photon counting as we 2D-scan the nanoantenna with nanometre resolution. For each pixel (100 ms) we build a histogram of photon arrival time relative to the laser pulse. By fitting to an exponential decay, we extract the lifetime (inverse of the rate) as a function of position, both with and without coupling, and using Eq. 7 we render a coupling strength map. The scanning approach allows us to get a full picture of the coupling strength as a function of the emitter position, and we can carefully position the emitter to obtain the desired coupling. The main drawback here is that the enhancements are not as high as those seen in gap structures as the mode is not as well confined.

A future challenge of plasmonic cavities coupled to nanoantennas is how to achieve the high confinement necessary and the precise and reproducible placement and alignment of a single emitter within such tiny mode volume. This challenge is especially important for the commercial prospects of this technology. Some interesting ideas for nanopositioning are being inspired by inject printing, which can use to position clusters of quantum dots rapidly with extraordinary accuracy, and which is now being extended to placing single quantum dots.[48]

Single emitter enhancement and brightness: the limits

A key factor of single emitter-cavity coupling, for almost all applications, is how many photons per second can be emitted, which corresponds, for example, to data transfer rates in quantum networks. As already discussed, in dielectric cavities the diffraction limit prevents further decrease in the mode volume size, which plasmonic cavities do overcome. This small volume coupled with the high radiative loss rate of plasmonic nanocavities allows for very high photon output or brightness.

The high loss-rate in plasmonic cavities results in Q-factors around Q = 10 or less, which means that for visible light with frequencies ~ 500 THz ($\hbar\omega = 2.1$ eV), the loss of plasmonic cavities puts a maximum limit of around $5\text{x}10^{13}$ photons/sec (210 meV) on the emission rate obtainable. This ultimate limit is extremely high and more than sufficient for single photon emitter sources based on weak coupling, where the cavity loss rate should be much higher than the actual photon emission rate to maintain purity (bad-cavity limit). As a result, the probability of storing two photons in the cavity at once is negligible and the possibility of simultaneous two photon emission is avoided. With this very high upper rate, the limit of photon output (brightness) in plasmonic antennas is rather limited by the following:

Coupling strength

After cavity loss, the coupling strength g is of course the key factor determining brightness and directly depends on how small an effective mode volume can be made, since $g \propto \frac{1}{\sqrt{V}}$. So far, the smallest mode volumes have been made by coupling two plasmonic particles together with increasingly smaller gap between them, where the mode becomes tightly confined. Exactly, how small this volume can be made remains to be seen, although it is rapidly approaching the ~ 1 nm^3 limit for visible light which is suggested to be a limit imposed by quantum tunnelling between the structures creating it.[49] Such small gap sizes theoretically, and recently, experimentally[44] give coupling strengths large enough to exceed the cavity loss rate, which represents the ultimate limit.

Non-radiative decay losses in cavity

The quantum efficiency of the cavity, i.e. how much light gets radiated, versus lost non-radiatively via ohmic mechanisms to the metal, also affects brightness. Despite high ohmic losses in typical plasmonic metals, such as gold and silver, plasmonic nanoantennas optimised for dipolar resonances have relatively large radiation efficiencies, approaching 50 %. As investigation into hybrid plasmonic materials continues[50], perhaps the non-radiative channels can be further reduced. In fact, the high radiation efficiency of plasmon nanoantennas means they are one of the few elements in the area of plasmonics where loss is not the principle limiting factor.

Quenching

A fluorescent emitter placed close to a metallic surface experiences new non-radiative decay channels causing quenching of the fluorescence despite the increased LDOS. On a flat metal surface this typically starts to happen at separations below 10 nm. In resonant nanoparticle systems the same thing can happen, with light from the emitter, that normally couples to the emissive bright dipole mode of the nanoparticle, instead coupling to higher-order dark modes with the energy eventually lost ohmically inside the metal.[51] The mode volumes of plasmonic systems are necessarily small to obtain large coupling strengths and it is necessary that the emitter must be placed extremely close to the metal to reside within the mode volume. Quenching therefore is a big problem for efficient spontaneous emission, with a trade-off between maximum coupling strength and quenching generally sought to maintain brightness output. As plasmonic mode volumes are squeezed smaller to increase coupling strengths, to reach the strong coupling regime, the obvious worry is that quenching begins to dominate and, despite strong coupling, light output becomes drastically reduced. Indeed experimentally, work such as that of Baumberg group[44] and Haran group[45] , which show impressive evidence of single molecules and quantum dots strongly coupled to plasmonic cavities, fail to show any fluorescence data, presumably due to low fluorescence light output. Strong coupling in such systems is nearly always detected through changes in the plasmonic scattering spectra rather than photoluminescence or fluorescence. Despite the lack of publication of fluorescence in these strong coupling cases, it has been suggested theoretically that in the strong coupling regime quenching is highly supressed, with the coupling to higher order modes actually a *necessity* to achieve strong coupling.[52] Further theoretical and recent experimental work shows that this might indeed be the case with fluorescence clearly visible from J-aggregates strongly coupled to single nanoparticles[53,54] and more recently from averaged date of strongly coupled single molecules in 5 nm plasmonic nanogap cavities, where fluorescent emission is observed despite these close distances.[55] Indeed even in the weak coupling regime, the exact geometry of the plasmonic structure affects the coupling to the dark modes responsible for quenching; e.g. work performed in an STM environment[47] shows fano resonances in fluorescence emission spectra in the weak coupling regime despite the close distances of the plasmonic structure to the emitter. It seems the quenching mechanisms on these nanosystems coupled to single molecules remain incompletely understood and can even be surmounted with appropriate geometry or by pushing deep into the strong coupling regime; certainly further experimental evidence is needed in this area.

As a tangent, the suppression of quenching occurring in the deep strong coupling case could provide an interesting platform for highly localised fluorescence emission and even ultra-superresolution imaging. As an emitter is moved close to a plasmonic cavity quenching dominates and the fluorescence of the emitter is suppressed providing a dark emission region. However, as the emitter continues to

move right into the heart of the mode volume of a highly confined cavity mode where strong coupling can occur, this quenching can be suppressed and the emitter can shine brightly again. The region where strong coupling occurs is extremely small on the single cubic nanometre size-scale, and therefore this fluorescence too can only occur brightly in this small region. This highly localised emission could perhaps be used as a paradigm shift for superresolution imaging, surpassing by orders of magnitude the conventional confinement typically obtained using plasmonic hotspots while trying to avoid quenching.[56]

Photostability and integration

Critical to any single photon source is the choice of the type of single photon emitter. Many options are available and many have been enhanced in various plasmonic geometries including atoms,[57] quantum dots,[41,43] crystal-vacancy centres[46,58] and dye molecules.[38,41,42] Each system has benefits and drawbacks. Atoms require extreme environments to control, and so are not easy to integrate into solid-state systems. Molecules are more easily integrated and crucially possess a clean dipole moment and a very small size, meaning they can be placed into small gap cavities. However, they tend to bleach very easily, with probabilities of 10^{-8} to 10^{-6} at room temperature, giving them short shelf-lives. Modern style colloidal quantum dots can be much more robust than molecules and have higher dipole moments, however they take up roughly 10x more space ($\sim$ d = 10 nm), and so cannot be easily integrated into the most confined light systems. Defect centres such as nitrogen vacancies in diamond are very robust systems, yet with low excitation cross-section and extensive phonon side bands. Also, since they are embedded in a crystal, they are hard to place inside the most confined plasmonic modes. One new type of system, which remains to be fully explored, is defect centres in two-dimensional crystal structures, such as hexagonal boronitride.[59] Such systems might be able to provide a robust emitter even at room temperature, in a more easily accessible geometry.

It is also necessary to consider the photodamage any concentrated excitation light might exert, not only on the photon emitter (where organic molecules are especially sensitive) but also on the plasmonic structure itself. Under high excitation powers, plasmonic nanostructures can melt and deform at temperatures far below the melting point of the bulk materials. Appropriate encapsulation and choice of thermally stable geometries is thus highly desirable, while such measures must be carefully incorporated to maintain the desired resonance conditions.

Non-radiative decay channels in emitters

Apart from quenching to the metal, the emitter itself has internal non-radiative decay channels competing with the radiative ones. Through internal conversion, a molecule can decay to the ground

state without photon emission. By inter-system crossing molecules can pass from the singlet to the triplet excited state. The transition from the triplet back to the singlet ground or excited state is forbidden and thus the triplet is very long-lived (typically micro- to milli-seconds). Molecules in this state are dark or 'blinking' and prevent light illumination, which could heavily impede any useful application. Likewise, quantum dots and other emitters can pass into similar long-lived dark trap states. Routes to suppress such non-radiative decay in emitters should be taken not only by appropriate emitter choice but by considering the stability provided to them by their environment.

Output coupling

The collection efficiency is the last item which must be optimised to ensure all the light produced is usable. Here, again nanoantennas make a useful system as they can be designed to direct light emission of coupled single photon emitters.[60,61] By using secondary optics with such nanoantenna system, indeed it has been shown that 99 % of emitter light can be collected.[62]

Given all the above, for a non-blinking, non-bleaching emitter, the biggest obstacle in producing superfast single photon emission from emitters in plasmonic cavities is the non-radiative quenching of the fluorescence, at least in the weak coupling regime. Figure 6 is a schematic graph showing the increase in brightness when the coupling strength to the plasmonic cavity is increased (by reducing the cavity mode volume). In the perfect system, the brightness of the emitter (pumped in saturation) would increase quadratically from $\eta_0\Gamma_0$ (where η_0 is the quantum efficiency of emission) with the coupling strength as per Eq. 6. The increase would occur up to the limit set by the cavity loss rate $\sim \kappa$, which is further limited by the radiative efficiency of the cavity η_{cav} to be $\sim \eta_{\mathrm{cav}}\,\kappa$. As the mode volume becomes extremely small, the emitter will necessarily be placed closer to the metal surfaces involved. The proximity means that one cannot insert spacer layers to prevent direct Förster quenching of fluorescence to the metal, and quenching becomes inevitable. Therefore, the compromise between reducing volume and preventing quenching limits the maximum brightness level available as discussed above. Exactly how quenching behaves, however, depends on the exact geometry of the metal, and has clearly be shown to be different from the r^6 dependence, frequently observed on flat metal surfaces.[63] In Figure 6, the quenching offset can be shifted by the specific geometry. As strong coupling is achieved, it seems quenching may cease to become a problem, and the brightness previously lost to quenching can be somewhat restored, although to which extent this occurs remains to be determined both theoretically and experimentally. However, even if reduction of photon brightness is minimised and significant fluorescence obtained, at such small mode volumes other processes may prevent *pure* single photon emission, yet another necessity for quantum applications.

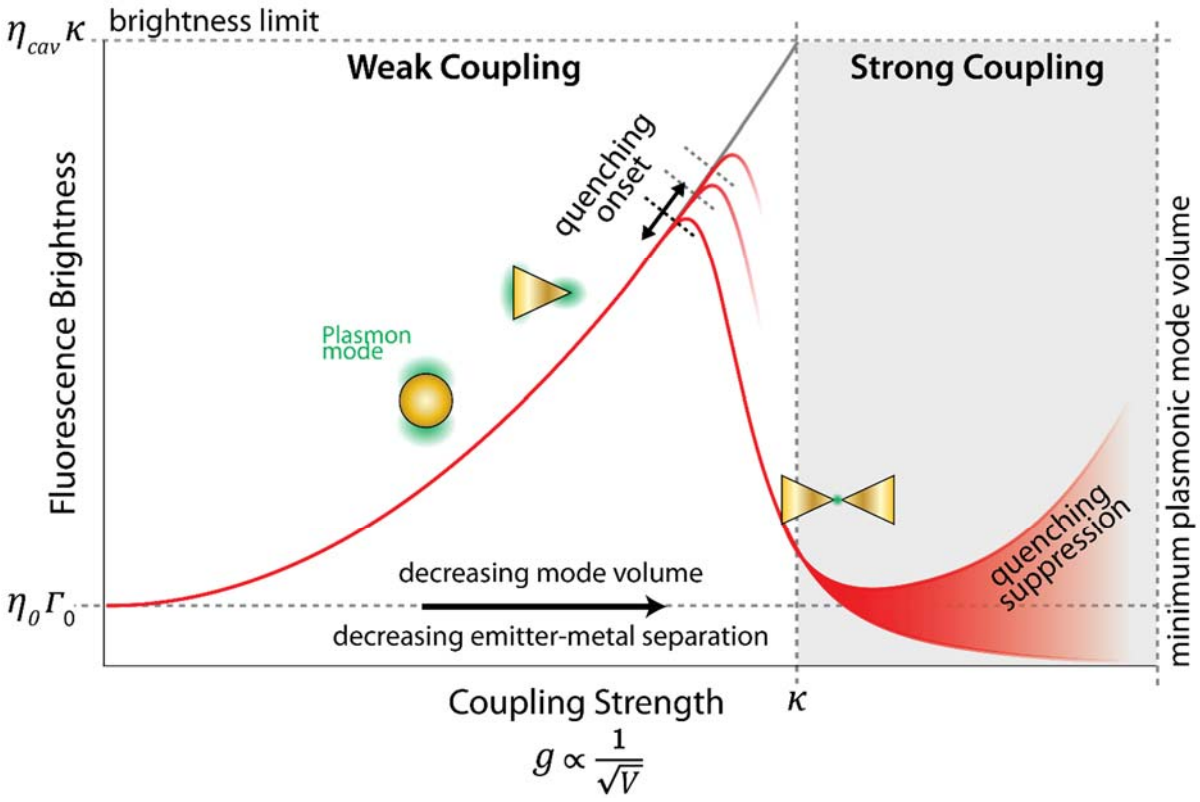

Figure 6 – Graphic illustrating the increase of brightness of a quantum emitter from the uncoupled free-space value to the theoretical maximum when coupled to a plasmonic nanocavity, given a saturated pumping regime. Here, η_0 is the emitter quantum efficiency, η_{cav} is the radiation efficiency of the cavity, Γ_0 the spontaneous emission rate of the uncoupled molecule, and κ the total cavity decay rate. Coupling strength obtainable increases as the mode volume is decreased, which is achieved using different plasmonic geometries. This decreased mode volume, consequently requires that the emitter is placed closer to metal surface to remain within the mode volume. However, as the molecule is placed closer to the surface quenching increases, reducing the photon output. The onset of this quenching depends on the exact geometry of the plasmonic system, but normally occurs before the strong coupling regime, and can severely reduce photon output close to zero. Once inside the strong coupling regime it is possible that quenching becomes suppressed, leading to the possibility of increased photon emission again. This exact process remains to be fully understood.

The Purity problem

As the spontaneous photon emission rate of the emitter is increased, it is necessary to provide sufficient excitation power to ensure the system is pumped in saturation such that the maximum rate of emission can be maintained. Since plasmonic resonances are rather broad ($\Delta\lambda \sim 100$ nm), they cover both emission and excitation wavelengths and thus the excitation light is also localised to small mode volumes by the plasmonic cavity, meaning that the energy density is greatly increased. This means that both linear and nonlinear processes, initially insignificant, do become important. These include Raman scattering[64,65] from the emitter and surrounding medium, electronic-Raman scattering

of the metal,[66] metal luminescence,[67] second harmonic generation and other nonlinear process in the metal[68] as well as bi-exciton creation in the emitter to name just a few. Some of these processes can be filtered out from the emission signal, however some, especially Raman signals, may overlap significantly with the spontaneous emission wavelength. The stronger these processes are the less pure the single photon emission becomes as this signal is contaminated with other sources of photons. Such loss of purity would show up as an increase in time-zero photon correlation statistics away from the ideal of *zero* for a true single photon source, typically measured in antibunching experiments. Indeed, in the work of the Baumberg group,[44] the enhanced Raman signal dominated over the quenched fluorescence signal, which would make such a source useless as a single photon source. It is therefore crucial to minimise background light generation, while still maintaining sufficient pump powers.

We note that a recent review by Koenderink explores in detail some of the other limitations and benefits of using plasmonic nanoantennas specifically in relation to creating bright single photon sources.[69] We also briefly note, that as well as purity, an important consideration for single photon sources for many quantum information applications is indistinguishability from one photon to the next. At room temperature the broad emission spectra of many single photon sources reduces the indistinguishability of photons, due to spectral uncertainty. This generally requires cooling to reduce the phonon broadened linewidths and thus increase indistinguishability. As plasmon devices are increasingly thought of for single photon sources, the implications on indistinguishability, and potential improvement for operation at room temperature, need to be carefully considered.

Conclusions

Picturing plasmonic systems in the same way as photonic cavities with ability to couple with strength *g* to a single photon emitter, provides an illuminating and intuitive way to understand the benefits and limits of such cavities for cavity-QED interactions and to compare them with traditional dielectric analogues. Using a simple formula the plasmonic cavity coupling strength can be calculated and directly compared to other rates in the system. We see that despite most plasmonic systems not obtaining strong coupling, the strength of plasmonic coupling is in fact much stronger than *strong coupling* in dielectric cavity systems, where the barrier to strong coupling is lowered by high quality factor cavities. In most real applications, high photon throughput is necessary, therefore the best cavities are the lossiest with smallest mode volumes and consequently highest coupling strengths, and to this end plasmonic cavities are an excellent choice. Care should be taken in the design of future plasmonic cavities for such applications to maximise brightness and avoid potential pitfalls as outlined

above. The challenge of effective, accurate and reproducible nanopositioning of the emitter is crucial and still remains to be solved. Further research must focus on the nature of quenching of emission in such picocavities and how this can be minimised to maximise photon brightness, not just the total decay rate of the system. Furthermore, a hazard of such small cavities is the generation of spurious photons, which decrease the purity of such system. In such tightly focused cavities, Raman and non-linear effects become increasingly important and need to be suitably handled to ensure usability of such single photon sources.

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Plasmonic Nanocavity Coupling

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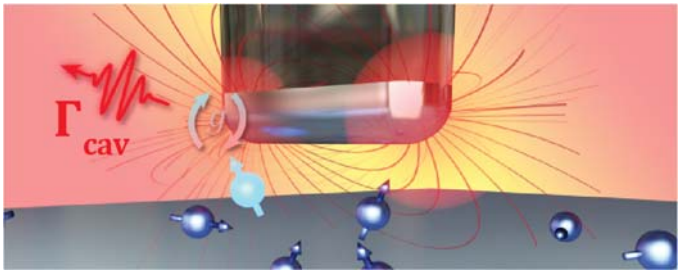

Artist impression of a quantum emitter coupling to a plasmonic nanocavity with coupling strength *g*. The plasmonic cavity enhances the single photon emission rate of the quantum emitter by an amount Γ_{cav} above the free-space spontaneous emission rate Γ_0.