

Room-temperature plexcitonic strong coupling: Ultrafast dynamics for quantum applications

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ABSTRACT

Strong light–matter interaction is at the heart of modern quantum technological applications and is the basis for a wide range of rich optical phenomena. Coupling a single quantum emitter strongly with electromagnetic fields provides an unprecedented control over its quantum states and enables high-fidelity quantum operations. However, single-emitter strong coupling is exceptionally fragile and has been realized mostly at cryogenic temperatures. Recent experiments have, however, demonstrated that single-emitter strong coupling can be realized at room temperature by using plasmonic nanocavities that confine optical fields via surface plasmons strongly on metal surfaces and facilitate sub-picosecond light–matter interaction. Here, we outline recent theoretical developments and experimental demonstrations of room-temperature strong coupling in the plasmonic platform, from emitter ensembles down to the single emitter limit, before placing a focus on selective studies that explore and provide insight into applications of plexcitonic strong coupling including sensing of single biological molecules, qubit entanglement generation, and reconfigurable single-photon sources and provide an outline of research directions in quantum sensing, quantum information processing, and ultrafast spectroscopy.

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I. INTRODUCTION

An optical cavity has the ability to confine electromagnetic waves and enhance light–matter interaction, facilitating rapid energy exchange between a quantum emitter and the optical field at the cavity resonance. When the energy exchange rate, traditionally defined by the coupling strength g , exceeds the total energy dissipation rate, the system reaches the strong coupling regime.^{1,2} This effect is at the core of modern quantum technological applications such as single-qubit coherent control,³ universal quantum gates,⁴ and quantum sensing.⁵ However, strong light–matter coupling with a single emitter is extremely fragile and has so far mostly been realized at cryogenic temperatures, in systems such as trapped atoms in reflective mirror cavities,^{6,7} trapped atoms in photonic crystal cavities,⁸ and solid-state qubits.⁹ In the past decade, tremendous progress has been made toward room-temperature single-emitter strong coupling by using nanoscale optical cavities formed by plasmonic resonances on metal

nanostructures.^{10–12} Although metals dissipate energy rapidly due to high Ohmic loss, plasmonic nanocavities are capable of confining and enhancing fields so intensely that this enhancement compensates for their dissipation and facilitates strong coupling.¹³ By realizing single-emitter strong coupling in an ambient environment,^{14,15} the plasmonic platform opens up vast possibilities for applications and limitless opportunities for fundamental studies.

In addition to their extreme field confinement property, plasmonic nanocavities also possess several unique optical properties. First, plasmonic nanocavities facilitate significant spatiotemporal field variations¹⁶ such that different emitters placed in the proximity of the nanocavities may experience vastly different optical environments. Consequently, this leads to distinguishable optical properties of nearby quantum emitters and was exploited in a sensing application¹⁷ and multimode control of near-field plasmonic coupling.¹⁸ Second, plasmonic nanocavities also facilitate ultrafast energy exchange between

quantum emitters in the timescale of a few tens of femtoseconds.^{13,17–20} Such a rapid energy exchange is significantly faster than typical dephasing rates and makes a plexcitonic system an ideal platform for room-temperature quantum technologies. In this perspective, we first outline some key aspects related to strong coupling in nanoplasmonic cavities, highlighting, in particular, quasi-normal mode (QNM) theory (Sec. II), followed by a summary of current experimental state-of-the-art configurations of plasmonic nanocavities and quantum emitters (Sec. III) for strong coupling. We then discuss several theoretical studies that explore applications of plexcitonic strong coupling using a single emitter (Sec. IV A) and two or more emitters (Sec. IV B). Finally, we present an outline of future research directions of room-temperature strong coupling based on plexcitonic systems (Sec. V).

II. QUASI-NORMAL MODE THEORY FOR PLEXCITONIC STRONG COUPLING

Resonances of a plasmonic nanostructure are characteristically non-conservative as their energy dissipates due to Ohmic losses and radiation to the (external) environment. Consequently, a plasmonic resonance is in terms of its photonic properties insufficiently captured by a simple real-frequency eigenmode. Generally, the photonics of a plasmonic resonance can be realistically described by taking Ohmic dissipation and radiation losses on board dynamically, such as within an appropriate finite-difference time-domain simulation¹³ or in terms of quasi-normal modes (QNM) with complex eigenfrequencies.^{21–24} The QNM description is also useful for understanding interaction between plasmons and quantum emitters. In a non-dissipative optical cavity, the emission properties of quantum emitters are modified by a sum of positive contributions from each cavity mode. In a system composed of a lossy plasmonic nanocavity and quantum emitters, on the other hand, the emitters' emission properties are determined by coherent superposition of the QNMs.²³ Here, key properties of a plasmonic mode, i.e., the mode volume and quality factor, and its interaction with quantum emitters are outlined within the QNM framework. More comprehensive introductions and further background can also be found in recent works of Lalanne *et al.*²² and Kristensen *et al.*²⁵

A. Quasi-normal modes

Each QNM has a complex eigenfrequency of $\tilde{\omega}_m = \omega_m - i\gamma_m$, where the real and imaginary parts correspond to its spectral frequency and dissipation rate, respectively. For a general non-conservative system, QNMs can be calculated by solving time-harmonic, source-free Maxwell's equations,²²

$$\begin{pmatrix} 0 & -i\mu^{-1}(\mathbf{r}; \tilde{\omega}_m) \nabla \times \\ ie^{-1}(\mathbf{r}; \tilde{\omega}_m) \nabla \times & 0 \end{pmatrix} \begin{pmatrix} \tilde{\mathbf{H}}_m \\ \tilde{\mathbf{E}}_m \end{pmatrix} = \tilde{\omega}_m \begin{pmatrix} \tilde{\mathbf{H}}_m \\ \tilde{\mathbf{E}}_m \end{pmatrix}, \quad (1)$$

where $\varepsilon(\mathbf{r}; \tilde{\omega}_m)$ and $\mu(\mathbf{r}; \tilde{\omega}_m)$ are the position- and frequency-dependent permittivity and permeability tensors. $\tilde{\mathbf{E}}_m$ and $\tilde{\mathbf{H}}_m$ are the QNM electric field and QNM magnetic field, respectively, which satisfy the Sommerfeld radiation condition for outgoing waves at $r = |\mathbf{r}| \rightarrow \infty$. The QNM fields also diverge at infinity and, thus, require special treatment for their normalization.²⁶ In numerical simulations, diverging QNM fields can in a finite computational space be taken care of by introducing absorbing boundary conditions, such as perfectly matched layers.^{22,27}

B. Mode volume and Purcell factor

For a quantum emitter placed in close proximity to a dissipative system, its enhanced emission properties and coupling strength can be described by a position-dependent complex-valued mode volume $\tilde{V}_m$ of each QNM, which defines the field confinement locally experienced by the emitter. This definition of the mode volume is in stark contrast to the conventional definition for a dielectric microcavity where its mode volume is defined as a real position-independent optical property of the whole system.²¹ For an emitter with transition frequency ω and dipole moment $\boldsymbol{\mu}$ placed at position $\mathbf{r}_0$, the mode volume of the m th QNM is given by²²

$$\tilde{V}_m(\mathbf{r}_0) = \frac{1}{2\varepsilon_0 n^2 [\tilde{\mathbf{E}}_m(\mathbf{r}_0) \cdot \hat{\mathbf{e}}_\mu]^2}, \quad (2)$$

where n is the refractive index at the emitter's position and $\hat{\mathbf{e}}_\mu = \boldsymbol{\mu}/|\boldsymbol{\mu}|$ is the dipole moment unit vector.

In the weak coupling regime, the emitter's emission property is modified by the local field confinement from QNMs, enhancing its emission rate by the Purcell factor as²²

$$F(\mathbf{r}_0; \omega) = -\frac{3}{4\pi^2} \left(\frac{\lambda}{n}\right)^3 \sum_m \text{Im} \left[\frac{\omega}{2(\omega - \tilde{\omega}_m)} \frac{1}{\tilde{V}_m(\mathbf{r}_0)} \right], \quad (3)$$

where $\lambda = 2\pi c/\omega$ is the emission wavelength in vacuum. When the emitter is in resonance with the m th QNM ($\omega \approx \omega_m$), the coefficient $\omega/2(\omega - \tilde{\omega}_m)$ becomes proportional to the quality factor $Q_m = \omega_m/2\gamma_m$. In the limit where the system is dominated by a single weakly dissipated QNM with $\gamma_m \rightarrow 0$ and $\tilde{V}_m \rightarrow \text{Re}[\tilde{V}_m]$, the Purcell factor recovers its conventional form $F_m = (3/4\pi^2)(\lambda/n)^3(Q_m/V_m)$.

C. QNM quantization

Although significant progress has been made in treating dissipative electromagnetic systems with the QNM theory, most quantum mechanical analyses of lossy optical cavities, such as plasmonic systems, are implemented heuristically in terms of a dissipative Jaynes–Cummings (JC) model where optical and plasmonic losses are treated phenomenologically.²⁸ Franke *et al.* have recently introduced the QNM-JC model based on a symmetrization scheme for creation and annihilation operators.^{23,29} In the QNM-JC model, the effective Hamiltonian that governs a plexcitonic system consists of three parts: $H = H_p + H_e + H_I$. (1) $H_p = \hbar \sum_{mn} \Omega_{mn} a_m^\dagger a_n$ represents the quantized QNM fields that include the coupling between different symmetrized QNMs m and n with a coupling constant Ω_{mn} . $a_m^\dagger$ (a_m) is the creation (annihilation) operator, obtained via a symmetrizing orthonormalization transformation; (2) $H_e = \hbar \sum_e \omega_e \sigma^+ \sigma^-$ describes the quantum emitters with different transition frequencies ω_e , where σ^+ (σ^-) is the raising (lowering) operator for the emitters; (3) $H_I = -i\hbar \sum_m g_m \sigma^+ a_m + \text{H.c.}$ is the interaction Hamiltonian in the symmetrized QNM basis, and $g_m = \sum_n (\mathbf{S}^{1/2})_{nm} \tilde{g}_n$ is the symmetrized coupling strength, where the symmetrizing matrix $(\mathbf{S})_{mn}$ characterizes the overlap/coupling between different QNMs m and n , and $\tilde{g}_n = \sqrt{\frac{\omega_n}{2\varepsilon_0 \hbar}} \boldsymbol{\mu} \cdot \tilde{\mathbf{f}}_n(\mathbf{r}_0)$ denotes the overlap between the emitter dipole moment and the QNM eigenfunction $\tilde{\mathbf{f}}_n(\mathbf{r}_0)$.

In similar spirit as the form of a local mode volume $\tilde{V}_m$, a local coupling strength $\tilde{g}_n$ emphasizes the electromagnetic field locally

experienced by an emitter. For a system with multiple emitters, the total coupling strength can be calculated as an integral of the local coupling strength $g_m(\mathbf{r}_0)$ over the whole system,³⁰

$$g_{\text{tot}} = \sqrt{\int d^3\mathbf{r} |g_m(\mathbf{r})|^2}, \quad (4)$$

where the integral is reduced to a summation in the case of discrete emitters, $g_{\text{tot}} = \sqrt{\sum_i |g_m(\mathbf{r}_i)|^2}$. In a high-Q optical cavity, this expression recovers its conventional form of $g_{\text{tot}} = \sqrt{N}g_0$ by assuming that all N emitters experience the same electromagnetic field with mode volume V and coupling strength $g_0 = \mu\sqrt{2\hbar\omega/\epsilon_0 n^2 V}$.

The QNM-JC model provides a rigorous theoretical foundation for analyzing room-temperature plexcitonic strong coupling, including optical phenomena related to quantum fluctuation and high photon number. It does, however, not come without an extra cost. A fully quantized model requires computational resources that grow exponentially with the number of plasmonic modes and emitters' quantum states. This may present a challenge for plasmonic nanocavities that often involve a large collection of spectrally overlapping higher-order quasi-normal modes.²⁴ Alternatively, a dynamic semi-classical model, which treats emitters quantum mechanically and optical fields classically, could be employed to capture many relevant physical phenomena, especially those in the limit where the external pumping rate is smaller than the system's total decay rate.

III. ROOM-TEMPERATURE PLEXCITONIC STRONG COUPLING: STATE-OF-THE-ART

This section outlines recent developments of different configurations of plasmonic nanocavities and representative quantum emitters that satisfy the criteria for room-temperature strong coupling.

A. Plasmonic nanocavity configurations

Rapid progress in nanofabrication has, in the past 20 years, enabled nanoscale manipulation of plasmonic nanostructures. This has provided the foundation of nanoplasmonic room-temperature strong coupling, which has been studied with a wide range of configurations for plasmonic nanostructures, including (a) plasmonic nanoparticle (NP) arrays, (b) plasmonic NP arrays with microcavities, (c) single plasmonic NPs, (d) dimer plasmonic NPs, and (e) probe-like slit nanoresonators.

1. Plasmonic nanoparticle arrays

Since the coupling strength increases with the emitter number as $g \propto \sqrt{N}$, strong coupling is more easily realized in a collective coupling setup involving a large number of emitters. Hence, early experiments on room-temperature strong coupling have been demonstrated between collective plasmons and ensembles of quantum emitters.¹⁰ A typical configuration includes NP arrays^{31,38,39} [Fig. 1(a)] in which each NP collectively contributes to the coupling and forms collective lattice resonances. This constitutes a favorable platform for strong coupling studies, which alters the original interaction between single NPs and emitters.³⁹

2. Plasmonic nanoparticle arrays with microcavities

The NP array configuration can also be optically improved by a sandwiching arrangement inside an external mesoscopic/microscopic cavity³² [Fig. 1(b)], where the plasmonic nanocavity is hybridized with a microcavity.^{15,40,41} The sandwich configuration takes advantage of both ultraconfinement from the plasmonic nanocavities and a low dissipation rate from the external cavity, making strong coupling more easily reachable across a wide spectral range.

3. Single plasmonic nanoparticles

In the past decade, the attention has been shifted from exploiting collective plasmons in NP arrays to reducing the mode volume of single NPs to enhance the interaction with individual quantum emitters. Example configurations of single NPs include core-shell nanospheres^{33,42} [Fig. 1(c)], nanoprisms^{34,43–45} [Fig. 1(d)], and elongated nanorods^{35,46,47} [Fig. 1(e)]. These configurations squeeze the plasmonic mode volume down to below $\sim 100 \text{ nm}^3$ [Fig. 1(e)] and successfully facilitated room-temperature strong coupling at the single emitter limit.³⁵

4. Dimer plasmonic nanoparticles

The field confinement property of single NPs can be enhanced even further at extremely small gap widths of only a few nm between the two NPs. At such a nanogap, plasmonic modes of the two NPs hybridize and form dimer plasmonic modes with an extreme field confinement property. Dimer plasmonic configurations include bowtie³⁶ [Fig. 1(f)], nanosphere on mirror^{11,48} [Fig. 1(g)], and nanocube on mirror^{37,49,50} [Fig. 1(h)]. Among these configurations, the NP-on-mirror (NPoM) nanocavity^{11,37,48–50} was the first to demonstrate room-temperature strong coupling with single quantum emitters.¹¹

5. Probe-like slit nanoresonator

Although nanogaps can provide enormous field enhancement, fabrication is generally challenging. Positioning emitters at the hotspot inside the nanogap are even more challenging and rely on probabilistic techniques¹¹ or DNA origami. A probe-like slit nanoresonator [Fig. 1(i)] that can be freely moved, however, enables deterministic and tunable near-field (cavity-free) strong coupling with colloidal quantum dots at room temperature.¹²

B. Plasmonic nanocavity modes

In practice, it still remains challenging to fabricate plasmonic NPs in perfect geometric shapes such as perfect spheres. In fact, NPs are always faceted and possess complex eigenmodes that are spectrally and spatially overlapping. As a result, an optical field incident on these nanostructures almost always excites multiple modes simultaneously, making it difficult to isolate individual modes and interpret near-field and far-field results.⁵¹ Hence, thorough theoretical and numerical investigations on eigenmodes of plasmonic nanocavities are essential for understanding their experimental behavior.^{24,52} Such understanding could lead to designs for functional plasmonic devices, as demonstrated by a recent work on single-molecule nanoscopy.⁵³

So far, most studies have focused on plasmonic gap modes that are confined within a nanoscale space between metal surfaces. The gap

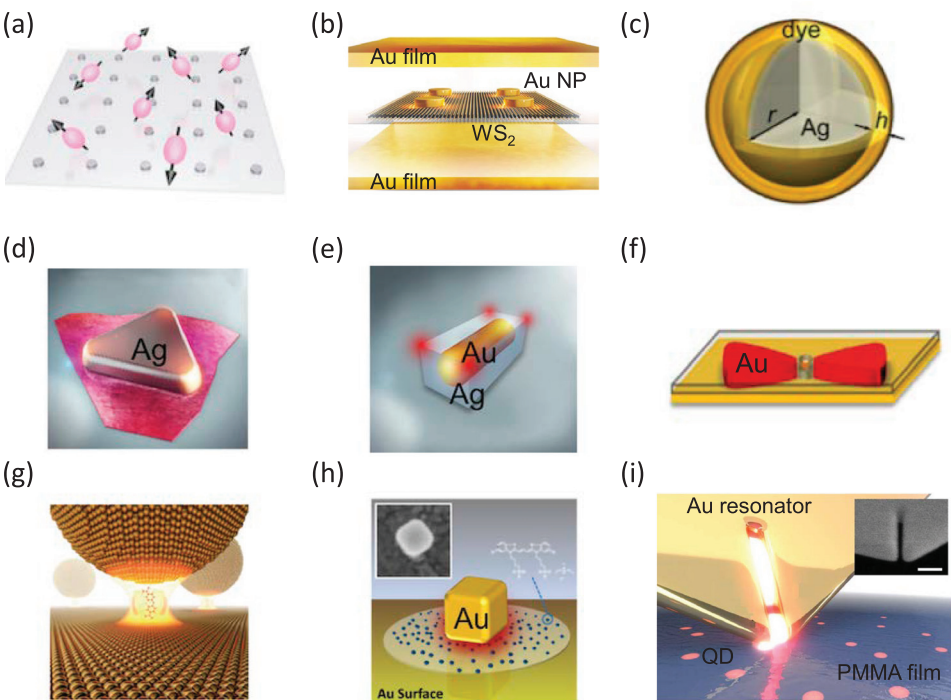


FIG. 1. Plasmonic nanocavity configurations for strong coupling. (a) Silver cylinder array on glass. Adapted with permission from Väkeväinen *et al.*, *Nano Lett.* **14**, 1721–1727 (2014).³¹ Copyright 2014 American Chemical Society. (b) Nanoparticle array sandwiched between gold films. Adapted with permission from Bisht *et al.*, *Nano Lett.* **19**, 189–196 (2019).³² Copyright 2019 American Chemical Society. (c) Nanosphere core with an emitter shell. Adapted with permission from Antosiewicz *et al.*, *ACS Photonics* **1**, 454–463 (2014).³³ Copyright 2014 American Chemical Society. (d) Nanoprism on the emitter sheet. Adapted with permission from Zengin *et al.*, *Phys. Rev. Lett.* **114**, 157401 (2015).³⁴ Copyright 2015 American Physical Society. (e) Nanorod coated with a cuboid nanoshell. Adapted with permission from Liu *et al.*, *Phys. Rev. Lett.* **118**, 237401 (2017).³⁵ Copyright 2017 American Physical Society. (f) Bowtie on glass. Adapted with permission from Santhosh *et al.*, *Nat. Commun.* **7**, 1–5 (2016).³⁶ Copyright 2016 Springer Nature. (g) Nanosphere on mirror. Adapted with permission from Chikkaraddy *et al.*, *Nature* **535**, 127–130 (2016).¹¹ Copyright 2016 Springer Nature. (h) Nanocube on mirror. Adapted with permission from Chen *et al.*, *Nano Lett.* **17**, 3246–3251 (2017).³⁷ Copyright 2017 American Chemical Society. (i) Slit-like nanoresonator. Adapted with permission from Groß *et al.*, *Sci. Adv.* **4**, eaar4906 (2018).¹² Copyright 2018 American Association for the Advancement of Science.

modes arise from a hybridization of the plasmonic modes from the opposite sides of the gap and provide a more intense field enhancement and stronger interaction with quantum emitters.⁵⁴ However, these gap modes couple weakly to the far field, except for a few lower-order modes.²⁴ On the other hand, plasmonic antenna modes of single NPs couple often strongly to the far field, while providing much weaker field enhancement. By hybridizing gap modes with antenna modes, a mode with both large field enhancement and large radiation efficiency can be achieved,⁵⁵ enabling subwavelength manipulation of light and an interface to the far field. Alternatively, an antenna mode with high field enhancement can also be realized by simply coating the NP with a layer of dielectric^{18,56} in a nanocube-on-mirror configuration.

C. Quantum emitters

Typical quantum emitters for realizing room-temperature strong coupling are summarized in Table I. This includes semiconductor quantum dots (QDs), dye molecules, and two-dimensional (2D) materials. At room temperature, quantum emitters experience large dephasing due to electron scattering, and plasmonic nanocavities are required to have a sufficiently small mode volume of $<10^{-5}\lambda^3$, in order for the systems to reach the strong coupling regime.

Semiconductor QDs, such as GaAs, often have a much larger dipole moment than other types of quantum emitters. However, the sizes of QDs are often larger than 2 nm and cannot fully exploit ultra-small mode volumes of plasmonic nanocavities. Strong coupling with QDs has been demonstrated with, e.g., a bowtie³⁶ and slit nanoresonator,¹² as shown in Figs. 1(f) and 1(i). On the other hand, dye molecules are much smaller than QDs but often have a smaller dipole moment. For example, a dye molecule such as a methylene blue could fit into a 0.9 nm gap in an NPoM nanocavity and reach the strong coupling

TABLE I. Typical emitters for the strong coupling study in plexcitonic systems, together with their transition dipole moment.

Emitters	μ (Debye)	Emitters	μ (Debye)
GaAs QD ⁶²	92	MAPbI ₃ ⁶³	46
CdSe QD ⁶⁴	~10	Graphene ⁶⁵	10
Methylene blue ¹¹	3.8	WS ₂ ⁶⁶	56
TDBC J-aggregate ³⁴	20	WSe ₂ ⁶⁷	7
PIC J-aggregate ³⁵	34	Defects in h-BN ⁶⁸	0.2–0.9
Rhodamine ^{69,70}	~5	Defects in diamond ⁷¹	~0.8

regime even though it has a dipole moment of 3.8 Debyes,¹¹ as shown in Fig. 1(g). Other promising candidate quantum emitters include defect color centers in hexagonal boron nitride (h-BN)⁵⁷ and nanodiamonds,^{58,59} whose emission properties are shown to be drastically altered by plasmonic nanocavities.^{60,61}

Recently, 2D materials such as transition metal dichalcogenides (TMDCs) have emerged as alternative quantum emitters for room-temperature strong coupling. TMDCs allow for electrostatic doping and are capable of tuning the strong coupling processes. However, the dominant directions of TMDC's transition dipole moments are usually aligned in-plane. This results in inefficient coupling between TMDCs with plasmonic modes that are dominantly aligned out-of-plane in most plasmonic configurations. As a result, most experiments on strong coupling with TMDCs so far report relatively low Rabi splittings of below 200 meV.^{48–50} The large dipole moment of TMDCs also arises from a collection of bound excitons that are delocalized throughout the TMDC sheets, and a direct analog to two-level atoms should be avoided while dealing with their excitonic excitation.³⁰

IV. APPLICATIONS OF ROOM-TEMPERATURE PLEXICITONIC STRONG COUPLING

In recent years, a wide range of theoretical and experimental studies have been devoted to quantum plasmonics.^{14,15,72} With the demonstration of single-emitter strong coupling in plexcitonic systems,^{11,12,35} we can now explore applications of plexcitonic strong coupling. In this section, we focus on several theoretical studies that attempt to bring plexcitonic strong coupling to different application scenarios. Starting from a single emitter that strongly couples to a plasmonic nanocavity, quantum immunoassay sensing has been proven to be feasible (Sec. IV A). It serves as a biochemical sensing scheme that utilizes light-matter strong coupling to drastically enhance the sensitivity down to the single-molecule limit.¹⁷ With two or more emitters that strongly couple to the same plasmonic nanocavity, entangled qubits¹⁸ and reconfigurable single-photon sources⁷³ are achievable (Sec. IV B), which form the basic building blocks for quantum information processing. With the development of the concept of microcavity plasmonics,^{15,19,40} we foresee a bright future of plexcitonic strong coupling in other areas as well, e.g., cavity-assisted ultrafast long-range periodic energy transfer between plasmonic nanoantennas.⁷⁴

A. Quantum plasmonic immunoassay sensing

1. Strong-coupling immunoassay setup

The proposed schematic is illustrated in Fig. 2(a) consisting of four main components: (i) a hemisphere dimer plasmonic nanocavity that provides a light-enhancing plasmonic hotspot, (ii) an antigen as the “analyte” to be detected, (iii) two antibodies that are paired with the target antigen, and (iv) a quantum emitter label that is chemically linked with the antibody-antigen-antibody complex. The quantum emitter label (such as a quantum dot or a dye molecule) is initially positioned such that it is optimally located at or close to the plasmonic hotspot and such that it couples strongly with plasmons. Figure 2(b) demonstrates the sensing capability of the proposed strong-coupling immunoassay by comparing its extinction cross section spectrum with those of conventional plasmonic immunoassays. The spectra of a conventional plasmonic immunoassays show a characteristic shift of the optical resonance. In contrast, the strong-coupling immunoassay

exhibits two split peaks, which is known as the characteristic Rabi splitting. This is in effect a bi-directional shift with higher sensitivity than those of conventional immunoassays.

2. Evidence of strong coupling

In an emitter-labeled plasmonic immunoassay, the extinction spectrum originates from stimulated absorption and emission processes whose signals interfere with the background excitation light. Hence, the “splitting” manifested in the extinction spectrum is not definitive proof that the coupled system is in the strong coupling regime. To provide stronger evidence that the proposed immunoassay is indeed in the strong coupling regime, we calculate photoluminescence (PL) spectra of the emitter labels. Unlike extinction spectra, the PL reveals the spontaneous emission of the coupled system without the background excitation light.

Figure 2(c) compares the PL and extinction spectra for strong-coupling immunoassays with gap sizes of 2–6 nm and emitter labels placed at the plasmonic hotspots. The discrepancy between the PL and extinction spectra becomes more significant at large gap sizes (>4 nm) where splittings only appear in the extinction spectra. The single peak in the PL spectrum implies that the emitter and plasmons are, in fact, in the weak coupling regime. For smaller gap sizes (<4 nm), splittings can be observed in both the PL and extinction spectra, indicating a strong coupling regime.

Strong coupling is also evident in the time dynamics of the system. The polarization dynamics $P(t)$ of the emitter is shown in Fig. 2(d) for gap sizes of 2–6 nm where $P(t)$ is normalized by the incident field amplitude $\epsilon_0|E_0|$. For small gap sizes of <4 nm, the dynamics clearly shows ultrafast Rabi oscillations with a period of less than 40 fs. These oscillations arise from rapid energy exchange between the emitter and plasmons.

3. Multianalyte detection

In a typical immunoassay measurement, multiple analytes are present in a liquid solution. To simulate more realistic experiments, let us consider an ensemble of emitter-labeled analyte complexes that are randomly scattered in the vicinity of a nanodimer, Fig. 2(a). In most cases, analyte-emitter complexes will be distributed around the nanodimer, and the emitters in these complexes couple weakly with plasmons. We define sensing in this scenario as sensing in the “classical” regime. However, there is a chance that a complex will be located optimally close to or within the gap between the two hemispheres, and the emitter label becomes strongly coupled with the nanodimer. Sensing in this case is defined as the “quantum” sensing regime. Figure 2(e) shows a statistical study on the extinction spectra of the nanodimer with different average surface densities of analyte-emitter complexes. At a large surface density, no boundary can be observed between the two regimes. However, the figure of merit (FoM) in the quantum regime remains roughly constant. This is because the spectrum in the quantum sensing is dominated by the dynamics of one emitter located at the plasmonic hotspot.

The results suggest that the proposed strong-coupling immunoassay protocol massively outperforms conventional shifting-type sensors. However, it is not without fabrication challenges related to the nanogap and alternative realizations such as such a plasmonic nanocube that provides sufficient field confinement at its corners is more

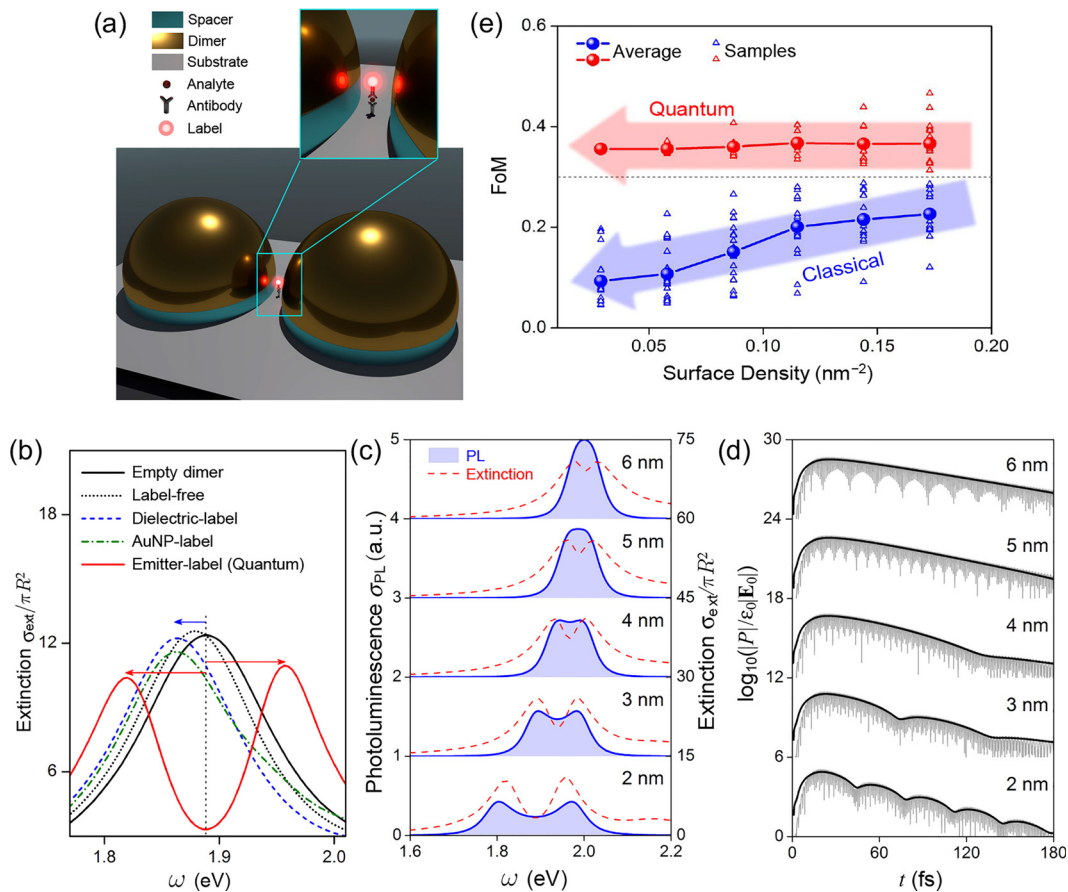


FIG. 2. Quantum plasmonic immunoassay sensing. (a) A schematic of the strong-coupling immunoassay where an analyte-emitter complex is captured at the plasmonic hot-spot of a gold hemisphere nanodimer. (b) Performance comparisons between the strong-coupling immunoassay sensor and different conventional plasmonic sensors. (c) Photoluminescence (blue solid lines) and extinction cross-sectional (red dashed lines) spectra for dimers with a gap size of 2–6 nm and a transition dipole moment of $\mu = 20\text{D}$. (d) The temporal dynamics of polarizations $|P(t)|$ (gray curves) and the corresponding envelopes (black curves) in the logarithmic scale. (e) Figure of merit (FoM) in classical and quantum regimes with different surface densities of analyte-emitter complexes. The triangles represent the FoMs of individual simulations, whereas the spheres correspond to the averages at each surface density. Adapted with permission from Kongsuwan *et al.*, *Nano Lett.* **19**, 5853–5861 (2019).¹⁷ Copyright 2019 American Chemical Society.

accessible for biomolecules.³⁵ Another alternative protocol uses artificial proteins to capture an antigen between a plasmonic dimer without using much larger antibodies.^{75–77}

B. Building blocks for quantum information processing

1. Qubit entanglement mediated by an antenna mode

An antenna mode in a coated nanocube-on-mirror (*c*-NCoM) nanocavity as depicted in Fig. 3 typically has multiple hotspots located at the upper corners of the nanocubes.¹⁸ These are relatively easy to access for enhancing various physical or chemical processes such as sensing.¹⁷ Remarkably, typical values of the field enhancement of the antenna mode in the *c*-NCoM geometry are comparable to the enhancement of the fields in coated nanosphere-on-mirror (*c*-NSoM) cavities. At the same time, due to the field confining effects of the

dielectric coatings, the enhancement is much stronger than that in the case of the layered nanocube-on-mirror (*l*-NCoM) system.

The most attractive feature of the antenna mode lies in its multiple exterior hotspots. It is, therefore, possible to consider entanglement of two single emitters placed at the upper corners of the nanocube via the antenna mode within a single *c*-NCoM nanocavity, as illustrated in the inset of Fig. 3(d). For a system where two quantum emitters QE1 and QE2 are coupled to a nanocavity with a typical single-emitter coupling strength of $g_0 = 80\text{ meV}$, we demonstrate the dynamics of the excited-state populations of QE1 and QE2 in Fig. 3(d). Clearly, there is an oscillatory exchange of excited state population between two of them. The concurrence C can be employed to systematically characterize the degree of entanglement between the two qubits.⁷⁸ It is found that the maximum concurrence of $C = 0.6$ can be achieved in the strong coupling regime for a carefully designed off-resonant system with an emitter-cavity detuning of $\Delta_{\text{e,c}} > 0.2\text{ eV}$. The dependence of the concurrence C on g_0 is exemplified in Fig. 3(e) in an off-resonant system

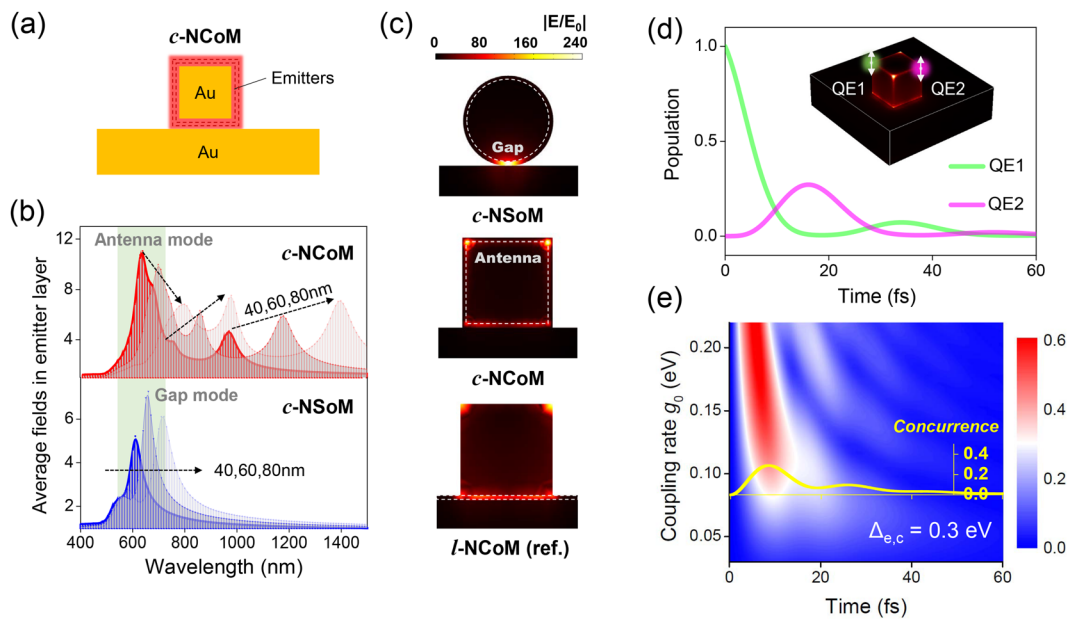


FIG. 3. Qubit entanglement mediated by an antenna mode. (a) Schematics of c-NCOM. (b) Modes in c-NCOM and c-NSoM for a fixed emitter thickness of 2 nm. (c) Near-field distributions of the modes in c-NSoM, c-NCOM, and l-NCOM. The nanoparticles have the same size of 40 nm with 2 nm emitter coating. (d) Two-emitter entanglement mediated via the antenna mode (inset: schematics) and the calculated dynamics of the excited state population, when QE1 and QE2 are simultaneously coupled to the nanocavity in resonance with $g_0 = 80$ meV. (e) The time evolution of the concurrence C for different values of the emitter-nanocavity coupling strength g_0 , with fixed detuning $\Delta_{e,c} = 0.3$ eV. Inset: a case study of $g_0 = 80$ meV. In all calculations, the resonant frequency of the nanocavity: $\omega_c = 640$ nm (1.94 eV) and decay rates of the nanocavity and emitters: $\kappa = 80$ meV and $\gamma_{e1(2)} = 40$ meV. Adapted with permission from Xiong *et al.*, *Nanophotonics* 9, 257–266 (2020).¹⁸ Copyright 2020 De Gruyter.

with $\Delta_{e,c} = 0.3$ eV. In the inset, we show the dynamics for a case study at $g_0 = 80$ meV, and a notable degree of entanglement $C \sim 0.4$ can be achieved. It should be noted that plasmon-mediated qubit entanglement has also been studied in plasmonic nanowires^{79–83} and metallic nanoparticles in the weak-to-intermediate coupling regime.⁸⁴ The work presented here¹⁸ extends the possibility to the strong coupling regime due to the remarkable three-dimensional field confinements provided by the antenna mode and reveals the dependence of the concurrence on the single-emitter coupling rate and the emitter-cavity detunings.

2. Reconfigurable single-photon sources

Single-emitter experiments such as summarized in Sec. III successfully propel active plasmonics into the quantum regime, typically characterized by an anharmonic energy structure as illustrated in Fig. 4(a), making the photon blockade (PB) highly feasible.⁸⁵ Meanwhile, an unconventional photon blockade (UPB) is also readily achievable in such a plexcitonic system by carefully engineering the quantum interference between different excitation pathways for multiple photons. With these concepts, we can now propose to operate a quantum plexcitonic system as a reconfigurable single-photon source⁷³ between the PB antibunched single photon beam and UPB antipaired photons with certain probability to emit bunched photons of three or more. It should be noted that for illustration purposes, a spherical Au nanoparticle is shown in Fig. 4(b). In practice, plasmonic nanocavities offering strong field localization as shown in Fig. 1 would be more feasible, e.g., a single nanoprism as shown in Figs. 4(c)–4(e).

To explain the concept of reconfiguration, we externally rotate the polarization angle α of the incident light in Figs. 4(c)–4(e) on a nanoprism-e₁ resonant plexcitonic system. The emitters coated around the nanoprism surface are now distinguished by their location, where we highlight the three apexes with strong plasmonic field enhancements: A, B, and C. Upon rotation of the polarization angle α from -30° to 150° , the electric fields at the three locations change periodically as shown in Fig. 4(d). These electric fields directly influence the local coupling rates³⁵ that can be approximated as $g_A = 85|\cos\alpha|$, $g_B = 85|\cos(\alpha - 60^\circ)|$, and $g_C = 85|\cos(\alpha + 60^\circ)|$ and led to the calculated correlation functions $g^{(2)}(0)$ and $g^{(3)}(0)$ in Fig. 4(e). Evidently, we observe a repeating reconfiguration pattern of PB-UPB with tuning the polarization angle α .

V. OUTLOOK

In this perspective, we have focused on recent progress and applications of plasmonic nanocavities that facilitated room-temperature plexcitonic strong coupling. While room-temperature plexcitonic strong coupling was initially realized with an ensemble of quantum emitters that respond collectively to plasmon excitation, advances in nanofabrication have provided sub-nanometer control over plasmonic nanostructures, bringing room-temperature plexcitonic strong coupling down to the single emitter limit. Of course, the natural next step is coherence control of a few quantum emitters and realization of multiple-emitter quantum operations at room temperature, and many more fascinating phenomena can be envisioned if advancing beyond the strong coupling into the ultrastrong coupling regime.^{86,87}

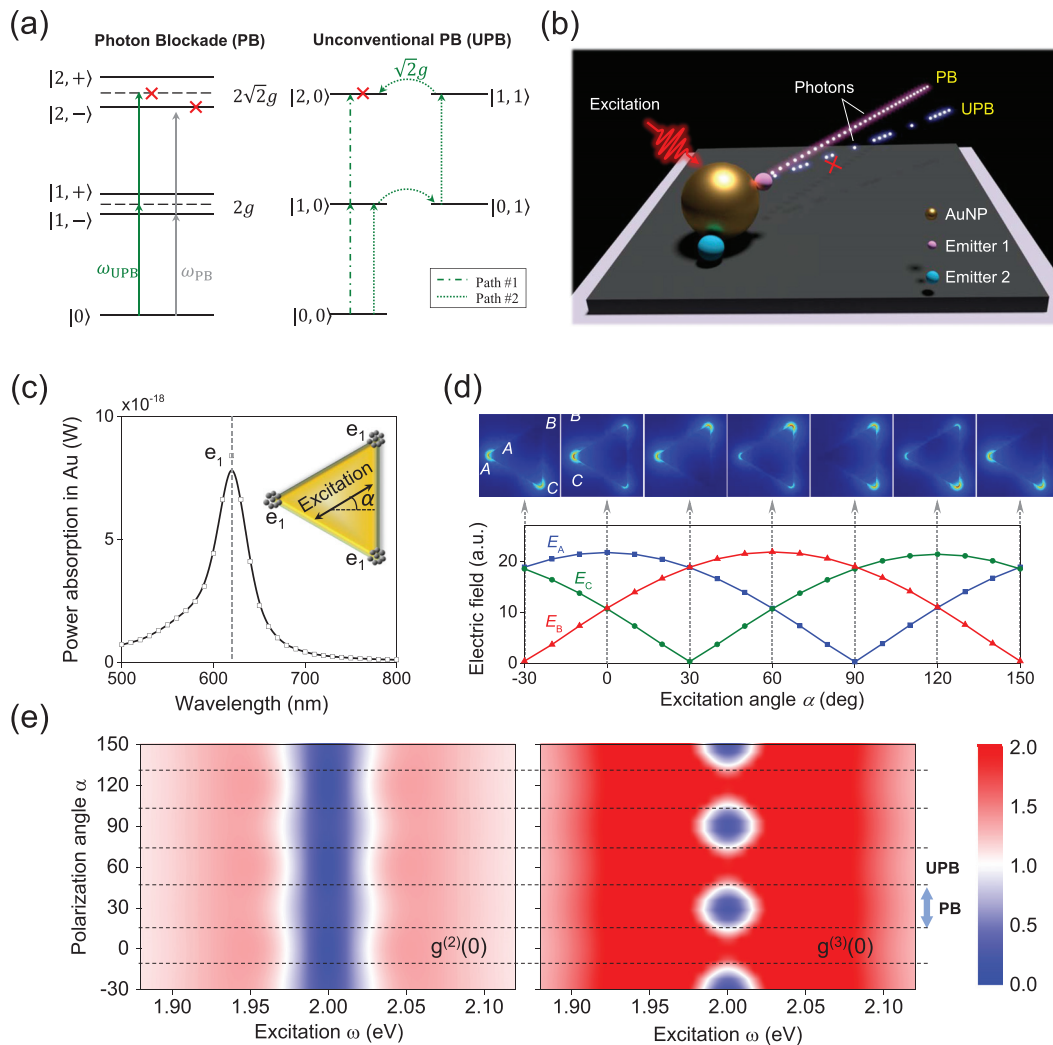


FIG. 4. Reconfigurable single-photon sources. (a) Energy level diagram showing a two-level quantum emitter coupled to a nanocavity in resonance with coupling rate g . The suppression of two-photon emission is due to the anharmonic Jaynes–Cummings ladder for PB and the destructive interference of two distinct dissipative-driven pathways for UPB. (b) Schematics of the proposed quantum plexcitonic system for a reconfigurable single-photon source. (c)–(e) Optically reconfigurable single-photon sources based on nanoprisms. (c) Reconfigurable single-photon source modulated by the polarization angle α of the incident light (inset: schematics) and the designed nanoprism plasmon mode in resonance with the emitters e_1 . (d) Electric field distributions of the nanoprism plasmon mode (top) and the local electric fields at the three apexes (bottom) as a function of α . (e) The effect of α on the correlation functions $g^{(2)}(0)$ and $g^{(3)}(0)$, with the PB region highlighted by the light blue arrow. Adapted with permission from You *et al.*, Nano Lett. **20**, 4645–4652 (2020).⁷³ Copyright 2020 American Chemical Society.

As particular examples, we have highlighted an immunoassay sensing scheme that employs strong coupling and quantum emitters as sensing labels.¹⁷ While a detailed statistical analysis with random positions of the analytes demonstrates that the proposed protocol works well and clearly serves as an important proof of principle for further designs of plasmonic immunoassay sensors, the concept could also be conceivably extended to detect other quantum objects such as electronic spins in nanodiamonds.⁸⁸ We have also deliberated on proposals for utilizing plexcitonic building blocks for quantum information processing, particularly for plasmon-mediated two-qubit entanglement and reconfigurable single-photon emission. These concepts build on designing multiple hotspots with deep sub-wavelength

field localizations in a single plasmonic nanocavity, which make attached quantum emitters spatially distinguishable while still strongly coupled to the same plasmonic nanocavity. Collating a few or an array of such building blocks together in a systematic and controlled manner is certainly a promising route toward scalable room-temperature quantum networks.

While allowing strong coupling at room temperature, nanoplasmonic cavities also facilitate—as directly uncovered in our numerical simulations—plexcitonic dynamics on timescales shorter than 20 fs. Such ultrafast dynamics conceivably enables sub-picosecond quantum operations at room temperature and allows, for example, nearfield-induced dynamic bipartite quantum entanglement through a CNOT

quantum operation⁸⁹ to be performed before decoherence effects become significant. Future research should investigate the potentials of plasmonic nanostructures as alternative or complementary platforms for noisy intermediate scale quantum (NISQ) technology.⁹⁰ Given the current pace of progress in the plasmonics community, we envision that room-temperature single- and multiple-qubit gates will soon be reliably realized in nanoplasmonic platforms, opening up a pathway toward room-temperature quantum technologies.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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