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Ultrastrong coupling in single plexcitonic nanocubes

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Abstract: Light-matter strong coupling is defined when the coupling strength exceeds the losses in the system, whereas ultrastrong coupling is not simply strong coupling with even larger coupling strength. Instead, ultrastrong coupling regime arises when the coupling strength is comparable to the transition frequency in the system. At present, ultrastrong light-matter interactions have been achieved in superconducting circuits, semiconductor polaritons, and organic molecules, where these systems are typically at the micrometer scale. In this work, we investigated ultrastrong coupling in a nanoparticle plexcitonic system, i.e. a single gold nanocube coated with quantum emitters and positioned on a gold film. We observed a normalized coupling rate $\eta \sim 0.12$ to the antenna mode in such coated nanocube-on-mirror (c-NCoM) configuration at the multilayer emitter level. In contrast to the gap mode that squeezes all the optical fields into the gap region, the antenna mode in c-NCoM provides multiple exterior hot spots at the upper corners of the nanocube, which can be exploited for qubit entanglement within a single nanocube. The concurrence between adjacent emitters is estimated up to 0.6. This theoretical study establishes a promising route toward building a scalable quantum network using single plexcitonic nanocubes as quantum nodes.

1 Introduction

The definitions of weak, strong, and ultrastrong coupling compare the light-matter coupling strength g with different parameters. In the weak coupling regime, g is smaller than the losses in the system; therefore, energy is lost before it can be exchanged between light and matter. In the strong coupling regime, where g exceeds the losses in the system, an oscillatory energy exchange is expected, which is called Rabi oscillation [1, 2]. Ultrastrong coupling, in contrast, compares g with bare energy ω in the system. The dimensionless parameter to quantify ultrastrong coupling, i.e. normalized coupling rate $\eta = g/\omega$, has been summarized for different experimental systems [3, 4], where $\eta = 0.1$ is often set as the ultrastrong coupling threshold due to the initial experimental demonstration in 2009 [5]. It is believed that ultrastrong coupling enables more efficient interactions and opens up new avenues for studying nonperturbatively coupled light-matter systems, leading to novel applications in quantum information processing (e.g. extremely fast quantum gate operations), higher-order processes and nonlinear optics, and photochemistry [3, 4].

In the past decade, ultrastrong coupling has been successfully realized in several different systems [3, 4], such as intersubband polaritons in microcavity-embedded doped quantum wells [6], Landau polariton systems [7], organic molecules [8], and superconducting circuits [9], and has also been extended to optomechanics [10]. Most of these systems are operating at the micrometer length scale [3, 4], except one optomechanical setup involving a plasmonic picocavity interacting with the vibrational mode of individual molecules, reaching $\eta = g/\omega_m = 0.3$ (ω_m is the mechanical frequency) [10]. The increased coupling strength benefits from the extremely small mode volume ($<1 \text{ nm}^3$) of the plasmonic picocavity. This experiment clearly points out the promising direction of accessing the ultrastrong coupling regime in a plexcitonic system, which

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involves the interactions between plasmon-polaritons and molecular excitons. Such system would take advantage of (i) extremely confined mode volume of plasmonic cavity and (ii) giant transition dipole moment of organic molecules, providing a possibility to reduce the overall system size to nanometer scale.

These properties are particularly meaningful in quantum information science, whose development has been hindered by some crucial problems, e.g. quantum decoherence, coherent connection between quantum nodes, and device scalability. To solve these problems, plasmonic systems emerge as a promising platform for future quantum technology [11–13]. First, due to its ability to concentrate light within ultra-small dimensions, plasmonic structures have gained notable reputations on constructing compact optoelectronic nanodevices with quantum features of photons, such as plasmonic quantum logic gates [14] and quantum interferometer [15]. Second, the study of strong coupling between plasmon-polaritons and quantum emitters (QEs) reveals Rabi oscillation periods shorter than the coherent time of the involved quantum plasmonic system, paving the way of overcoming the decoherence effect. It is worth noting that strong coupling between plasmon-polaritons and a single QE has been experimentally demonstrated at room temperature [16–18], showing the potential of fast coherent manipulation at a single qubit level in ambient conditions. Third, coherent connection between quantum nodes relies on entangled qubits, which has also been explored in plasmonic systems showing robustness and a high degree of entanglement [19–21]. On top of these achievements, plasmonic systems that are able to simultaneously address all the above-mentioned problems are highly desirable.

Nanoparticle-on-mirror (NPoM) structures have shown outstanding potentials for quantum plasmonics. Due to the small gap between the metal nanoparticle (e.g. cube and sphere) and the metal film (i.e. the mirror), light can be extremely concentrated down to picometer scale [10, 22–24], bringing about unparalleled progresses in a single photon source [25, 26], strong coupling [16, 27–30], and quantum entanglement [31]. These pioneering studies of NPoM are mostly focused on gap plasmons. In this work, to be more specific, we differentiate NPoM into nanosphere-on-mirror (NSoM) and nanocube-on-mirror (NCoM) and coat QEs around the entire surface of the nanoparticles to take advantage of all the enhanced fields [32]. We will demonstrate the advantages of the antenna mode of the NCoM configuration. Based on this antenna mode, both ultrastrong plexcitonic coupling and high degree of entanglement can be achieved within a single NCoM, which could represent a nanoscale quantum node

in a highly scalable quantum network, enabling ultra-fast operation at femtosecond scale. Beyond the antenna mode, NCoM configuration is also shown to be a good platform that allows QEs to strongly couple to different cavity modes simultaneously.

2 Antenna mode

The schematic of coated NCoM (c-NCoM) in our study is shown in Figure 1A, where an Au nanocube is coated with layers of emitters and positioned on an Au film. It differs vastly from the most frequently studied NCoM configuration where the emitters are dispersed on the Au film [29], which we refer to as layered NCoM (*l*-NCoM). As most previous studies have been focused on the gap mode for the nanoparticle on mirror configurations (either a sphere or a cube) [16, 29], the potentials of the antenna mode have not been well explored. As illustrated in Figure 1B, the optical response of c-NCoM is compared to that of coated NSoM (c-NSoM) for various particle sizes driven by plane-wave excitation along the *x*-axis with only the E_z component. Note that the particle size refers to the side length of the cube for NCoM or the diameter of the sphere for NSoM. It is clear to see that c-NCoM has three sets of modes extending its working wavelength from 500 to 1500 nm for cube size from 40 to 80 nm. In contrast, c-NSoM has only one optical mode—gap mode in 500–800 nm range for the same sphere size from 40 to 80 nm.

We pick the 40 nm nanoparticles and focus on their optical modes in the visible range. We can clearly observe the mode profiles of the gap mode of c-NSoM (top) and the antenna mode of c-NCoM (middle) in Figure 1C. Different from the gap mode that squeezes all the fields into a single hot spot in the gap, the antenna mode supports multiple hot spots at the upper corners of the nanocubes. The field enhancements at these exterior hot spots of antenna mode in NCoM are comparable to that of gap mode in NSoM, which is induced by the incident E_z component. We have also performed simulations with incident E_x component or changing to glass substrates. The results reveal much weaker field enhancements, proving that the antenna mode originates from the combined effects of sharp corners of nanocube and strong reflection from the Au mirror substrate. It is interesting to note that the previously studied *l*-NCoM (Figure 1C, bottom) also supports a similar antenna mode, but the fields at the upper corners are much weaker. We attribute this antenna mode enhancement of c-NCoM to the field confining effects from the emitter coatings (with refractive index of 1.6).

Figure 1: Ultrastrong coupling in c-NCoM.

(A) Schematics of c-NCoM. (B) Optical modes in c-NCoM and c-NSoM configurations for nanoparticle sizes of 40, 60, and 80 nm (indicated by the direction of arrows) and an emitter thickness of 2 nm. The green block represents the interested wavelength range of the coated emitters, which are coupled to the antenna mode of c-NCoM and the gap mode of c-NSoM, respectively. (C) Near-field distributions of the optical modes coupled to the studied emitters in three different configurations: c-NSoM, c-NCoM, and l-NCoM. The nanoparticles have the same size of 40 nm with 2-nm-thick emitter coating. (D) Simulated normalized coupling rate η as a function of the number of emitter layers (where each emitter layer is assumed to be 1 nm thick) in the three configurations in (C). The blue-shaded area with $\eta > 0.1$ defines the ultrastrong coupling regime.

By coupling multiple layers of emitters (each layer is assumed to be 1 nm thick) to c-NSoM, c-NCoM, or l-NCoM configuration, we compare their normalized coupling rate η in Figure 1D (calculation details shown below). In all cases, the nanoparticles have a size of 40 nm. It has been found that the c-NSoM configuration (blue curve) supports the strongest coupling for single-layer coated emitters, with a normalized coupling rate $\eta > 0.1$, i.e. the ultrastrong coupling regime. This setup has been demonstrated in 2017 [16]. As the emitter coating gets thicker, the normalized coupling rate η drops and saturates, getting out of the ultrastrong coupling regime, due to the compromising effects of the rapidly dropped field enhancements in the gap and the increasing number of emitters. In contrast, c-NCoM (red curve) enters the ultrastrong coupling regime when there are at least six layers of coated emitters; for the reference case l-NCoM (black curve), it is generally more difficult to get into ultrastrong coupling regime as the antenna mode is not well exploited. It should be noted that the present study has used emitters with relatively small transition dipole moment $\mu = 3.8D$. All the curves in Figure 1D could be lifted up once emitters with larger μ are employed. We therefore conclude that both c-NSoM and

c-NCoM configurations are promising in single nanoparticle ultrastrong coupling.

However, it is worth noting that there are critical differences between c-NSoM and c-NCoM. The antenna mode in c-NCoM has multiple hot spots and these hot spots are located at the upper corners of the nanocubes, which are more easily accessible to enhance various physical or chemical processes such as sensing or catalysis, e.g. the recently proposed quantum plasmonic immunoassay sensing [33]. Additionally, the optical resonance of the antenna mode, as well as its strong field enhancement, is less sensitive to the gap size (see Supplementary Section S1), which makes it easier to be used in many practical applications. In the following, we will elaborate the detailed calculations on single nanoparticle ultrastrong coupling and how we can apply it for qubit entanglement.

2.1 Ultrastrong coupling to antenna mode

Ultrastrong coupling compares the coupling rate g with bare energies ω in the system (in our case, the exciton transition frequency ω_e). To calculate the normalized

strong coupling rate $\eta = g/\omega_e$, we extract the coupling rate g as half of the minimum Rabi splitting when the emitter resonance is swept across the cavity resonance, whereas the energy ω_e is taken as the energy at which the minimum Rabi splitting occurs. In our simulations, the emitters are modeled as dispersive medium with a Lorentzian permittivity:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{f\omega_e^2}{\omega_e^2 - \omega^2 - i\gamma_e\omega}, \quad (1)$$

where ε_∞ is the base material permittivity, f is the oscillator strength, ω_e is the exciton transition frequency, and γ_e is the exciton linewidth. Note that the oscillator strength f used here is directly related to the transition dipole moment μ of the emitters as $f = 2N_d\mu^2/\hbar\varepsilon_0\omega_e$, with N_d as the emitter density. These parameters for emitters are taken from Ref. [16], and the permittivity for gold is taken from Ref. [34]. All simulations are performed using finite-difference time-domain (FDTD) solutions from Lumerical, Inc. to calculate the scattering cross-sections of the plexcitonic systems under excitation of p -polarized light incident at 45° in the xz -plane to better mimic the experimental setup.

As shown in Figure 2A, we use c -NCoM and c -NSoM cavities with particle sizes of 40 nm, which have the fixed cavity resonance denoted as black dotted lines. The resonances of one-layer (1-nm-thick) emitters are then swept as indicated by green dashed lines. Here, the bare cavity resonance is obtained by coating the cube/sphere with one-layer dielectric with a refractive index of $n = 1.6$ to reproduce the electromagnetic environment of emitter coating. The bare emitter resonance is obtained by modeling the emitter layer as a hollow cube/sphere suspended in air with a thickness of 1 nm. All the spectra for the bare emitter have been normalized to the response of bare cavity. When the cavity and emitters are coupled to each other, the plexcitonic systems exhibit the scattering spectra denoted as shaded red and blue curves, respectively. The Rabi splittings signifying the strong coupling are subsequently extracted and plotted in Figure 2B as a function of the emitter wavelength λ_e . At the minimum point, the coupling rate g and the corresponding $\omega_e = 2\pi c/\lambda_e$ are recorded to calculate the normalized coupling rate η as shown in Figure 1D. It is noteworthy that, in Figure 2A, except for the upper and lower branches of the splitting spectra, there is a tiny peak in between, which consistently appears at the spectral location of the bare

Figure 2: Strong coupling simulations of the plexcitonic system.

(A) Simulated strong coupling between fixed cavities and emitters (1 nm thick, single layer), with emitter resonance λ_e swept from 640 to 720 nm for c -NCoM (left) and from 625 to 705 nm for c -NSoM (right). Dashed black/green lines represent the responses from bare cavities/emitters. (B) Rabi splittings extracted from the scattering cross-section spectra in (A) across different emitter wavelengths. The coupling rate g and the corresponding emitter wavelength λ_e or energy ω_e can be read at the minimum Rabi splitting. Two cases of 1- and 10-layer emitters are illustrated. (C) Near-field distributions in the 1-layer emitters (top) or 10-layer emitters (bottom) for the antenna mode of c -NCoM and gap mode of c -NSoM, respectively. In all cases, nanoparticles have the same size of 40 nm. Each emitter layer is assumed to be 1 nm thick with fixed oscillation strength $f = 0.27$, e.g. methylene blue molecules.

emitter (dashed green lines). This originates from those emitters sitting away from hot spots and not contributing to strong coupling (see Supplementary Section S2).

To understand the trend in Figure 1D, one should get clues from the near-field distributions shown in Figure 2C. For *c*-NSoM configuration, as the coated emitter or the gap gets thicker, it always has a single hot spot at the gap between the sphere and the mirror, and the field enhancement monotonically decreases. Meanwhile, the number of emitters in the hot spot that are involved in the strong coupling process gets larger. This compromising effect will eventually lead to a saturated coupling rate g . In contrast, *c*-NCoM has multiple hot spots. It is interesting to see in Figure 2C that *c*-NCoM with one-layer emitters has four major hot spots at the upper corners of the cube, whereas *c*-NCoM with 10-layer emitters holds eight hot spots at all corners as the cube is lifted up further away from the mirror (more examples in Supplementary Section S1). The increased number of hot spots, together with the increased number of participating emitters, enables an rapidly increasing coupling rate. In contrast, *l*-NCoM does not benefit from the hot spots at the upper corners and therefore exhibit a slower increasing trend for coupling rate.

It should be emphasized here that, from a theoretical point of view, absorption cross-section or photoluminescence spectrum could provide more accurate information to identify the interaction regime between emitters and cavity, especially for the transition regime from weak to strong coupling [33, 35]. In our case, plexcitonic systems are in the ultrastrong coupling regime; hence, the scattering cross-section is good enough to reveal the information of an interaction regime. Besides, the scattering cross-section also better mimics our experimental measurements [32]. Nevertheless, a simple comparison between absorption and scattering cross-sections is presented in Supplementary Section S3.

2.2 Antenna mode for qubit entanglement

The most fascinating feature of the antenna mode lies in its multiple hot spots. In this section, we will explore the possibility of entangling two single emitters at upper corners through the antenna mode within a single *c*-NCoM cavity. Entanglement lays the foundation in many areas of quantum information processing [36], e.g. quantum secret sharing [37, 38], quantum teleportation [39, 40], and quantum key distribution [41, 42]. Additionally, the exponentially increased degrees of freedom provided by quantum nodes also accelerate the development of quantum computation [43]. From the integration point of

view, entanglement within a single nanoparticle will drastically reduce the footprint of chips.

As illustrated in Figure 3A (inset), it is ideal to coat a single layer of emitters so that *c*-NCoM will have higher chance to interact with single emitters at the upper corners. Meanwhile, a larger coupling rate g_0 between those single emitters and the *c*-NCoM cavity is favorable. Intuitively, a larger coupling rate g_0 leads to a more rapid energy exchange, which effectively allows more rounds of quantum manipulation within the same decoherence time. In this study, the coupling rate g_0 between the single emitter and the *c*-NCoM cavity is derived from the collective coupling rate g between the single-layer emitters and the cavity from our FDTD simulations. Considering the single-layer emitters in *c*-NCoM consisting of N emitters, each emitter is individually coupled to the cavity with a coupling rate of g_i . Then, the collective coupling rate between single-layer emitters and the cavity can be derived via $g^2 = \sum_{i=1}^N g_i^2$. For the antenna mode of single-layer *c*-NCoM supporting only four hot spots at the upper corners, we assume that the four emitters sitting at the hot spots experience the same coupling rate g_0 , whereas the other emitters away from hot spots have negligible contributions to Rabi splitting. This assumption simplifies the collective coupling rate as $g \approx \sqrt{4g_0^2} = 2g_0$. In our FDTD study above (Figure 2B), the emitter layer has an oscillator strength of $f=0.27$ (or $\mu=3.8D$) [16], resulting in a collective coupling rate of $g=0.11$ eV between the one-layer emitter coating and *c*-NCoM. By varying the oscillator strength f representing various types of emitters, we show the corresponding collective coupling rate g in Figure 3B, which is found to be proportional to $\sqrt{f}$. Here, the same *c*-NCoM is used, with a cube size of 40 nm and one-layer/1-nm-thick emitter coating. We expect an increased collective coupling rate if other emitters with larger f are used, such as WS₂ monolayer [44] or heptamethine cyanine dye [45]. For example, if the oscillator strength goes up to $f=1$, the collective coupling rate reaches $g=0.16$ eV, whereas the corresponding single-emitter coupling rate could be $g_0=0.08$ eV.

In the following, we analyze the possibility of entanglement generation using single *c*-NCoM within the framework of quantum mechanics. For a system where two QEs, QE1 and QE2, are coupled to a cavity, the Hamiltonian is given by

$$H = \frac{\omega_c}{2} a^\dagger a + \frac{\omega_{e1}}{2} \sigma_1^+ \sigma_1^- + \frac{\omega_{e2}}{2} \sigma_2^+ \sigma_2^- + g_1 \sigma_1^+ a + g_2 \sigma_2^+ a + \text{H.c.}, \quad (2)$$

where ω_c and $\omega_{c(2)}$ are the frequencies for cavity and emitters, and $g_{1(2)}$ is the coupling strength between the cavity

Figure 3: Antenna mode for qubit entanglement.

(A) Dynamics of the excited-state population when QE1 and QE2 are entangled, with coupling rate $g_0 = 0.08$ eV and emitter-cavity detuning $\Delta_{e,c} = \omega_e - \omega_c = 0$. Inset, schematics of two-emitter entanglement in c-NCoM configuration. (B) Calculated collective coupling rate g for various types of QE layer with different oscillator strength f from FDTD simulations. The dashed line is fitted to $\sqrt{f}$. (C) Dynamics of concurrence C at different emitter-cavity detuning $\Delta_{e,c}$, with single-emitter coupling rate $g_0 = 0.1$ eV (left) and $g_0 = 0.2$ eV (right). (D) Dynamics of concurrence C at different single-emitter coupling rate g_0 , with the emitter-cavity detuning of $\Delta_{e,c} = 0$ (left) and $\Delta_{e,c} = 0.3$ eV (right). Inset, dynamics of concurrence C at the single-emitter coupling rate $g_0 = 0.08$ eV. In this study, the resonant frequency of cavity is fixed at $\omega_c = 1.94$ eV (640 nm) from Figure 2A. The decay rates of cavity and emitters are chosen as $\kappa = 0.08$ eV and $\gamma_{e1(2)} = 0.04$ eV, respectively.

and the emitter QE1(2). Here, $a^\dagger$ and $\sigma_{1(2)}^+$ are the creation operators for cavity and emitters, a and $\sigma_{1(2)}^-$ are the annihilation operators for cavity and emitters, and H.c. stands for Hermitian conjugation. The c-NCoM cavity and emitters are exposed in a dissipative environment, which is described by the Lindblad master equation:

$$\partial_t \rho = i[\rho, H] + \frac{\kappa}{2} \mathcal{D}[a]\rho + \frac{\gamma_{e1}}{2} \mathcal{D}[\sigma_1^-]\rho + \frac{\gamma_{e2}}{2} \mathcal{D}[\sigma_2^-]\rho, \quad (3)$$

where ρ is the density matrix of the coupled system and κ and $\gamma_{e1(2)}$ are the decay rates of cavity and emitters. The Lindblad terms $\mathcal{D}[\hat{o}]\rho = 2\hat{o}\rho\hat{o}^\dagger - \rho\hat{o}^\dagger\hat{o} - \hat{o}^\dagger\hat{o}\rho$ ($\hat{o} = a, \sigma_1^-, \sigma_2^-$) describe different dissipation channels from cavity and emitters to environment. We set the initial state of the system as $|1\rangle_{e1} \otimes |0\rangle_{e2} \otimes |0\rangle_c$, i.e. the qubit QE1/QE2 is in excited/ground state and the cavity is in vacuum state, and allow the system to evolve following Eq. (3). Employing a typical single-emitter coupling rate of $g_0 = 0.08$ eV derived from the collective coupling rate in Figure 3B, we demonstrate the dynamics of the excited-state populations of QE1 and QE2, as shown in Figure 3A. Here, the expectation value of the excited-state population is obtained by $n_i = \text{tr}(\rho \sigma_i^+ \sigma_i^-)$ ($i = e1, e2$). The Rabi oscillations

clearly indicate that the system enters into the strong coupling regime. More interestingly, there is an oscillatory exchange of excited-state population between QE1 and QE2.

To estimate the entanglement between the QEs numerically, we perform partial trace over the c-NCoM cavity for the density matrix ρ of coupled system and obtain the reduced density matrix $\rho = \text{tr}_c(\rho)$ describing a mixed state of qubits QE1 and QE2. We can then use concurrence C to characterize the degree of entanglement between two qubits [46], which is defined as

$$C(\rho) = \max\{0, \Lambda_1 - \Lambda_2 - \Lambda_3 - \Lambda_4\}, \quad (4)$$

where $\Lambda_1, \dots, \Lambda_4$ are the eigenvalues, in decreasing order, of the matrix $\rho \tilde{\rho}$. Here, $\tilde{\rho} = (\sigma_y \otimes \sigma_y) \rho^* (\sigma_y \otimes \sigma_y)$ is the spin-flipped state of ρ , where ρ^* is the complex conjugate of ρ and σ_y is the Pauli matrix.

The dependence of concurrence C on emitter-cavity detuning $\Delta_{e,c} = \omega_e - \omega_c$ and coupling rate g_0 is shown in Figure 3C and D. For the cases in Figure 3C, we study the dynamics of concurrence C for different emitter-cavity detuning $\Delta_{e,c}$ at two regimes: strong coupling regime with $g_0 = 0.1$ eV and ultrastrong coupling regime with $g_0 = 0.2$ eV.

We find that the maximal concurrence of $C=0.6$ is achieved in the ultrastrong coupling regime for a carefully designed off-resonant system with $\Delta_{e,c} > 0.2$ eV. As for the cases in Figure 3D, we study the dynamics of concurrence C for different coupling rate g_0 in either resonant systems with $\Delta_{e,c} = 0$ eV or off-resonant systems with $\Delta_{e,c} = 0.3$ eV. Similarly, the larger concurrence is obtained in those off-resonant systems. In Figure 3D (inset), we show the dynamics of concurrence for a case study of $\Delta_{e,c} = 0.3$ eV at the coupling rate of $g_0 = 0.08$ eV, and a notable degree of entanglement $C \sim 0.4$ is revealed. According to these results, we conclude that the higher concurrence can be obtained with an off-resonant system in the ultrastrong coupling regime.

3 More possibilities with other modes

Up to this point, we have been focused on the antenna mode of c -NCoM. In fact, as suggested in Figure 1B, there

exists two other modes at larger wavelengths for the c -NCoM configuration. When the cube gets bigger in size from 40 to 80 nm, along with the red shift, the antenna mode gradually decreases in magnitude, whereas the other two modes become more prominent. In Figure 4A, we adopt the quasi-normal mode (QNM) method [47] to analyze the three modes in more detail, with their mode profiles plotted in Figure 4B. Different from the antenna mode, the other two modes, face and edge modes, are both gap modes, as all the electromagnetic fields are concentrated in the gap. Figure 4B also confirms that the antenna mode indeed dominates for smaller cubes (e.g. size of 40 nm), whereas the face and edge modes become more notable for larger cubes like the size of 80 nm.

Among all these sub-100 nm nanoparticles, compared to NSoM that supports only gap mode in visible range, c -NCoM offering multiple optical modes across visible to near-infrared range could serve as a more interesting and diversified playground for QEs. In particular, QEs in the near-infrared range have a smaller exciton transition frequency ω_e (e.g. 1100 nm $\rightarrow$ 1.1 eV vs.

Figure 4: Multimode strong coupling in c -NCoM.

(A) Eigenmode analysis by the QNM method for c -NCoM, with cube size of 80 nm and emitter thickness of 2 nm. Here, the higher-order modes at wavelength below 650 nm are omitted as we focus on the coupling between near-infrared emitters and antenna/face modes. (B) Mode profiles of the three eigenmodes identified from QNM simulations: antenna, face, and edge modes for c -NCoM with cube size of 40 nm (top row) and 80 nm (bottom row), respectively. (C) FDTD simulations demonstrating strong coupling for c -NCoM (cube size of 80 nm) with three different coating scenarios: (i) fully coated, (ii) partially coated only at the sbottom surface, and (iii) partially coated only at the top surface. The emitter wavelength λ_e is swept from 700 to 1100 nm to couple to multiple optical modes. The bare cavity resonances are denoted for antenna mode (dashed green line) and face mode (dashed orange line). The corresponding split branches due to their coupling with emitters are denoted as A/A' for antenna mode (solid green curves) and F/F' for face mode (solid orange curves).

600 nm $\rightarrow$ 2.1 eV), making ultrastrong coupling regime easier to be reached [45]. Now, we employ such near-infrared QEs and demonstrate the possibility of multimode strong coupling using a larger *c*-NCoM with a size of 80 nm, as shown in Figure 4C. Here, *c*-NCoM is first coated with two-layer (2 nm thick) QEs (resonance swept from 700 to 1100 nm) at all six surfaces (Figure 4C, top). The scattering cross-section spectral map suggests that the emitters are separately coupled to either antenna mode (dashed green line) or face mode (dashed orange line), as clearly manifested by the four separated branches. We identify them as two sets of strongly coupled plasmon-emitter pairs: (i) emitters and antenna mode (solid green curves, denoted as A/A') and (ii) emitters and face mode (solid orange curves, denoted as F/F'). The anti-crossing feature is clearly seen for each pair of A/A' and F/F' . Although the antenna and face modes overlap spatially and spectrally, such that the branches F and A' seem unlikely to arise separately from the two modes, the nonidentical distributions of hot spots from the two modes in fact enable the distinguishable strong coupling between the emitters and different cavity modes (see Supplementary Section S4). This is drastically different from the case where indistinguishable emitters are coupled to two cavity modes, resulting in only three branches [48].

To get more insight about the contributions from different modes, we investigate different coating scenarios. For example, when emitters are coated only at the bottom surface or the gap region, the NCoM gap has fields contributed from both antenna and face modes, which are strongly coupled with the emitters. Thus, in Figure 4C (middle), the four distinguishable branches A/A' and F/F' still remain. In contrast, when the emitters are coated only at the top surface, they can only couple to the antenna mode as the face mode has negligible fields at the top surface. Therefore, only the branch A/A' shows up in Figure 4C (bottom). These two maps undoubtedly verify that the two strong coupling pairs originate from the location variations of emitter ensembles. The emitters on top of the cubes are preferentially coupled to antenna mode, whereas the emitters in the gap region would be able to couple to both antenna and face modes.

On a separate note, it is interesting to note that, in Figure 4C (bottom), the uncoupled face mode is blue shifted. This is simply because of the air gap in our simulation when *c*-NCoM is partially coated only at the top surface. If the gap is filled with dielectric (refractive index of 1.6), the face mode will shift back to 975 nm.

4 Conclusions and outlook

We have demonstrated ultrastrong coupling in a single *c*-NCoM plexcitonic system, which supports antenna mode but has been overlooked. When NCoM is coated with multiple layers of emitters, the plexcitonic system reveals a notable normalized coupling rate of $\eta \sim 0.12$ that is well into the ultrastrong coupling regime. The antenna mode of *c*-NCoM is distinct from those gap modes studied previously, in terms of providing multiple exterior hot spots at the upper corners, which is considered as open cavity and easily accessible. In practice, sharp corners of nanocubes should be favored for *c*-NCoM to support such hot spots, and experimentalists have been making their progresses [18, 49]. Nevertheless, it is encouraging that our initial strong coupling experiment on *c*-NCoM with rounded cube corners and nonoptimized designs has already achieved Rabi splittings above 300 meV [32]. Going further, the antenna mode with its multiple hot spots would enable the entanglement within single nanocubes, where many such quantum nodes constitute a scalable quantum network. Our calculation proves that the concurrence between adjacent emitters can go up to 0.6 with a single-emitter coupling rate of $g_0 > 0.15$ eV and emitter-cavity detuning of 0.3 eV.

In addition to the antenna mode, *c*-NCoM also simultaneously supports gap modes such as face and edge modes at longer wavelengths. When the emitter resonance covers the range of multiple cavity modes, every cavity mode can be strongly coupled to the emitters, resulting in multiple pairs of Rabi splitting branches. More interestingly, we can selectively enable or disable some strong coupling pairs by controlling the locations of the emitter coatings. It provides extra freedom in engineering the strongly coupled plexcitonic system. In short, our study not only reveals the values of antenna mode of NCoM but also inspires the construction of novel quantum plexcitonic systems.

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References

- [1] Brune M, Schmidt-Kaler F, Maali A, et al. Quantum rabi oscillation: a direct test of field quantization in a cavity. *Phys Rev Lett* 1996;76:1800–3.
- [2] Meekhof DM, Monroe C, King BE, Itano WM, Wineland DJ. Generation of nonclassical motional states of a trapped atom. *Phys Rev Lett* 1996;76:1796–9.
- [3] Kockum AF, Miranowicz A, De Liberato S, Savasta S, Nori F. Ultrastrong coupling between light and matter. *Nat Rev Phys* 2019;1:19.
- [4] Forn-Daz P, Lamata L, Rico E, Kono J, Solano E. Ultrastrong coupling regimes of light-matter interaction. *Rev Mod Phys* 2019;91:025005.
- [5] Anappara AA, De Liberato S, Tredicucci A, et al. Signatures of the ultrastrong light-matter coupling regime. *Phys Rev B* 2009;79:201303.
- [6] Askenazi B, Vasanelli A, Todorov Y, et al. Midinfrared ultrastrong light-matter coupling for thz thermal emission. *ACS Photonics* 2017;4:2550–5.
- [7] Bayer A, Pozimski M, Schambeck S, et al. Terahertz light-matter interaction beyond unity coupling strength. *Nano Lett* 2017;17:6340–4.
- [8] Wang H, Wang H-Y, Chen Q-D, et al. Hybrid-state dynamics of dye molecules and surface plasmon polaritons under ultrastrong coupling regime. *Laser Photonics Rev* 2018;12:1700176.
- [9] Yoshihara F, Fuse T, Ashhab S, Kakuyanagi K, Saito S, Semba K. Superconducting qubit-oscillator circuit beyond the ultrastrong-coupling regime. *Nat Phys* 2017;13:44.
- [10] Benz F, Schmidt MK, Dreismann A, et al. Single-molecule optomechanics in “picocavities”. *Science* 2016;354:726–9.
- [11] Tame MS, McEnery KR, Özdemir SK, Lee J, Maier SA, Kim MS. Quantum plasmonics. *Nat Phys* 2013;9:329.
- [12] Xu D, Xiong X, Wu L, et al. Quantum plasmonics: new opportunity in fundamental and applied photonics. *Adv Opt Photonics* 2018;10:703–56.
- [13] Zhou Z-K, Liu J, Bao Y, et al. Quantum plasmonics get applied. *Prog Quant Electron* 2019;65:1–20.
- [14] Yang X, Hu X, Yang H, Gong Q. Ultracompact all-optical logic gates based on nonlinear plasmonic nanocavities. *Nanophotonics* 2017;6:365.
- [15] Fakonas JS, Lee H, Kelaita YA, Atwater HA. Two-plasmon quantum interference. *Nat Photonics* 2014;8:317.
- [16] Chikkaraddy R, De Nijs B, Benz F, et al. Single-molecule strong coupling at room temperature in plasmonic nanocavities. *Nature* 2016;535:127.
- [17] Santhosh K, Bitton O, Chuntanov L, Haran G. Vacuum rabi splitting in a plasmonic cavity at the single quantum emitter limit. *Nat Commun* 2016;7:ncmms11823.
- [18] Liu R, Zhou Z-K, Yu Y-C, et al. Strong light-matter interactions in single open plasmonic nanocavities at the quantum optics limit. *Phys Rev Lett* 2017;118:237401.
- [19] Gonzalez-Tudela A, Martin-Cano D, Moreno E, et al. Entanglement of two qubits mediated by one-dimensional plasmonic waveguides. *Phys Rev Lett* 2011;106:020501.
- [20] Li M, Zou C-L, Ren X-F, et al. Transmission of photonic quantum polarization entanglement in a nanoscale hybrid plasmonic waveguide. *Nano Lett* 2015;15:2380–4.
- [21] Holtfrerich MW, Dowran M, Davidson R, Lawrie BJ, Pooser RC, Marino AM. Toward quantum plasmonic networks. *Optica* 2016;3:985–8.
- [22] Lei DY, Fernández-Domínguez AI, Sonnefraud Y, et al. Revealing plasmonic gap modes in particle-on-film systems using dark-field spectroscopy. *ACS Nano* 2012;6:1380–6.
- [23] Chikkaraddy R, Zheng X, Benz F, et al. How ultranarrow gap symmetries control plasmonic nanocavity modes: from cubes to spheres in the nanoparticle-on-mirror. *ACS Photonics* 2017;4:469–75.
- [24] Baumberg JJ, Aizpurua J, Mikkelsen MH, Smith DR. Extreme nanophotonics from ultrathin metallic gaps. *Nat Mater* 2019;18:668–78.
- [25] Hoang TB, Akselrod GM, Mikkelsen MH. Ultrafast room-temperature single photon emission from quantum dots coupled to plasmonic nanocavities. *Nano Lett* 2015;16:270–5.
- [26] Luo Y, Shepard GD, Ardelean JV, et al. Deterministic coupling of site-controlled quantum emitters in monolayer wse₂ to plasmonic nanocavities. *Nat Nanotechnol* 2018;13:1137.
- [27] Leng H, Szychowski B, Daniel M-C, Pelton M. Strong coupling and induced transparency at room temperature with single quantum dots and gap plasmons. *Nat Commun* 2018;9:4012.
- [28] Kleemann ME, Chikkaraddy R, Alexeev EM, et al. Strong-coupling of WSe₂ in ultra-compact plasmonic nanocavities at room temperature. *Nat Commun* 2017;8:1296.
- [29] Chen X, Chen Y-H, Qin J, et al. Mode modification of plasmonic gap resonances induced by strong coupling with molecular excitons. *Nano Lett* 2017;17:3246–51.
- [30] Lo TW, Zhang Q, Qiu M, et al. Thermal redistribution of exciton population in monolayer transition metal dichalcogenides probed with plasmon-exciton coupling spectroscopy. *ACS Photonics* 2019;6:411–21.
- [31] Hensen M, Heilpern T, Gray SK, Pfeiffer W. Strong coupling and entanglement of quantum emitters embedded in a nanoantenna-enhanced plasmonic cavity. *ACS Photonics* 2017;5:240–8.
- [32] Song T, Chen Z, Zhang W, et al. Compounding plasmon-exciton strong coupling system with gold nanofilm to boost rabi splitting. *Nanomaterials* 2019;9:564.
- [33] Kongsuwan N, Xiong X, Bai P, et al. Quantum plasmonic immunoassay sensing. *Nano Lett* 2019;19:5853–61.
- [34] Johnson PB, Christy RW. Optical constants of the noble metals. *Phys Rev B* 1972;6:4370.
- [35] Antosiewicz TJ, Apell SP, Shegai T. Plasmon–exciton interactions in a core-shell geometry: from enhanced absorption to strong coupling. *ACS Photonics* 2014;1:454–63.
- [36] Zeilinger A. Experiment and the foundations of quantum physics. *Rev Mod Phys* 1999;71:S288.
- [37] Hillery M, Bužek V, Berthiaume A. Quantum secret sharing. *Phys Rev A* 1999;59:1829.
- [38] Zhou Y, Yu J, Yan Z, et al. Quantum secret sharing among four players using multipartite bound entanglement of an optical field. *Phys Rev Lett* 2018;121:150502.
- [39] Bouwmeester D, Pan J-W, Mattle K, Eibl M, Weinfurter H, Zeilinger A. Experimental quantum teleportation. *Nature* 1997;390:575.
- [40] Ren J-G, Xu P, Yong H-L, et al. Ground-to-satellite quantum teleportation. *Nature* 2017;549:70.

- [41] Yin J, Cao Y, Li Y-H, et al. Satellite-based entanglement distribution over 1200 kilometers. *Science* 2017;356:1140–4.
 - [42] Wengerowsky S, Joshi SK, Steinlechner F, Hübel H, Ursin R. An entanglement-based wavelength-multiplexed quantum communication network. *Nature* 2018;564:225.
 - [43] Kimble HJ. The quantum internet. *Nature* 2008;453:1023.
 - [44] Wang S, Li S, Chervy T, et al. Coherent coupling of WS_2 monolayers with metallic photonic nanostructures at room temperature. *Nano Lett* 2016;16:4368–74.
 - [45] Todisco F, De Giorgi M, Esposito M, et al. Ultrastrong plasmon-exciton coupling by dynamic molecular aggregation. *ACS Photonics* 2017;5:143–50.
 - [46] Horodecki R, Horodecki P, Horodecki M, Horodecki K. Quantum entanglement. *Rev Mod Phys* 2009;81:865–942.
 - [47] Yan W, Faggiani R, Lalanne P. Rigorous modal analysis of plasmonic nanoresonators. *Phys Rev B* 2018;97:205422.
 - [48] Parkins S, Aoki T. Microtoroidal cavity qed with fiber overcoupling and strong atom-field coupling: a single-atom quantum switch for coherent light fields. *Phys Rev A* 2014;90:053822.
 - [49] Clark BD, Jacobson CR, Lou M, et al. Aluminum nanocubes have sharp corners. *ACS Nano* 2019;13:9682–91.
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