

Plasmon–Exciton Interactions: Spontaneous Emission and Strong Coupling

Hong Wei,* Xiaohong Yan, Yijie Niu, Qiang Li, Zhili Jia, and Hongxing Xu

The extraordinary optical properties of surface plasmons in metal nanostructures provide the possibilities to enhance and accelerate the spontaneous emission, and manipulate the decay and emission processes of quantum emitters. The extremely small mode volume of plasmonic nanocavities also benefits the realization of plasmon-exciton strong coupling. Here, the progress on the study of plasmon modified spontaneous emission and plasmon-exciton strong coupling are reviewed. The fundamentals of surface plasmons and quantum emitters, and the methods for assembling coupling systems of plasmonic nanostructures and quantum emitters are first introduced. Then the major aspects of plasmon modified spontaneous emission, including emission intensity, lifetime, spectral profile, direction, polarization, and energy transfer are reviewed. The coupling of quantum emitters and plasmonic waveguides is then discussed. Next, the developments of strong coupling between plasmonic structures and various quantum emitters are reviewed. Finally a few applications are highlighted followed by conclusions and outlook.

H. Wei, X. H. Yan, Y. J. Niu Beijing National Laboratory for Condensed Matter Physics Institute of Physics Chinese Academy of Sciences Beijing 100190, China E-mail: weihong@iphy.ac.cn H. Wei Songshan Lake Materials Laboratory Dongguan 523808, China X. H. Yan School of Physical Sciences University of Chinese Academy of Sciences Beijing 100049, China Y. J. Niu, H. X. Xu School of Physics and Technology Wuhan University Wuhan 430072, China Q. Li Guangdong Provincial Key Laboratory of Nanophotonic Functional Materials and Devices School of Information and Optoelectronic Science and Engineering South China Normal University Guangzhou 510006, China Z. L. Jia Center for Advanced Measurement Science National Institute of Metrology Beijing 100029, China

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.202100889.

DOI: 10.1002/adfm.202100889

1. Introduction

Metal nanostructures support surface plasmons (SPs), quanta of collective oscillations of free electrons at metaldielectric interfaces. Their coupling with photons leads to the formation of surface plasmon polaritons, which enables the manipulation of light beyond the diffraction limit. Due to the excitation of SPs, metal nanostructures show many extraordinary optical properties. One of the most prominent properties of SPs is the confinement of electromagnetic field into nanoscale volume, leading to the enhancement of local electromagnetic field and local density of optical states (LDOS). In nanogaps of nearby metal nanostructures, the enhancement is extremely prominent.^[1–3] The field enhancement effect has been used for enhancing various optical processes, such as Raman scattering,^[4]

fluorescence,^[5–7] optical forces,^[8,9] lasing,^[10,11] and various nonlinear processes.^[12–14] The SP resonance frequencies can be finely tuned by controlling the nanostructure geometries, and are very sensitive to the dielectric environment.^[15] The SPs can propagate in 1D nanostructures with the field tightly confined in the transverse cross section, providing nanowaveguides for electromagnetic energy guiding.^[16] These extraordinary properties offer powerful abilities to manipulate light and light–matter interaction at nanoscale for both fundamental sciences and the applications in various fields such as information technology,^[16,17] ultrasensitive sensing and detection,^[15,18] medical diagnosis and therapy,^[19] chemical reactions,^[20–22] and energy resources.^[23]

Quantum emitters (QEs) with nanoscale sizes are important for various applications such as light emitting devices, display devices, and single-photon sources. SPs offer a very useful tool to enhance and control the performances of QEs. For QEs in the proximity of plasmonic nanostructures, the excitation of SPs may modify the excitation rate and the spontaneous emission of the QEs, depending on the wavelength of the SPs. Since the frequency of SP resonance can be finely tuned by tailoring the geometries of the metal nanostructures, it is feasible to match the SP resonance wavelengths with the excitation or/ and emission wavelengths. For SPs resonant with the excitation light, the local electromagnetic field intensity is largely enhanced, resulting in the enhancement of excitation rate. If the emission wavelength of the QEs is located within the SP resonance band, the decay rates of the excitons in QEs will



be modified due to the modified LDOS according to Purcell effect.^[24,25] Coupling with plasmonic nanostructures usually leads to the increase of the spontaneous emission rate, corresponding to shorter lifetime. The intensity of fluorescence (also called photoluminescence, PL) can be enhanced or weakened, jointly affected by both the excitation enhancement and the emission modification. The plasmon–exciton interaction can also modulate the emission spectra, direction and polarization, mediate interaction between different emitters, and influence multiexciton processes, providing a versatile platform to manipulate the decay processes of QEs.

In addition to the efforts to manipulate the spontaneous emission by careful design and construction of plasmon coupled systems, two research topics about the plasmon-exciton coupling have received much attention in recent years. One is the coupling between QEs and plasmonic waveguides. Plasmonic waveguides enable the propagation of SPs in a well defined direction, and the hybrid systems of QEs coupling with plasmonic waveguides can be used as building blocks for quantum plasmonic circuits.^[16,26] Another hot topic is the strong coupling between QEs and plasmonic nanostructures.^[27,28] When the coupling strength exceeds the mean damping rate of SPs and excitons, the plasmon-exciton interaction enters the strong coupling regime. Under strong coupling condition, plasmon-exciton polaritons, also called plexcitons, are formed. Due to the unique properties of plexcitons, the strong coupling systems provide a promising platform for many quantum optics applications. Strong coupling has been realized using a variety of plasmonic nanostructures, with the number of QEs decreased to the single emitter level.

Here, we review the main progress on the spontaneous emission and strong coupling in hybrid systems of plasmonic nanostructures and optical nanoemitters. We first concisely introduce the fundamentals of SPs and QEs in Sections 2 and 3, respectively. Then we review the typical methods for preparing the coupled systems of metal nanostructures and QEs in Section 4. In Section 5, different aspects of SP modified spontaneous emission are reviewed, mainly including fundamentals for excitation enhancement and Purcell effect, SP modified fluorescence brightness, decay rates, spectra, emission direction and polarization, and SP assisted energy transfer between emitters. Plasmonic waveguide modified spontaneous emission is introduced in Section 6. Section 7 covers the progress of strong coupling between different types of emitters and various plasmonic nanostructures. In Section 8, we briefly summarize some applications relating to the weak and strong coupling between SPs and QEs. At last, this review is concluded with some thoughts on the future developments.

2. Surface Plasmons in Metal Nanostructures

SPs are collective oscillations of conduction electrons at the metal–dielectric interface. At the surface of extended metal structures, SPs propagate as surface-confined electromagnetic waves, while in small metal nanoparticles (NPs), SPs are featured as highly localized electromagnetic field on the NP surface. The two forms of SPs in metal nanostructures are usually called propagating SPs and localized SPs, respectively.

2.1. Localized Surface Plasmon Resonances

A metal nanosphere in uniform dielectric environment is the simplest structure to show the fundamentals of localized SPs. Driven by the external field, electrons move away from the positive ion core, so that opposite charges accumulate on the two sides of the nanosphere, as schematically shown in the left panel of Figure 1a. The accumulation of charges will result in a Coulomb restoring force to pull the electrons back, so that a repetitive back and forth oscillation occurs. If the frequency of the incident light matches the oscillation frequency, a resonance occurs, corresponding to the peak in extinction spectrum (right panel of Figure 1a). This is called localized SP resonance (LSPR). The absorption and scattering lead to the damping of the SP mode, corresponding to the linewidth of the extinction spectrum. Increasing the refractive index of the dielectric medium will lead to the redshift of resonance wavelength. The sensitive dependence of resonance wavelength on the environmental refractive index can be used for sensing applications.

The LSPR frequency is dependent on the size and shape of the NPs. The spectral peak is redshifted as the nanosphere becomes larger. For a metal nanorod, depending on the polarization of the driving field, two classes of SP modes can be excited, corresponding to the charge oscillations along the major and minor axis (usually called longitudinal modes and transverse modes, respectively).^[29] With the increase of the aspect ratio, the longitudinal dipolar SP resonance is redshifted. For metal nanorods with larger aspect ratio, the high order longitudinal SP modes can appear within the visible to near infrared spectral range.^[30] The multiple resonances provide more options for matching the LSPR wavelength with excitation laser wavelength and emission wavelength of QEs. The aggregation of metal NPs can change the SP response of individual NPs due to the electromagnetic coupling. The simplest nanoaggregate is a dimer composed of two metal NPs. The coupling of two NPs forms new SP modes. For the excitation light polarized parallel to the dimer axis, the longitudinal coupling of the dipolar mode results in a mode with LSPR wavelength redshifted relative to that of single NP, while for the excitation light polarized perpendicular to the dimer axis, the transverse coupling results in a mode with slightly blueshifted LSPR wavelength.^[31] The decrease of the nanogap redshifts the resonance wavelength of the longitudinal mode until quantum effects become noticeable.

Under resonance frequency, the electric field near the nanosphere surface is largely enhanced compared with the incident field.^[32] The in-phase coupling of two dipoles excited by incident light polarized parallel to the interparticle axis leads to strong localization and large enhancement of electric field in the nanogap between the two NPs.^[1,2] The field enhancement factor decreases as the polarization is rotated away from the parallel direction, as clearly shown in Figure 1b.^[33] The nanogap between two plasmonic nanostructures form a nanocavity, which is the "hot spot" that can significantly amplify weak optical signals. This nanogap effect enables the giant enhancement of light–matter interactions at nanometer scale and is the foundation for many plasmonic applications. The field enhancement in the nanogap is generally increased with the decrease of the gap size. In the sub-nanometer gaps, the



FUNCTIONAL MATERIALS



Figure 1. a) Schematic illustrations of SP resonance. Left: Under excitation of light polarized in horizontal direction, the positive and negative charges are separated on two sides of a metal NP. Right: The extinction spectrum of the NP. ω_{SP} and γ_{SP} represent the resonance frequency and the damping rate of SPs, respectively. b) Local electric field intensity enhancement in logarithmic scale in a plane through the centers of the Ag nanospheres and perpendicular to the incident wave vector. The arrows represent the different polarizations of the incident light. c) Left: Schematic of SPs propagating on a metal NW with pentagonal cross section. Right: Illustration of the dispersion relations of different order SP modes in a metal NW. d) Left: Electric field distributions of TM₀ and HE₁ modes in a Ag NW with a radius of 60 nm at vacuum wavelength of 633 nm. Right: Effective refractive index and propagation length of the TM₀ and HE₁ modes as a function of the NW radius. (b) Reproduced with permission.^[39] Copyright 2018, American Chemical Society. (d) Reproduced with permission.^[39]

quantum effects make the field enhancement factor smaller than what predicted by classical electromagnetic theory,^[34,35] and could reduce the electric field enhancement for extremely small gap distance.^[36–38]

2.2. Propagating Surface Plasmons

In 2D and 1D metal structures, SPs can propagate in the extended directions with the electric field confined in the perpendicular directions. The 1D plasmonic nanostructures can function as nanowaveguides to realize light guiding with lateral confinement beyond the diffraction limit, which provides a fundamental building block for constructing on-chip integrated nanophotonic circuits. Figure 1c shows the illustration of propagating SPs on a metal nanowire (NW) and the dispersion relations of different order SP modes. Compared with the light in vacuum, the wave vector of the SPs is larger. Therefore, they cannot directly interact with free-space light. To excite the propagating SPs by light, some schemes that can compensate the momentum mismatch can be employed, for example, scattering at the NW end, and near-field coupling. The emission of optical nanoemitters can also excite the propagating SPs on nanowaveguides. The single photon emission property of some QEs renders the excitation of single quantized plasmons. The coupling of QEs and plasmonic waveguides not only modifies the spontaneous emission, but also enables the propagation of the radiation from the QEs along the waveguides, providing more possibilities to manipulate the spontaneous emission. In addition to metal NW, several 1D nanostructures based on metal film can also function as plasmonic waveguides, such as groove or slot in metal film, wedge protrusion on metal film, dielectric NW or nanostripe on metal film (usually called dielectric-loaded plasmonic waveguide), and high-refractive-index NW on metal film with low-refractive-index spacer between them (usually called hybrid plasmonic waveguide). These waveguides support propagating SP modes with different field confinement and propagation loss.

The simple structure of a metal NW makes it a promising candidate to construct compact integrated nanophotonic circuits, and has been widely used for coupling with single QEs as will be seen in Section 6. Here we briefly introduce the properties of propagating SPs on metal NWs. The electric field of propagating SPs can be confined around the metal NW even if the NW diameter is much smaller than the light wavelength, making it a nanowaveguide breaking the diffraction limit. The left panel of Figure 1d shows the electric field distributions of the two lowest order SP modes, TM₀ mode and HE₁ mode, of a cylindrical silver NW. The effective refractive index of the SP mode, which equals to k/k_0 (k and k_0 are the SP wave vector and vacuum wave vector, respectively), reflects the degree of field confinement. As shown in the right panel of Figure 1d, the effective refractive index for TM₀ mode is increased with the decrease of the NW radius, indicating tighter field confinement for thinner NWs. For HE1 mode, the effective refractive index is smaller and shows an opposite trend with the change of the NW radius. The tighter field confinement leads to the larger loss in metal. Therefore, the propagation length of the TM₀ mode is shorter and is decreased with the decrease of the NW radius, while the propagation length of the HE₁ mode shows opposite behavior. When the TM₀ and one or two degenerate HE1 modes are excited simultaneously in the NW, the coherent superposition of these modes can lead to zigzag or chiral electric field distribution along the NW.^[16,40,41] At the end of the NW, the propagating SPs are converted to photons. The SP modes, the NW geometries and dielectric environments determine







Figure 2. a) Energy diagram illustrating the absorption and decay of a QE. b) Schematic of the optical setup for measuring the second order correlation function of the emitted photons. The curve at top-right corner shows the second order correlation function for a single-photon source.

the characteristics, such as direction and polarization, of the emitted light at the NW ends, which can be utilized to manipulate the emission of the QEs coupled with the NW. Moreover, a NW of finite length can function as a Fabry–Pérot resonator, which can modulate the emission spectra of QEs coupling with the NW.

3. Quantum Emitters

The QEs used in SP-involved optical experiments mainly include molecules, quantum dots (QDs), color centers in diamond nanocrystals, and atomic layer 2D materials like transition metal dichalcogenides (TMDCs). In quantum confined systems, the electronic states are discrete. The interaction of light with QEs can be described by two steps: the absorption and the spontaneous emission. For simplicity, the QE can be described as a two-level system, which can well describe the main optical properties of different QEs, in spite of their different structures. By absorbing the photon energy, the electron is excited from the ground state to the excited state. The electron in the excited state experiences vibrational relaxation before returning to the ground state, as schematically shown in Figure 2a. Due to the vibrational relaxation, the fluorescence emitted by the QE is redshifted, enabling the easy detection of the fluorescence.

The relaxation to the ground state can be achieved by different channels, for example, radiative decay by emitting photons, and nonradiative decay generating heat. The duration in the excited state is usually called the lifetime of the excited state, and is the reciprocal of the total decay rate, that is, $\tau = 1/\gamma = 1/(\gamma_{rad} + \gamma_{nrad})$, where γ_{rad} and γ_{nrad} are the decay rates of the radiative decay channel and nonradiative decay channel, respectively. The total decay rate γ is usually called spontaneous emission rate, which means the rate at which an emitter in excited state returning to the ground state by dissipating energy through different channels. The quantum yield of the fluorescence is defined as $\eta = \gamma_{rad}/(\gamma_{rad} + \gamma_{nrad})$, which reflects the probability of the QE emitting light after absorbing a photon. Some QEs show blinking behavior in their fluorescence due to the transition to dark states. The fluorescence intensity detected in experiment can be described by $I = C\gamma_{exc}\eta$, where *C* is the collection/detection efficiency of the experimental setup, γ_{exc} is the excitation rate, and η is the quantum yield. In structured environment as the case of coupling with plasmonic nanostructures, the modification of the fluorescence intensity is caused by the changes of the above three parameters, which will be discussed in Section 5.

One significant property of some QEs is the single photon emission, that is, a QE excited under proper conditions can emit only one photon at a time, which manifests as a photon antibunching behavior as can be measured from the second order correlation function of the emitted photons. Figure 2b shows the sketch for measuring the antibunching behavior in the time domain by Hanbury Brown and Twiss experiment. The emitted light is split into two paths by a 50/50 beam splitter, and recorded by two detectors. The single photon emission determines that the two detectors cannot detect photons at the same time. This makes QEs nanoscale single-photon sources which are important for various quantum optics applications. In addition to atoms, molecules, QDs, and color centers, defects in 2D materials and carbon nanotubes are found to show single photon emission behaviors.^[42,43]

The spontaneous emission rate can be obtained according to Fermi's golden rule, and is determined by the transition dipole moment and the LDOS. When the emitter-field coupling constant is much smaller than the decay rate γ , it is assigned as weak coupling. In the weak coupling regime, the modification of the spontaneous emission rate can be described by classical theory, and the enhancement of the radiative decay rate can be obtained by the enhancement of the radiated power.^[44] When the coupling constant is larger than the decay rate, the strong coupling regime is reached. In the strong coupling regime, hybrid states are formed, which can result in the splitting of emission spectra. The small mode volume of SPs facilitates the realization of strong coupling between QEs and plasmonic nanostructures, as will be discussed in Section 7.

4. Methods for Preparing the Coupled Systems of Metal Nanostructures and Quantum Emitters

Precisely controlling the relative position and orientation of QEs and plasmonic nanostructures is vital to manipulate the

ADVANCED SCIENCE NEWS _____ www.advancedsciencenews.com



exciton–plasmon coupling and is a challenging task. Various kinds of methods for constructing the hybrid systems have been developed, including self-assembly by molecular linkers, silica encapsulation, nanomanipulation and nanopositioning, lithographically fabricated masks, microfluidic flow control,^[45] electrohydrodynamic nanoprinting,^[46] two-photon polymerization,^[47] etc. In this section, we briefly introduce some typical methods.

4.1. Self-Assembly

Self-assembly is the process by which individual components spontaneously form organized structures due to specific interactions. Self-assembly can occur in systems with a wide range of sizes, and is a very useful method to construct hybrid structures by connecting individual components with high precision and high yield.^[48] Therefore, it is a very flexible and easy method for preparing the hybrid systems of metal nanostructures and optical nanoemitters. Here we will mainly introduce some schemes of assembling plasmonic NPs and nanoemitters by linkers. The linkers commonly used in direct self-assembly process mainly include polymers, thiol molecules, biological molecules, and DNA origami. For gold nanostructures, the thiols and thiolated ligands have been used mostly as functional linkers due to the stabilized Au–S bond.^[49,50] Nepal et al. demonstrated the assembly of QDs and Au nanorods with precisely tuned separation and number of QDs on each nanorod.^[49] As shown in **Figure 3**a, the amino functional alkythiol was chosen as ligand and bonded with gold surface. The terminal amines on QDs and nanorods will be converted to thiols through the excess of Traut's reagent, and the assembly is realized through dithiol coupling. By employing aminoalkylthiols with different lengths of alkyl chain, the separation of QD and nanorod can be controlled. In addition, the number of QDs surrounding the Au nanorod can be tuned by changing the stoichiometric ratio of QD to Au nanorod, as shown in the transmission electron microscopy (TEM) images in Figure 3a.

The biological molecule linkers are also widely employed in self-assembly based on the processes such as the hybridization of complementary single-strand DNA, and the biotin– streptavidin coupling.^[51,52] Cohen–Hoshen et al. reported the assembly of Au NPs functionalized by thiol-DNA-biotin molecules with QDs covered with streptavidin.^[53] As shown in Figure 3b, Au NPs attached by one or multiple QDs were obtained by controlling the number ratio of QD to NP. In



Figure 3. a) Top: Schematic of directed assembly of QD-Au nanorod architectures in water. Bottom: TEM images of QD-Au nanorod coupled structures. Scale bars are 25 nm. b) Different QD-NP complexes assembled by streptavidin molecules on QDs and biotin-dsDNA-thiol molecules on Au NPs. c) TEM image of a single QD (marked by yellow circle) attached to a silica-coated Au NP. d) Schematic of the hybrid NP architecture consisting of a Au nanorod core and a silica shell, with the dye molecules (RhBITC) embedded throughout the silica shell. e) Scheme of assembling Au NP and nanodiamond using AFM. f) Sketch of Au NP on a nanofiber tip over the molecules on the glass slide. Inset: SEM image of a Au NP attached to the end of a pointed optical fiber. g) Top: Schematic illustration of the two-step lithography process for making holes at the center of bowtie structures and the interfacial capillary force assisted method for driving QDs into the holes. Bottom: SEM images of nanobowties with a nanohole in the resist (left) and with QDs in the nanogaps. Scale bars are 20 nm. (a) Reproduced with permission.^[69] Copyright 2012, American Chemical Society. (c) Reproduced with permission.^[67] Copyright 2011, American Chemical Society. (d) Reproduced with permission.^[66] Copyright 2012, American Chemical Society. (e) Reproduced with permission.^[67] Copyright 2016, Wiley. (f) Reproduced with permission.^[67] Copyright 2016, Mature Publishing Group.



particular, NP-QD-NP structure can be constructed when a few molecules are attached to a single QD (right panel of Figure 3b). Through the hybridization of complimentary DNA strands, Au NP dimers with a single QD in the nanogap was successfully assembled.^[54] By using DNA origami technique, similar coupled systems with a single molecule or a single QD positioned in the nanogap of a plasmonic NP dimer can also be obtained.^[55–58]

Metal nanostructures can be coated with silica shells, and silica can be easily modified with ligands for connecting with fluorescent emitters.^[59-61] The controlled thickness of the silica shell provides a simple method for tuning the interactions between the emitters and the metal core.^[60,61] It was demonstrated that, by modifying the surface of Au@SiO2 core-shell NPs with a positively charged polyelectrolyte, single QDs coated by negatively charged ligands were successfully attached to the NPs (Figure 3c).^[62] The silica shells coated on metal NPs can be highly porous under proper experimental conditions.^[63] The mesostructured silica shell can be doped with molecules, leading to the formation of the coupled systems of plasmonic NPs and emitters.^[64,65] Figure 3d shows the sketch for the hybrid nanostructure of a Au nanorod with rhodamine B isothiocyanate (RhBITC) molecules embedded in the silica shell.^[65–72]

4.2. Manipulation and Nanopositioning

The hybrid system can be assembled by manipulating plasmonic nanostructure or QE through the tip of a scanning probe microscope, such as atomic force microscope (AFM). The typical steps of nanomanipulation using AFM probe are the so-called "imaging-moving" process. First, topography is measured by using tapping mode of AFM and the locations of the nanocomponents are obtained. Then, nanomanipulation is performed by utilizing contact mode to move one component close to the other. After finishing the construction of the hybrid system, the optical measurements can be performed in situ for the same hybrid structure. The distance between different building blocks can be controlled with high accuracy. Figure 3e shows the sketch for manipulating a Au nanorod by the AFM tip to move toward a fluorescent nanodiamond. By moving the Au nanorod to different positions relative to the nanodiamond, different configurations of the nanorod-nanodiamond hybrid structure were constructed, leading to different emission patterns.[66] By utilizing this technique, composites of different plasmonic nanostructures and different QEs were assembled, such as Au NPs and QDs,^[68-70] and Ag NWs and nanodiamonds.^[71] Complex hybrid systems consisting of multiple components can also be constructed by careful nanomanipulation. A nanodiamond containing a single nitrogen vacancy (NV) center and two Au nanospheres were assembled step-by-step, with the nanodiamond located in the gap between the two nanospheres.^[72] A U-shaped nanostructure consisting of three gold nanorods and two silica-encapsulated QDs was built by AFM nanomanipulation.^[73]

Metal NPs or QEs can be attached to the end of the scanning probe. The nanopositioning ability of scanning probe

microscope enables the precise control of the interaction between plasmonic nanostructures and QEs. The coupling between a single Au NP and a fluorescent molecule was controlled by scanning a Au nanosphere attached to the tip of an optical nanofiber over the molecules on the glass slide (Figure 3f).^[5,6] By controlling the lateral and vertical distance between the NP and the molecule, the fluorescence enhancement or quenching was observed. On the contrary, the emitters can be attached to the probe tip with the plasmonic nanostructures on the substrate. The fluorescence lifetime imaging on metal NWs was performed by attaching a fluorescent nanobead to a nanofiber tip,^[74] or attaching a nanodiamond containing a single NV center to an AFM tip.^[75] The QEs on the probe tip can be placed on the sample surface under proper conditions. By inducing long-range electrostatic forces between an AFM tip and an opaque conductive substrate, a nanodiamond containing a NV center was transferred to the center of a silver bullseve structure.^[76]

4.3. Mask and Template

The development of top-down nanofabrication techniques has enabled the highly controllable fabrication of plasmonic nanostructures and nanodevices. Electron beam lithography (EBL) is a widely used technique for fabricating nanostructures with high accuracy. The hybrid systems of plasmonic nanostructures and QEs can be prepared by a two-step EBL process. The first lithography step defines the pattern of the plasmonic nanostructures on the resist followed by deposition of metal layer. The second lithography step opens windows of nanoscale sizes in the resist at specific positions of the metal nanostructures for subsequent deposition of QEs.

Santhosh et al. prepared Ag nanobowties with QDs in the nanogaps by the two-step EBL process (Figure 3g).^[67] The nanobowties were first fabricated by EBL with the gap size of ≈ 20 nm. Then the nanoholes were patterned in the resist with EBL at the center of the nanogap between the two nanotriangles, and the QDs were driven into the nanoholes by the interfacial capillary force during the solvent evaporation.^[77] As confirmed by the scanning electron microscopy (SEM) images in Figure 3g, the QDs were positioned in the nanogaps of the bowtie nanoantennas. Using similar method, Gruber et al. fabricated Ag NWs with QDs assembled at the ends of the NWs.^[78] It is also possible to first deposit QDs in the areas defined by EBL, and then fabricate the metal NWs in the second step EBL process.^[79] Recently, Meng et al. developed a method to make nanoholes in polymer by using hot scanning nanoprobe, and demonstrated the assembly of single QDs and a Ag NW.^[80]

The assembly of QEs into the nanoholes can also be realized by chemically modifying the nanohole areas for chemical binding of QEs to the metal nanostructures. Curto et al. functionalized the nanohole areas created by the second EBL step by a self-assembled monolayer of mercaptoundecanoic acid. The QDs were successfully immobilized at the desired positions of gold nanorods and Yagi–Uda antennas.^[81,82] Similar procedures were employed to assemble single QDs with single Au nanodisks and nanodisk dimers.^[83] www.advancedsciencenews.com

5.1. Excitation Enhancement and Purcell Effect

When a QE is placed close to a plasmonic structure, both the excitation rate and decay rate are modified due to the excitation of SP modes. As introduced in Section 3, the fluorescence intensity of the QE is determined by three factors: the excitation rate, the quantum yield, and the collection efficiency. In this section, we will mainly discuss the influence of plasmonic nanostructure to the excitation rate and decay rate. The quantum yield can be modified by coupling to SP modes due to the change of decay rates to different channels. The collection efficiency can be influenced because the nanostructure can modify the direction of the fluorescence emission, which will be discussed in Section 5.3.

The plasmonic nanostructure can function as an optical nanoantenna to concentrate light into nanoscale volumes around the nanostructure, leading to largely enhanced local electromagnetic filed. Since the excitation rate $\gamma_{exc} \propto |\boldsymbol{\mu} \cdot \boldsymbol{E}|^2$, where $\boldsymbol{\mu}$ is transition dipole moment and \boldsymbol{E} is local electric field, the plasmon-enhanced local electric field around the metal nanostructure can largely enhance the excitation rate of the nearby QE. As discussed in Section 2, the field enhancement is extremely strong in the nanogaps of coupled nanostructures. Thus, placing the QE into the nanogap with large field enhancement is an effective way to enhance the emission intensity.

The spontaneous emission is not an intrinsic property of a QE, but can be modulated by the interaction with the environment. The decay rate in a structured environment is modified compared with that in free space, and is proportional to the LDOS. This phenomenon is known as Purcell effect, as Purcell first discovered in 1946 that the spontaneous transition rate of a nuclear magnetic moment can be enhanced by coupling to a resonant electrical circuit.^[24] For a QE coupled with a metal nanostructure, the total decay rate can be expressed as $\gamma_{\text{tot}} = \gamma_{\text{rad,m}} + \gamma_{\text{nrad,m}}$, where $\gamma_{\text{rad,m}}$ is the radiative decay rate, $\gamma_{\text{nrad,m}}$ is the nonradiative decay rate, and the letter m in the subscripts represents the QE coupling with the metal nanostructure. In literature, the ratio of the total decay rate for the QE coupled with plasmonic structure and for the bare QE is

often called Purcell factor, although other definition of Purcell factor is also used in some papers. As the total decay rate is the reciprocal of the lifetime of the excited state measured in experiments, it is convenient to obtain the Purcell factor in experiments by this definition.

FUNCTIONAL

www.afm-journal.de

For a cavity mode resonant with the QE transition frequency, under optimal position and orientation of the QE, the Purcell factor is $F_{\rm P} = \frac{\gamma}{\gamma_0} = \frac{3Q\lambda^3}{4\pi^2 V}$, where γ and γ_0 are the spontaneous emission rate for a QE coupled with an optical cavity and for a QE in free space, respectively, Q is the quality factor of the cavity mode, and V is the effective volume.^[25] Therefore, there are two strategies to increase the decay rate, that is coupling the QE with a cavity of high Q or small V. In spite of the low quality factor of plasmonic nanocavities, the small mode volume can efficiently enhance the decay rate. The small size of plasmonic nanostructures determines the coupling system can be ultra-compact, and the low Q guarantees a broader spectral band for engineering the spontaneous emission of the QE. Moreover, theoretical study shows that the maximum rate of single photon emission for the QE coupled with plasmonic nanostructures is two orders of magnitude higher than that for the QE coupled with dielectric resonators.^[84]

The coupling between a QE and a plasmonic nanostructure, taking a metal nanosphere as an example, can be intuitively understood by the dipole-dipole interaction, in analogy to Förster resonance energy transfer (FRET). The exciton in the excited QE will transfer part energy to the metal nanosphere, exciting the SP mode (Figure 4a). The energy transfer rate depends on the orientation of the dipole and the plasmon mode, the separation distance, and the spectral overlap between the SP resonance and the QE emission. The energy of the SPs will be partly radiated as photons and partly absorbed by the metal NP and finally converted to heat. The fluorescence detected in the far field can be classified into two parts. One part is the far-field emission radiated directly by the QE, and the other part is the scattering of the SP mode in the NP excited by the exciton in the QE due to energy transfer. Under proper conditions, the latter part can be dominant. The quantum yield of the fluorescence for the QE coupled with a plasmonic nanostructure can be expressed



Figure 4. a) Schematic illustration of the decay channels of a QE coupling with a metal nanostructure. b,c) Calculated excitation rate (red), quantum yield (blue), and fluorescence rate (black) as a function of molecule-particle separation. The solid curves are the results of calculations using multiple multipole method (max. error 2%) whereas the dashed curves correspond to the dipole approximation which fails for short distances *z*. In (b) the particle diameter is 80 nm and in (c) it is indicated in the figure. Excitation wavelength is 650 nm. (b) and (c) Reproduced with permission.^[6] Copyright 2006, American Physical Society.

as $\eta_m = \gamma_{rad,m} / \gamma_{tot} = [\gamma'_{rad} + \gamma_{ET} \gamma_{SP-rad} / (\gamma_{SP-rad} + \gamma_{SP-nrad})] / \gamma_{tot}$, where γ'_{rad} is the rate of direct free-space radiation, γ_{ET} is the energy transfer rate between the QE and the plasmonic structure, γ_{SP-rad} and $\gamma_{SP-nrad}$ are the rates at which the SPs are radiated as photons and damped by absorption, respectively. Due to the increase of the nonradiative decay rate, the fluorescence quantum yield can be decreased compared with the QE without coupling to plasmonic nanostructures, especially for QEs with originally high quantum yield. However, for the QEs with low quantum yield, the fluorescence quantum yield can be enhanced by plasmonic nanostructures.

DVANCED

SCIENCE NEWS ______

Usually, the part of the fluorescence directly emitted by the QE without coupling to SPs and the part of fluorescence emitted by the QE-SP coupling cannot be distinguished. In the coupled system of a single QE and a metal NW, by using the propagation properties of SPs on the NW, the decay rates of the exciton into each channel (free-space radiation, nonradiative decay, exciting SPs) can be experimentally obtained, as will be discussed in Section 6. It is noted that, in some papers, the enhancement factor of the radiative decay rate $\gamma_{\rm rad,m}/\gamma_{\rm rad,0}$ was used as the enhancement factor of fluorescence quantum yield to evaluate the fluorescence intensity enhancement, but this replacement is only valid when the change of the total decay rate induced by the plasmonic nanostructure is very small. Making the above replacement without careful analysis may lead to unreliable results.

Without considering the detection efficiency, the fluorescence intensity of the QE is jointly determined by the excitation rate enhancement and the modified quantum yield. Figure 4b shows the theoretically calculated excitation rate, quantum yield, and emission rate as a function of the separation between an electric dipole and a gold nanosphere. With the decrease of the separation distance, the excitation rate is increased due to the enhancement of local electric field, while the quantum yield is decreased from its original value 1 due to the increased nonradiative decay rate. Therefore, the emission rate is first increased with the decrease of the distance, reaching a maximum at a certain distance, and then decreased by further decreasing the distance.

5.2. Plasmon Modified Fluorescence Brightness, Decay Rates, and Spectra

The influence of a single metal nanostructure to the QE fluorescence was experimentally demonstrated by positioning a gold nanosphere close to a molecule by scanning probe microscopy technique with the gold nanosphere attached at the tip of the probe.^[5,6] By carefully controlling the distance between the gold nanosphere and the molecule, it is found that the maximum enhancement of the fluorescence intensity appears when the separation distance is about 5 nm.^[6] Further decreasing the distance leads to the decrease of the fluorescence intensity, agreeing with the theoretical results in Figure 4c. The obtained fluorescence intensity enhancement is moderate due to the moderate field enhancement of single gold nanosphere and the decrease of fluorescence quantum yield.

Au nanorod can also strongly modify the spontaneous emission of QEs. It is reported that more than 1000-fold

enhancement of single crystal violet (CV) molecule fluorescence can be achieved by individual gold nanorods.^[85,86] The simulation result shows that this large enhancement includes an excitation enhancement of about 130 and an emission enhancement of about 9.^[86] To achieve the maximum enhancement, the CV molecule is placed at the end of the nanorod with dipole moment along the long axis of the nanorod. Here the relatively large emission enhancement is achieved because of the low quantum yield of CV molecules (2%). For QEs with high quantum yield, the emission enhancement can be quite limited, and the emission can even be suppressed. For highly luminescent dye molecules and QDs with the initial quantum yield approaching 100%, coupling with plasmonic structures usually decreases the quantum yield. For such a case, the main contribution to the fluorescence intensity enhancement is the excitation enhancement due to the enhanced local electric field. The maximum excitation enhancement occurs when the excitation wavelength matches the SP resonance of the metal nanostructure. This is experimentally demonstrated by measuring QDs coupled with single Ag nanoprisms with laser light of varied wavelengths.^[87] As the local electromagnetic field corresponding to SP resonance wavelength depends on the polarization of the excitation light, the fluorescence intensity also shows a dependence on the excitation polarization.[64]

Since the electric field enhancement in the nanogaps of coupled nanostructures is much larger compared with separated nanostructures, various nanogap structures are fabricated to enhance the fluorescence of QEs. NP dimers composed of two metal NPs (Figure 5a-d) are typical nanogap structures with large field enhancement. Using the gold bowtie nanoantenna (Figure 5a), the fluorescence of single molecules can be enhanced up to 1340-fold when the molecule is located in the nanogap between two triangles and excited by laser light polarized parallel to the long axis of the nanobowtie.[88] This large enhancement results from the enhancement of both excitation rate and fluorescence quantum yield, and the enhancement factor is decreased with the increase of the nanogap size. The random position and orientation of the molecular dipole moments result in the variation of the fluorescence brightness.^[88] Single molecule fluorescence enhancement up to 1100-fold is reported in the structure of a NP dimer in an aperture in a gold film (Figure 5b) with the molecules diffusing in the solution covered the antenna structure.^[89] The fluorescence enhancement is also mainly due to the large field enhancement in the nanogap of the dimer. The presence of the gold film can screen the background fluorescence by preventing direct excitation of molecules diffusing away from the nanodimer. Through the hybridization of complimentary DNA strands, a single QD can be positioned in the nanogap of Au or Ag NP dimers (Figure 5c). PL intensity enhancement up to 30-fold was obtained.^[54] By chemically modifying the NP dimer using the two-step EBL method, a similar system can also be obtained.^[83] However, due to the low excitation enhancement and the reduced quantum yield, noticeable PL enhancement was not observed. By using an AFM tip to manipulate two silver nanocubes to hold a nanodiamond containing a single NV center (Figure 5d), the brightness of single photon emission from the NV center was enhanced and a photon rate of 8.5×10^5 counts per second near the saturation limit was achieved.^[90]





Figure 5. a) Top: Schematic of a Au bowtie nanoantenna coated with molecules (black arrows) in PMMA (light blue) on a transparent substrate. Bottom: SEM image of a Au bowtie nanoantenna. Scale bar is 100 nm. b) SEM image of a fabricated nanoantenna consisting of a NP dimer inside a rectangular aperture in a Au film. c) TEM image of a Au NP dimer with a QD in the gap region. d) Illustration of a nanodiamond containing a single NV center situated in the gap between two Ag nanocubes. e) Cross-sectional schematic of a single QD embedded in the gap between a Ag nanocube and a Au film. f) Schematic of a Ag nanocube over a Au film substrate, separated by an alumina layer, monolayer WSe₂, and the PVP layer around the nanocube. (a) Reproduced with permission.^[88] Copyright 2009, Nature Publishing Group. (b) Reproduced with permission.^[89] Copyright 2013, Nature Publishing Group. (c) Reproduced with permission.^[54] Copyright 2019, Wiley. (d) Reproduced with permission.^[90] Copyright 2017, American Chemical Society. (e) Reproduced with permission.^[93] Copyright 2016, American Chemical Society. (f) Reproduced with permission.^[98] Copyright 2018, American Chemical Society.

Another kind of plasmonic nanogap is formed between a NP and a metal film.^[3,91] Compared with NP dimers, the NP-film coupled system, also called NP-on-mirror (NPOM), can be easily prepared by depositing metal NPs over a metal film. A dielectric layer can be deposited on the film surface to function as a spacer. By controlling the thickness of the spacer layer, the nanogap thickness can be well controlled.[35,92] The spontaneous emission of the QE in the nanogap between the NP and the metal film will be strongly modified. Among NPs of various geometries, metal nanocube is of high interest due to its flat facet, which facilitates the formation of nanogaps with larger area and the coupling of QEs with the plasmonic nanogap. For a QD coupled with the NPOM structure (Figure 5e), a 1900-fold enhancement of fluorescence intensity and a 540-fold decrease in lifetime were observed, increasing the maximum single photon emission rate of the QD.^[93] By tuning the SP resonance wavelength of the NPOM through changing the size of the nanocube to match the excitation wavelength and close to the emission peak wavelength, fluorescence intensity enhancement over 30 000 times was demonstrated.^[94] With the decrease of the spacer thickness, the electric field enhancement in the nanogap increases and the fluorescence quantum yield decreases, which leads to the maximum fluorescence intensity at a certain gap thickness.^[95] For a nanodiamond containing a single NV center located in the nanogap of NPOM, the average PL lifetime shortening of 70 times and the average saturated intensity increase of 90 times were observed, with up to 35 million photon counts per second.^[96] By illuminating the coupled structure with a continuous-wave laser for 30 s, the lifetime and intensity were further decreased and increased, respectively, which was attributed to the decrease of the gap size caused by the sintering of the nanocube.^[97] PL enhancement of monolayer semiconductors was also reported in the NPOM structures (Figure 5f). PL enhancement factor of 1700 and 6000 were obtained for monolayer WSe2 and MoSe2 coupled with the NPOM, respectively.^[98,99] For single defects in monolayer WSe₂, coupling with the NPOM cavity led to a Purcell factor up to 551 (average 181) and enhancement of quantum yield from 1% to 65% (average 44%).^[100] Moreover, large enhancement of upconversion PL using NPOM was realized, with the intensity enhanced by four orders of magnitude and the Purcell factor of 166.^[101] Placing a silver NW over a silver film with a dielectric spacer also forms a coupled plasmonic cavity. It was shown that the radiative decay rate of the fluorescent molecules in the nanogap was enhanced by a factor approaching 1000.^[102]

 Table 1 summarizes the enhancement factor of PL intensity

 and Purcell factor in some typical plasmonic nanostructures.

By careful design of experiment, it is possible to separate the excitation enhancement and emission enhancement. Exciting the nanosystem with the laser wavelength off resonance with the plasmonic nanostructure can eliminate the excitation enhancement. Under this condition, the change of the spontaneous emission will be caused only by the emission modification. Figure 6a shows the dark-field scattering spectra of two silver nanoprisms on the monolayer of QDs and the PL spectrum of the QDs.^[109] As can be seen, the nanoprism 2 shows a SP resonance at the wavelength of the PL spectral peak. Figure 6b shows the PL image of the QDs excited by laser light of 405 nm wavelength in the area containing the two Ag nanoprisms. Clearly, the QDs at the position of the nanoprism 2 show stronger PL intensity. The PL decay curves in Figure 6c show that the PL lifetime of the QDs near nanoprism 2 is shortened, while the lifetime of the QDs near nanoprism 1 remains similar to that of the background QDs.

Figure 6d,e show the PL intensity enhancement and lifetime as a function of SP resonance wavelength of the Ag nanoprisms, respectively.^[109] As can be seen, when the SP resonance wavelength matches the PL spectrum of the QDs, the enhancement factor of PL intensity is maximum, while the lifetime is shortest. In absence of excitation enhancement, the enhancement of the

www.advancedsciencenews.com

 Table 1. Spontaneous emission of QEs coupled with various plasmonic nanostructures.

Plasmonic nanostructures	QEs	Nanostructure size [nm] ^{a)}	Separation distance [nm]	PL intensity enhancement	Purcell factor ^{b)}	Ref.
Au NP	Single terrylene molecules	<i>d</i> ≈ 100	_	≈25	≈20	[5]
Au NP	Single Nile blue molecules	$d \approx 80$	≈5	≈7	-	[6]
Au NP	Lissamine molecules	$d \approx 2$ $d \approx 30$ $d \approx 60$	1	<1	≈9.1 ≈15.6 ≈21.4	[103]
Au NP	Single ATTO647N molecules	$d \approx 10$	≈10.1	<1	≈2	[104]
Au NP	Single QDs	<i>d</i> ≈ 35	_	≈1	≈20	[68]
Au NP	A single QD	$d \approx 30$	_	-	≈18	[70]
Au nanocube	A single QD	<i>l</i> ≈ 127	_	-	24	[47]
Au nanocube	A single QD	/ ≈ 88	_	1.3	74	[69]
Au nanorod	Single crystal violet molecules	<i>l</i> ≈ 58, <i>d</i> ≈ 25	In solution	1100	-	[85]
Au nanorod	Single crystal violet molecules	<i>l</i> ≈ 60, <i>d</i> ≈ 25	In solution	≈1000	≈7	[86]
Au nanorod	800CW molecules	<i>l</i> ≈ 113, <i>d</i> ≈ 38	Polymer $t \approx 3$	≈120	-	[105]
Al nanorod	Single terrylene diimide molecules	<i>l</i> ≈ 175, <i>d</i> ≈ 50	≈10	3–4	10	[106]
Au@Ag nanocuboid	Alexa Fluor 647 molecules	Au nanorod <i>l</i> ≈ 50.3, <i>d</i> ≈ 12.8, Ag shell t ≈ 7.44, 4.08	-	186	-	[107]
Ag nanoprism	Dye molecules	$l \approx 100, t \approx 12$	DNA spacer ≈5.5	≈9–30	_	[108]
Ag nanoprism	QD monolayer	<i>l</i> ≈ 50–100, <i>t</i> ≈ 10–15	_	≈1.2–1.5	≈3–4	[109]
Ag nanoprism	Single QDs	/ ≈ 47	PMMA $t \approx 10$	2.5	5	[110]
Ag nanoprism Au nanosphere Ag nanocube	QDs	Prism $l \approx 100$ Sphere $d \approx 80$ Cube $l \approx 50$	<5	≈25 ≈6 ≈9	-	[87]
Au NP with SiO_2 shell	Single QDs	Au core $d \approx 55$	$SiO_2 t \approx 7$ $t \approx 14$	2.4 1.7	≈3.9 ≈1.3	[62]
Ag NP with SiO ₂ shell	Fluorophores	Ag core $d \approx 130$	Molecules in SiO ₂	≈20	<10	[111]
Au nanorod with SiO ₂ shell	IRDye 800CW DBCO	Au nanorod <i>l</i> ≈ 50, aspect ratio 3.7	$SiO_2 t \approx 17$	≈10	-	[61]
Au nanorod with SiO ₂ shell	Oxazine 725 molecules	Au nanorod $l \approx 89$, $d \approx 42$, SiO ₂ $t \approx 21$	Molecules in SiO ₂	Average 29	-	[64]
Au nanorod with SiO ₂ shell	Oxazine 725 molecules	Nanorod $l \approx 100$, $d \approx 44$, SiO ₂ $t \approx 23$	Molecules in SiO ₂	20.8	≈3.5	[112]
Au NP dimer	Single QDs	$d \approx 40$	Gap ≈ 5	<30	-	[54]
Au NP dimer	Single ATTO647N molecules	$d \approx 80$ $d \approx 100$	Gap ≈ 23	Average 13.8 Average 28, maximum 117	≈17.3	[55]
Au NP dimer	Single ATTO647N molecules	$d \approx 60$	Gap ≈ 21	Maximum 4	Average 3	[57]
Au NP dimer	Single ATTO647N molecules	$d \approx 100$	Gap ≈ 12–17	Maximum 471	-	[113]
Au NP dimer	Single Cy5 molecules	$d \approx 60$	Gap ≈ 13	≈37	8.5	[114]
Au NP dimer	Single Cy7 molecules	$d \approx 100$	Gap ≈ 12–16	-	75*	[115]
Au NP dimer	Single Alexa Fluor 647 molecules (quencher added)	<i>d</i> ≈ 80	Gap ≈ 6	600	-	[116]
Au NP dimer	Nile blue molecules	$d \approx 60$	Gap ≈ 5	610 for TiO ₂ gap, 1526 for Al ₂ O ₃ gap	-	[117]
Au nanobowtie	Single dye molecules	-	Gap < 20	≈1340	≈28	[88]
Au NP monomer dimer	Single NV centers	$d \approx 60$	-	≈12 ≈14	≈7.5 ≈9.5	[72]

www.advancedsciencenews.com

Table 1. Continued.



	امیں سما م
www.arm-	journal.de

Plasmonic nanostructures	QEs	Nanostructure size [nm] ^{a)}	Separation distance [nm]	PL intensity	Purcell	Ref.
Au NP monomer	Single QDs	$d \approx$ 90, $t \approx$ 40	Gap ≈ 14	2.7	11.1	[83]
Ag NP monomer dimer	Single Cy5 molecules	<i>d</i> ≈ 20	≈8	≈7 ≈13	≈3.1 ≈3.8	[118]
Ag nanocube monomer dimer	Single NV centers	<i>l</i> ≈ 80	Nanodiamond size ≈30–35	2.1–4.0 2.7–18.0	1.8–3.4 2.1–5.9	[90]
Au NP monomer dimer	Single fluorescent polystyrene beads	Au NP $d \approx 60$, bead $d \approx 40$	-	1.5 2.72 (maximum 3.64)	_	[119]
Au nanorod monomer dimer	ATTO-655 molecules	<i>l</i> ≈ 43.5, <i>d</i> ≈ 20.4	Gap ≈6.1	120 470	-	[120]
Ag NP dimer	Single molecules	<i>d</i> ≈ 80	Gap ≈12	139 (Alexa488) 149 (Atto542) 162 (Atto647N)	-	[56]
Ag NP dimer	Single Alexa Fluor 647 molecules	<i>d</i> ≈ 100	Gap ≈12	Average 89, maximum 461	-	[121]
Asymmetric Ag nanobar dimer	NIR dye molecules	Short bar <i>l</i> ≈ 150, Long bar <i>l</i> ≈ 210	Gap ≈40	405	-	[122]
Au NP dimer in an aperture in Au film	Single Alexa Fluor 647 molecules (quencher added)	NP $d \approx$ 76, Au film $t \approx$ 50	Gap ≈12	1100	_	[89]
Three Au nanorods arranged in U shape	Single silica-encapsulated QDs	Nanorod $l \approx 85$, $d \approx 25$	Gap ≈ 26 Gap ≈ 29	-	≈132 ≈45	[73]
Ag nanocube on Ag film	Cy5 molecules	Nanocube <i>I</i> ≈ 83.6	$PVP \approx 3$, polyelectrolyte ≈ 5	30 000	74	[94]
Ag nanocube on Ag film	Single NV centers	Nanocube <i>I</i> ≈ 100	Spacer ≈6	≈90 (NA = 1.49), ≈300 (NA = 0.9)	≈70	[96]
Ag nanocube on Au film	Ru dye molecules	Nanocube <i>l</i> ≈ 80	Gap ≈8	≈65	≈1000	[95]
Ag nanocube on Au film	QDs	Nanocube <i>l</i> ≈ 75	$PVP \approx 3$, polyelectrolyte ≈ 1	177–2300	190-880	[123]
Ag nanocube on Au film	Single QDs	Nanocube <i>l</i> ≈ 75	Gap ≈ 12	1900	540	[93]
Ag nanocube on Au film	$Monolayer\ WSe_2$	Nanocube <i>I</i> ≈ 50–100	$Al_2O_3 t \approx 4$, PVP $t \approx 2-3$	≈1700	-	[98]
Ag nanocube on Au film	Monolayer MoSe ₂	Nanocube <i>l</i> ≈ 65	$Al_2O_3 t \approx 2$	≈6000	-	[99]
Au NP on Au film	Monolayer MoS ₂	NP $d \approx 200$	$Al_2O_3 t \approx 5$ on both sides of MoS ₂	7.74	-	[124]
Au NP on Ag film	Single QDs	NP <i>d</i> ≈ 100	-	-	20	[125]
Au nanocube on Au film	Single defects in monolayer WSe ₂	Nanocube $l \approx 110, h \approx 90$	Gap ≈5	13	Average 181, maximum 551	[100]
Au nanocube on Au film	Single defects in carbon nanotubes	Nanocube $l \approx 160, h \approx 30$	≈5	415	70	[126]
Ag nanocube on Au film surrounded by a circular grating	QDs	Nanocube $l \approx 90$, ring $w \approx 280$, $h \approx 50$, $p \approx 560$	Gap ≈10 (QD diameter)	121	424	[127]
Au nanorod on Au film	Nile blue molecules	Nanorod $I \approx 82.5$, $d \approx 33$	Gap ≈5–50	Maximum 311.8 (gap ≈10)	Maximum 58.6 (gap ≈5)	[128]
Au nanopatch on Au film	Single QDs	Nanopatch $d \approx 200-2500$, $t \approx 20$	PMMA $t \approx 30-40$	70	72	[129]
Au microdisk on Au film	QDs	Microdisk $d \approx 1500-2100$, $t \approx 20$	Silica t ≈ 15 on both sides of QDs	-	≈20–80	[130]
Ag NW on Au film	Single QDs	NW <i>d</i> ≈ 160–280	-	-	≈7.9	[131]
Ag NW on Ag film	Alq ₃	NW $d \approx 100$	$Al_2O_3 t \approx 1.8$, $Alq_3 t \approx 2.5$	-	≈1000*	[102]
Si NP on Au film	QDs	NP <i>d</i> ≈ 80–200	$Al_2O_3 t \approx 1-30$	69 ($t \approx 5$)	42 (<i>t</i> ≈ 1)	[132]

www.advancedsciencenews.com

Table 1. Continued.



www.afm-jou	urnal.de
-------------	----------

Plasmonic nanostructures	QEs	Nanostructure size [nm] ^{a)}	Separation distance [nm]	PL intensity enhancement	Purcell factor ^{b)}	Ref.
Au nanobowtie on Au film	Carbon nanotubes	Nanotriangle $l \approx 250, h \approx 30,$ gap $\approx 10-20$	Carbon nanotube on Au nanobowtie with 2 nm Al ₂ O ₃ spacer	Average 44, maximum 98	Average 57, maximum 180	[133]
Au NP dimer on Au film	Monolayer MoS ₂	NP <i>d</i> ≈ 140	$Al_2O_3 t \approx 6$	1350	-	[134]
Au nanoshell coated on a QD encapsulated in a SiO ₂ shell	single QDs	Au shell t ≈ 20	$SiO_2 t \approx 35$	_	≈6	[135]
Ag coated on InGaN QD with Al_2O_3 as spacer	Single QDs	Ag $t \approx 30$	$Al_2O_3 t \approx 20$	≈7.33	≈12.8	[136]
Nanoaperture in Al film	R6G molecules	<i>d</i> ≈ 150, Al <i>t</i> ≈ 300	In solution	≈6.5	>4.1	[137]
Au bullseye structure	Alexa Fluor 647 molecules	Aperture $d \approx 135$, groove $w \approx 200$, $h \approx 65$, $p \approx 440$	In solution	≈120	-	[138]
Au bullseye structure	Alexa Fluor 647 molecules	Aperture $d \approx 140$, groove $w \approx 200$, $h \approx 65$, $p \approx 440$	In solution	80	-	[139]
Au bullseye structure	Single PMMA-encapsulated QDs	Aperture $d \approx 250-350$, groove $w \approx 220$, $h \approx 110$, $p \approx 520-570$	PMMA $t \approx 25$	≈5.5	≈7 (exciton A), ≈28 (exciton F)	[140]
Ag bullseye structure	Single NV centers	Aperture $d \approx 100-140$, groove $w \approx 80$, $h \approx 100$, $p \approx 280-300$	-	-	≈6	[141]
Au film on Si nanopillar	Single defects in monolayer WSe ₂	Au $t \approx 10$, nanopillar $d \approx 180$, overall $h \approx 300$	$Al_2O_3 t \approx 6$	≈7.3	≈2.4	[142]
Au and Ag NP array	Single defects in h-BN	NP $d \approx 80, h \approx 50,$ spacing ≈ 400	Al ₂ O ₃ t ≈ 5 for Ag NP array	2.4 (Au) 2.6 (Ag)	≈6.7 (Au) ≈30 (Ag)	[143]
Au NP array	LDS 750 dye molecules	NP $d \approx 135$, $h \approx 70$, $p \approx 400$	$AI_2O_3 t \approx 5$	≈7	≈2.2	[144]
Au NP film	Single silica coated QDs	NP <i>d</i> ≈ 17	Silica $t \approx 5$	≈3	≈10	[145]
Ag NP film	Single QDs	-	-	<1	≈2.5	[146]
Ag nanocube film	QDs	Nanocube <i>I</i> ≈ 55	PVP $t \approx 5$	3.5	4.5	[147]
SiO ₂ @Au core-shell NP film	Indocyanine green molecules	Inner radius ≈112, outer radius ≈123	Human serum albumin 3.8–12	-	≈50	[148]
Vertically aligned Au nanorod monolayer	QDs	Nanorod $l \approx 100.5$, $d \approx 39.8$	Silica $t \approx 20$	≈10.4	≈4.5	[149]
Disordered Au nanorods	Defects in h-BN	Nanorod $l \approx 20$	-	>100	26.75	[150]
Hexagonal array of nanoholes in Au film	Alexa Fluor 647 molecules	Nanohole $d \approx 140$, $p \approx 440$, Au $t \approx 150$	In solution	40	2.1	[151]
Ag nanohole array	Monolayer MoS_2	Nanohole <i>d</i> ≈ 170, <i>p</i> ≈ 260, 440, Ag <i>t</i> ≈ 60	SiN $t \approx 20$	77 104	_	[152]
Trenches in Au substrate	Monolayer WSe ₂	Trench <i>w</i> < 20, <i>p</i> ≈ 200	0	≈20 000	-	[153]
Au nanogroove array	Monolayer MoS ₂	Au $t \approx 150$ groove $h \approx 55-105$, $p \approx 500$	0	62	-	[154]
Rough Au film	Single QDs	Au film t ≈ 120, size of rough valleys and peaks ≈10–50	-	5	>1000	[155]
Rough Au film	Single QDs	Au film t ≈ 100, size of rough valleys and peaks ≈20–50	-	≈7	≈50	[156]
Au film	Single NV centers	$t \approx 50$	-	≈5–10	≈1.8	[157]
Bowtie nanoaperture in Al film on near-field probe	Single TDI molecules	Nanogap region \approx 70 \times 140	>30	<5	-	[158]
Tip of tapered slot	Alexa Fluor 750 molecules	Tip <i>l</i> ≈ 20	-	≈2200	-	[159]

a)d, t, w, h, l, and p represent diameter, thickness, width, height or depth, length or side length, and period, respectively; b)* marks the values corresponding to the enhancement factor of radiative decay rate.







Figure 6. a) Single particle scattering spectra of two Ag nanoprisms on top of a homogeneous QD film. The shaded graph is the emission spectrum of the QD film. b) A confocal scanning PL intensity image excited with a 405 nm laser. c) PL decays of the QDs near the two Ag nanoprisms and background QDs. d–f) The average enhancement factors of PL intensity (d), the average lifetime (e), and the average decay rate enhancement factors (f, black circles are for radiative decay rates, blue squares are for nonradiative decay rates) are plotted against scattering peak positions of Ag nanoprisms on top of a film of QDs with emission peak centered at 598 nm. Emission spectrum of the QDs (shaded spectra) are also plotted for reference. Horizontal dotted line in (e) is the average lifetime of the background QDs. Red and blue dotted lines are the Gaussian fits. g) Experimental scattering (top) and fluorescence (bottom) spectra of single NP dimers with incorporated Cy3 dye molecules. Spectra with identical colors are measured on the same dimer. h) Experimental and theoretical correlation between the wavelengths of maximum fluorescence enhancement and the wavelengths of maximum scattering. (a–f) Reproduced with permission.^[109] Copyright 2010, American Chemical Society. (g) and (h) Reproduced with permission.^[163] Copyright 2008, American Physical Society.

radiative decay rate $\gamma_{rad,m}/\gamma_{rad,0}$ can be obtained by taking the ratio of the PL intensities obtained at the initial time. As $\gamma_{rad,0}$ can be obtained from the measured PL quantum yield of the QDs and the total decay rate, $\gamma_{rad,m}$ can be obtained. Since the total decay rate of the QDs coupled with the nanoprism can be obtained from the measured lifetime, the nonradiative decay rate is then also obtained. The maximal enhancement factor for the radiative decay rate and nonradiative decay rate also appear at the wavelength of resonance (Figure 6f). Usually the lifetime and quantum yield of fluorescence are independent of the excitation wavelength. However, for the QDs coupled with silver nanoprisms, wavelength dependent lifetime and quantum yield were observed. This phenomenon was attributed to wavelength dependent coupling of high-order SP modes to different spatial subpopulations of QDs.^[160] This indicates more possibilities to tailor the spontaneous emission by SP modes in metal nanostructures.

To fully utilize the plasmonic enhancement to increase the fluorescence brightness, metal nanostructures of double SP

resonances with one resonance matching the excitation wavelength and one resonance matching the emission wavelength can be used. This double resonance enhancement was demonstrated in gold nanorods coated with silica shells with the molecules dispersed therein. When the transverse and longitudinal SP resonances of the gold nanorod match the excitation and emission wavelengths, respectively, higher fluorescence intensity and shorter lifetime were observed.^[112]

DVANCED

SCIENCE NEWS ______

The coupling of QEs with SP modes can not only modify the PL intensity and lifetime, but also change the PL spectral profile.^[161-164] Figure 6g shows the dark-field scattering spectra and fluorescence spectra for four gold NP dimers coupled with Cv3 molecules.^[163] With the decrease of the distance between the two NPs, the scattering peak of the longitudinal mode redshifts, and the fluorescence spectrum is reshaped. The change of the relative intensity of different wavelengths can be clearly seen, indicating the wavelength dependence of fluorescence enhancement. The wavelength of maximum fluorescence enhancement is linearly dependent on the scattering peak wavelength with a slope of 0.95 (Figure 6h). This indicates that efficient energy transfer occurs between the exciton and the SP mode. The SP induced spectral reshaping of fluorescence was also observed in gold nanorod coated by silica shell with molecules embedded in the shell.^[164] As the SP resonance wavelength of the longitudinal mode is shifted away from the intrinsic fluorescence wavelength of the molecules, a new fluorescence peak appears at the wavelength of the SP resonance. For the nanorods of the same resonance wavelength, the intensity of the SP induced fluorescence peak is stronger for nanorods of bigger size.

5.3. Emission Direction and Collection Efficiency

It is challenging to fully collect and use the generated photons from OEs due to the wide angular distributions of the fluorescent emission. Plasmonic nanostructures have been shown to provide a solution to modify the emission pattern and enhance the collection efficiency. The plasmon-coupled directional emission was first realized for fluorophores coupled with metal film. The excited fluorophores can generate propagating SPs on the metal film, and the SPs radiate to the side of the substrate at a certain angle depending on the wavelength.^[165,166] This emission can be regarded as the reverse process of exciting SPs on the film by light, and the emission angle is determined by the phase matching condition for the SPs and light. More recently, directional fluorescent emission was reported in different kinds of plasmonic nanostructures with well-designed geometries, such as Yagi-Uda antenna,^[81,167] bullseye structure composed of multiple grooves in/on metal film,^[138,139,141,168-173] hexagonal array of nanoapertures in metal film,^[151] microdisk on metal film,^[130] split ring resonator,^[174] V-shaped nanoantenna,^[175] nanorod,^[66,82,176] nanowire,^[177,178] and metasurface.^[179]

A single metal NP can be regarded as an antenna with the radiation pattern determined by the antenna mode. By efficiently coupling to the plasmonic nanoantenna, the QE emission follows the pattern of the SP mode. A metal nanorod can support multipolar SP modes, and the interaction of these modes with a QD placed at the end of the nanorod modifies the QD emission pattern.^[82] Figure 7a shows the experimental

results of back focal plane imaging (also called Fourier imaging) of the fluorescence from QD-nanorod coupled systems for Au nanorods of different lengths. The emission shows clear dipolar and quadrupolar radiation patterns, because the QD emission wavelength of about 800 nm matches the dipolar (j = 1) and quadrupolar (j = 2) modes of the two nanorods, respectively. By increasing the nanorod length to match the higher order SP resonance wavelength with the QD emission wavelength, the radiation patterns corresponding to higher order modes were observed. These results show that the emission of a dipolar transition can be converted into higher order radiation by coupling to properly designed plasmonic antennas. For a QD or a fluorophore in the nanogap of a NP dimer, dipolar radiation pattern determined by the SP mode was also observed.^[83,114]

By coupling a single QD to an optical Yagi-Uda antenna, unidirectional emission of the QD was achieved (Figure 7b).^[81] In this nanoantenna structure, the resonant feed element which was assembled with a QD was surrounded by a set of parasitic elements acting as reflector and directors. As shown in Figure 7b, the radiation pattern of the QD shows a single lobe because of the coupling with the optical antenna. A frontto-back intensity ratio of 6 dB was achieved, which was defined as the intensity ratio between the point with maximum intensity and the point diametrically opposite in the Fourier plane image. The directionality can be controlled by tuning the antenna dimensions. Similarly, unidirectional emission was demonstrated in U-shaped split ring resonator coupled with QDs, V-shaped antennas coupled with dye molecules, and gold nanorod coupled with fluorescent nanodiamond.^[66,174,175] Unidirectional radiation of a single QE can also be realized by coupling the QE to propagating SP mode on a metal NW. As shown in Figure 7c, the QD coupled with a silver NW emits mainly along the NW with two lobes symmetric with respect to the NW axis (Figure 7c (ii)), resembling the emission of a dipolar source perpendicular to the NW. The emission into propagating SPs was guided along the NW and coupled out as photons at the NW end. The emission at the NW end shows a clear unidirectional behavior (Figure 7c (iii)).^[177]

The light transmitted through an aperture in a metal film surrounded by circular grooves (called bullseye structure) emerges as a beam with a small angular divergence due to interference.^[180] The light beaming capability of the bullseye structure can be used to collimate the fluorescent emission of QEs. The left panel of Figure 7d shows the SEM image of a bullseve structure that is a nanoaperture in a gold film surrounded by five grooves.^[138] The corrugations improve the local electric field intensity in the nanoaperture, leading to enhanced emission count rate. The dye molecules in the nanoaperture emitted into a cone of $\pm 15^{\circ}$ in the direction normal to the sample plane, as shown in the right panel of Figure 7d. This normal emission with small spreading angle guarantees that the fluorescence can be effectively collected by an objective or other optical components (for example, optical fiber) with low numerical aperture. The radiation direction can be shifted if the circular symmetry of the antenna is broken, for example, by shifting the aperture position relative to the center of the grooves.^[139] By carefully designing the antenna parameters to tune the interference conditions for different wavelengths, the fluorescence of different wavelengths is emitted into different directions, leading to the

ADVANCED SCIENCE NEWS ______





Figure 7. a) Angular radiation patterns of QDs coupled to nanorod antennas. Left: Schematic of an angular radiation pattern highlighting the critical angle of the glass-air interface and the numerical aperture of the objective. Middle and right: Experimental Fourier-space patterns of the first two resonant antenna modes. b) Unidirectional emission of a QD coupled to an optical Yagi–Uda antenna. Left: SEM image of a five-element Yagi–Uda antenna. A QD is attached to one end of the feed element inside the marked area. Right: Radiation pattern from a QD coupled to an Yagi-Uda antenna. c) Bidirectional and unidirectional emission from a QD coupled to a Ag NW. (i) Fluorescence image showing the coupling of a single QD to a Ag NW with an Al₂O₃ spacer layer of 10 nm thickness. The larger emission spot is the QD position, while two smaller spots correspond to the NW ends. The inset is the bright-field optical image of the NW. The scale bar is 2 µm. (ii, iii) Fourier images obtained from the areas marked in (i) by the green and white dashed squares, respectively. The green dashed lines indicate the direction of the NW. d) Directional emission from molecules coupled to a nanoaperture with periodic corrugations. Left: SEM image of the fabricated nanoaperture with five corrugations. Right: Angular radiation patterns in the polar angle for a single nanoaperture with (red) and without (blue) periodic corrugations. The intensity for the noncorrugated aperture is multiplied by a factor of 4. e) Directional emission from QDs coupled to a nanocube-bullseye hybrid plasmonic nanoantenna. (i) 3D illustration of the hybrid plasmonic nanoantenna consisting of Au concentric rings on a Au film and a Ag nanocube situated at the center of the rings. The nanocube and the gold film are separated by a monolayer of QDs. (ii, iii) Fourier image and angular emission pattern of QDs coupled to a nanocube-bullseye antenna. The angular pattern in (iii) is retrieved along the dashed line in (ii). (a) Reproduced with permission.^[82] Copyright 2013, Nature Publishing Group. (b) Reproduced with permission.^[81] Copyright 2010, American Association for the Advancement of Science. (c) Reproduced with permission.^[177] Copyright 2015, American Chemical Society. (d) Reproduced with permission.^[138] Copyright 2011, American Chemical Society. (e) Reproduced with permission.^[127] Copyright 2020, Wiley.

color sorting. The color sorting of fluorescence with central wavelength 560 and 670 nm was demonstrated by tuning the distance between the nanoaperture and the first groove. When the groove–aperture distance is equal to a multiple of SP wavelength at the gold–glass interface, the emission is centered in the direction normal to the sample plane due to the constructive interference between the fluorescence emitted from the central aperture distance is equal to an odd multiple of half wavelength of SPs, the destructive interference leads to significant intensity drop in the direction normal to the sample and the maximum emission toward 30° with respect to the normal direction.

Depositing a circular metal grating on a metal film also forms a bullseye antenna that shows light beaming behavior. In spite of the enhanced directionality, the enhancement of PL intensity on the bulleseye antenna is moderate. To further enhance the PL intensity, a nanogap structure can be built as discussed in Section 5.2. By placing a Ag nanocube onto the center of the Au bullseye structure, the PL intensity and decay rate for the QDs located in the nanogap beneath the nanocube can be significantly enhanced, while the directionality of the emission is maintained.^[127] The emitted photons are mostly directed to the center of the Fourier plane and distributed in the range of about $\pm 7^{\circ}$ around the normal direction (Figure 7e).

5.4. Emission Polarization

When a QE is efficiently coupled to a plasmonic nanoantenna, its emission is converted to the radiation of the antenna mode. Therefore, not only the angular emission pattern, but also the emission polarization is determined by the antenna mode. The nanoantenna modified emission polarization has been studied in the coupled systems of QEs with plasmonic nanoantennas of gold nanorods,^[81,82,181,182] probe-based aluminum nanorods,^[176] multiple-NP antenna,^[183,184] multiple-nanorod antenna,^[73] NP dimer,^[90] split ring resonator,^[185] metal tip,^[186] and sawtooth nanoslit array.^[187] Figure 8a shows the fluorescence of single QDs coupled with Au nanorods, and the degree of linear polarization (DOLP) is encoded in color, with red being linear polarization parallel to the long axis of the nanorod.^[81] DOLP (also called depolarization ratio) is defined as DOLP = $(I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$, where I_{\parallel} and I_{\perp} are the emission intensities at two orthogonal polarization directions, respectively. The QDs were excited by circularly polarized laser light of 633 nm wavelength. As can be







Figure 8. a) PL images of QDs on half-wave dipole antennas (left), and Yagi-Uda antennas (right). Different colors show variations in DOLP. Scale bar, 2 µm. b) Depolarization ratio of the dipole emission from a Ag NP trimer antenna with linear (left) and right-angle (right) configurations. c) Polarization angle (solid line) and the maximum depolarization ratio ρ_{max} (dashed line) of the emission as a function of angle γ . The radii of all three Ag NPs are 40 nm. The separations between the NP 1 and 2, and 2 and 3 are kept at 1 nm. The wavelength of the dipole emission is 555 nm. d) Polarization angle (solid lines) and the maximum depolarization ratio (dashed lines) as a function of the wavelength of the dipole emission for the right-angle configuration of a Ag trimer antenna with identical NPs of radius 40 nm. The separation between the NP 1 and 2 is either 1 nm (red) or 5 nm (blue). The separation between the NP 2 and 3 is always kept at 1 nm. e) A nanoantenna consisting of three Au nanorods coupled to two QDs located in the gaps between the two vertical nanorods and the horizontal one. Left: Simulated maps of electric field intensities and electric displacement vectors of the plasmonic mode excited at 808 nm wavelength by a y-oriented dipole at QD1 (top-left panel) and QD2 (bottom-left panel). Right: Simulated polarization states (shown by the polarization ellipses) of the emissions from QDI and QD2, respectively. f) Top: Sketch of a split ring resonator nanoantenna driven by a QD emitting photons with opposite spin in different directions. Bottom: Experimentally measured polarization states of emission of the coupled split ring resonator and QD system in different directions (with different k-vectors). The polarization state is encoded in the color as well as in the rotation angle and the elliptical shape of the arrows. The inset in the center shows the orientation of the split ring resonator. (a) Reproduced with permission.^[81] Copyright 2010, American Association for the Advancement of Science. (b-d) Reproduced with permission.^[184] Copyright 2009, American Chemical Society. (e) Reproduced with permission.^[73] Copyright 2018, Nature Publishing Group. (f) Reproduced with permission.^[785] Copyright 2014, American Chemical Society.

seen, the fluorescence of the QDs coupled with Au nanorods is linearly polarized along the long axis of the nanorod with a degree of linear polarization of about 0.8. The emission of the QDs coupled with Yagi–Uda antennas composed of Au nanorods is also linearly polarized parallel to the long axis of the nanorod with similar DOLP. For the coupling system of Au NP core and molecules embedded in silica shell, the DOLP of the fluorescence excited by circularly polarized light was found to be the same as the DOLP of the scattering light of the NPs.^[181] Simulations show the efficiency of energy transfer from the dipole to the nanorod is above 0.9, when the dipole is located within a distance of 20 nm away from the nanorod surface. This high efficiency guarantees the high DOLP of the fluorescence.

Although the dipolar SP modes in a metal nanosphere does not have a preferred polarization direction, the coupling of two metal nanosphere forms a dipolar nanoantenna polarized along the axis connecting the centers of the two nanospheres. Therefore, the emitted light of the QE in the nanogap between the two nanospheres is linearly polarized parallel to the dimer axis. For the nanoantenna composed of three nanospheres, the emission polarization can be different depending on the geometry.^[183,184] Figure 8b shows the DOLP for Ag nanosphere trimers of different geometries. For linear arrangement of the nanospheres, the polarization of the emitted light is still along the central axis as the axial symmetry holds. When the third nanosphere is moved away from the axis, the polarization of the emitted light is rotated to a new direction. For the right-angle geometry (right panel of Figure 8b), the emitted light is mainly polarized along the direction of 40° with respect to the axis. Figure 8c shows the polarization angle as a function of the rotation angle γ of the third nanosphere relative to the dimer. As can be seen, the polarization angle is first rotated clockwise to 40° with the increase of γ , and then is rotated counterclockwise. For $\gamma = 120^{\circ}$, the



emission becomes linearly polarized along the axis again. This is because the three nanospheres are now in an equilateral triangle configuration with the third nanosphere coupling symmetrically with the other two nanospheres. Figure 8c also shows the DOLP is decreased with the increase of the polarization angle. The polarization angle and DOLP for a nanosphere trimer antenna is strongly dependent on the wavelength, as shown in Figure 8d. This is totally different from the dimer case, where the emission is always linearly polarized along the dimer axis independent of wavelength. There is a sharp shift of the polarization angle from -30° to 40° at about 520 nm, which may be caused by the phase difference of the SP modes as illustrated in the inset. At this transition wavelength, the emission is almost circularly polarized with DOLP close to 0. When the nanogap between the nanospheres 1 and 2 is increased from 1 to 5 nm, the results stay almost the same, which facilitates the coupling of this nanoantenna structure with QEs of different sizes. The polarization behavior can be further controlled by tuning the size of the third nanosphere, the distance between the third nanosphere and the dimer, and the refractive index of the surrounding medium.^[183,184] The nanosphere tetramer antenna consisting of four nanospheres shows a similar polarization rotation behavior. The maximum polarization rotation angle of 56° was obtained when the third and fourth nanospheres are both rotated 90° relative to the dimer axis.^[184]

Metal NPs of other shapes can also be used to compose an antenna to modulate the emission polarization of QEs. A U-shaped nanoantenna consisting of three Au nanorods was constructed to modify the excitation and emission of the QDs located at the two junctions between the nanorods.^[73] The excited QDs within the nanogaps couple to different SP modes in the structure, as shown in Figure 8e. The three nanorods can be regarded as three linearly polarized electric dipoles. The QD in the right junction couples to nanorod 1 and 3, while the QD in the left junction couples to nanorod 2 and 3. The difference of the two modes in the top-left and bottom-left panels of Figure 8e is the phase relation between the dipolar modes of two nanorods. The two orthogonal dipoles with similar amplitude combine to form a nearly linearly polarized effective dipole oriented at an angle of about 45° or 135°. These effective diploes produce far-field radiation with roughly orthogonal linear polarizations (right panels of Figure 8e). Simulation results show that the DOLP is about 0.98 for the emission of the two QDs, and the polarization angle is 41° and 137°, respectively. The nearly orthogonal linear polarization indicates that the emission of the two QDs can be selectively detected by using a polarizer.

The U-shaped split ring resonator support multiple SP modes. The superposition of the radiation patterns from different modes can lead to different polarization states of the radiated light. For QDs coupled with the split ring resonator, the emission polarization can vary from linear to elliptical polarization. Figure 8f shows the distribution of polarization ellipticity in the Fourier plane. As can be seen, the emission along the symmetry plane of the antenna ($k_x = 0$) is linearly polarized, while the emission with opposite signs of ellipticity up to ±0.5 radiates to the opposite sides of the symmetry plane. Chiral plasmonic nanostructures with different handedness show different responses to the circularly polarized light and

circularly polarized excitons, which have been used to modify the degree of circular polarization of the PL from valley-polarized excitons in monolayer TMDCs.^[188–191]

5.5. Plasmon Assisted Energy Transfer between Emitters

The energy transfer between fluorescent emitters has attracted a lot of attention over the past decades, due to its wide applications in the fields such as chemical physics and life science. The FRET is near-field nonradiative energy transfer from an emitter called donor to an emitter called acceptor. The FRET occurs through dipole-dipole interaction, and is the main energy transfer mechanism between emitters in nanometer distance. The FRET efficiency falls as $1/r^6$ (r is the distance between donor and acceptor), leading to an energy transfer distance of smaller than 10 nm. Since plasmonic nanostructures can effectively couple fluorescent emission into SP modes, assisted by the SP modes, energy transfer between donor and acceptor emitters over longer distance can be realized. The SP mediated long-range energy transfer was first demonstrated in a sandwiched structure of donor-Ag film-acceptor (Figure 9a).^[192] The donor molecules (Alq₃) and acceptor molecules (R6G) were doped in PMMA films and located on opposite sides of the Ag film. Figure 9b shows the PL spectra of control samples of donor-only and acceptor-only, and the sample containing both donor and acceptor layers. The PL spectrum of the donor-Agacceptor sample contains the emission peaks of both donor and acceptor molecules, and the intensity of the acceptor PL is larger than the spectrum for acceptor-only sample. These spectra indicate the occurrence of energy transfer from donor to acceptor molecules mediated by the SPs on the Ag film. Experiments for Ag films of varied thickness show that the energy transfer is present for Ag film thickness up to 120 nm. Analysis for the PL spectra shows that the proportion of emission due to energy transfer is largest for Ag film of 60 nm thick, although the absolute amount of energy transferred decreases as the Ag thickness increases. This is caused by the interplay between the probability of direct light transmission through the film and that of SP mediated energy transfer. Time-resolved PL measurements (Figure 9c) show that the lifetime of acceptor PL in the donor-Ag-acceptor sample is longer than that of the acceptoronly sample, and close to the PL lifetime of donor molecules, which further confirms the energy transfer between the donor and acceptor molecules. SP mediated energy transfer was also investigated in similar sandwiched structures replacing the metal film by a layer of metal NPs and depositing donor and acceptor emitters on the opposite sides of the NP layer with spacers between metal NPs and emitters. The energy transfer efficiency and PL intensity of the acceptor is dependent on the distance between the Au NPs and the emitters.^[193,194]

The propagating SPs on metal films or 1D nanowaveguides can be utilized to further increase the energy transfer distance. Putting donor and acceptor on the same side of a metal film can realize energy transfer over longer distances, by virtue of the propagation of SPs. For donor fluorescent nanobead and acceptor molecules dispersed in PVA film deposited on a Ag film of 50 nm thick with a 10 nm thick silica spacer, the donor excited by laser light can decay by exciting propagating SPs on www.advancedsciencenews.com





Figure 9. a) Schematic sample cross section superposed with field profiles associated with the symmetric SP mode (calculated for maximum Alq₃ emission wavelength 520 nm) illustrating how the fields span the Ag film. b) PL spectra from a planar sample with Ag film of thickness 30 nm. Data are shown for donor-only sample (Alq3:PMMA|Ag|PMMA) (blue spectrum), acceptor-only sample (PMMA|Ag|R6G:PMMA) (red spectrum), and sample containing both donor and acceptor layers (Alq3:PMMA/Ag|R6G:PMMA) (black spectrum). c) Time-resolved PL of samples with a Ag film thickness of 60 nm measured in the spectral region dominated by acceptor emission (λ > 648 nm). Data are shown for donor-only, acceptor-only, and donor and acceptor samples. d) Illustration of the sample structure with Ag NWs grown in the AAO template, the donor QDs adsorbed on the surface of the Al₂O₃ barrier layer, and the acceptor QDs deposited in the rest of the nanopores of the AAO template. e) Top: Schematic of a QD (donor) and a fluorescent nanobead (acceptor) coupled to a Ag NW. Bottom: Fluorescence image taken while the laser is focused on the QD. Bright spots are detected at the position of both emitters as well as both ends of the NW. f) Scattering (top) and fluorescence (bottom) spectra of the hybrid nanostructure of donor and acceptor molecules embedded in the silica shell on a Au@Ag core-shell nanorod. The blue and pink shades are the intrinsic emission spectrum of donor and the absorption spectrum of acceptor, respectively. The sharp cutoff at the short-wavelength side of the fluorescence spectrum is caused by the long-pass filter at 530 nm. g) Top: Donor and acceptor fluorescence decay traces from the sample of FRET-conjugates coupled with Au NP dimers. Bottom: Donor fluorescence decay traces of the donor-conjugate dimer sample (orange triangle), the FRET-conjugate in water (blue circle), and the FRET-conjugate dimer sample (green rectangle) providing evidence for FRET acceleration through nanoresonators. Black lines represent best biexponential fits. The donor is selectively excited at 480 nm. (a-c) Reproduced with permission.^[192] Copyright 2004, American Association for the Advancement of Science. (d) Reproduced with permission.^[196] Copyright 2010, American Chemical Society. (e) Reproduced with permission.^[199] Copyright 2017, American Physical Society. (f) Reproduced with permission.^[206] Copyright 2012, American Chemical Society. (g) Reproduced with permission.^[209] Copyright 2011, Elsevier.

the Ag film, which excite the acceptor molecules on the Ag film. As the SPs can propagate several microns over the Ag surface, the acceptors located microns away were excited, leading to the long-range energy transfer between the donor and acceptor molecules with separation distance up to 7 μ m.^[195] 1D plasmonic nanowaveguides can provide better control on the direction of SP propagation. Metal NWs are a typical kind of plasmonic waveguides supporting propagating SP modes with tight field confinement in the transverse cross section. By depositing donor and acceptor QDs on opposite ends of an array of Ag NWs (Figure 9d), the energy transfer was demonstrated for NW length up to 560 nm.^[196] Simulation shows that the enhancement factor of the energy transfer rate is different for

NWs with different shapes of cross section. Circular nanorod shows the strongest enhancement. For donor and acceptor with nonparallel polarizations, V-shaped nanorod structures show larger enhancement of energy transfer rate compared with single nanorod.^[197] By assembling a donor nanobead and an acceptor nanobead onto a Ag NW, energy transfer between the donor and acceptor nanobeads with a distance about 1 μ m was observed.^[198] The long-range energy transfer between a single QD (donor) and a fluorescent nanobead (acceptor) was also realized by coupling to a Ag NW, as shown in Figure 9e.^[199] The excited QD generates single SPs on the NW, which propagate and transfer energy to the acceptor located on the same NW with a distance of 8.7 μ m. The characterization of the

correlation between the fluorescence intensities of the QD and the acceptor nanobead shows that the QD and the nanobead blink simultaneously, confirming the energy transfer process between them. Simulation results show that large energy transfer rate between donor and acceptor can be obtained by coupling to wedge waveguide and V-groove channel waveguide,^[200] and the energy transfer rate can be further improved by coupling the emitters to an epsilon-near-zero plasmonic waveguide.^[201]

For conjugated or randomly distributed donor-acceptor pairs, metal nanostructure in their vicinity can also influence the Förster type energy transfer. The energy transfer rate, efficiency, and Förster radius can be modified because of the coupling of the fluorophores with SPs. The energy transfer for donor-acceptor pairs coupled with various metal nanostructures have been investigated, for example, metal NPs,^[202-205] nanorods,^[206,207] NP dimers,^[208,209] multilayer core-shell NPs,^[210] metal film,^[211] nanoapertures,^[212] and NPs over metal film.^[213] The energy transfer efficiency can be expressed as $E = \gamma_{\rm FT}/(\gamma_{\rm D} + \gamma_{\rm FT})$, where $\gamma_{\rm FT}$ is the energy transfer rate between donor and acceptor, and $\gamma_{\rm D}$ is the sum of the radiative and nonradiative decay rate of the donor. Since the plasmonic structures can influence γ_{D} and γ_{FT} , the energy transfer efficiency depends on the configuration of the plasmonic structures and fluorophores, and SP resonance wavelength. Figure 9f shows the scattering and fluorescence spectra of a single Au@Ag core-shell nanorod with donor and acceptor molecules embedded in outer silica shell.^[206] The scattering spectrum partly overlaps with the absorption spectrum of acceptor molecules (pink shade in top panel of Figure 9f). The rightmost peak in the fluorescence spectrum is the emission from the acceptor molecules due to the energy transfer from the donor molecules. The experimental results show that when the SP resonance wavelength overlaps with the emission peak of the donor, the energy transfer efficiency is low.

For a donor-acceptor pair coupled to a gold NP dimer, time resolved PL in the top panel of Figure 9g shows a risetime in the acceptor fluorescence before the decay, resulting from the energy transfer. The bottom panel of Figure 9g shows the donor fluorescence decay traces of different samples. The donor coupled to the dimer shows the slowest decay (orange data), while the FRET between the donor and acceptor significantly increases the decay rate (blue data). For donor-acceptor pair coupled with the dimer, the decay rate is increased further (green data), which is mainly due to the increased energy transfer rate caused by the coupling of the donor-acceptor pair with the NP dimer.^[209] In donor-acceptor pairs with fixed separation achieved by linking the donor and acceptor molecules to the opposite ends of double-stranded DNA, experiments show the energy transfer efficiency changes with LDOS that is tuned by the distance of the emitter pair to a Ag mirror, but the energy transfer rate is independent of LDOS.^[211]

The FRET rate and efficiency are strongly dependent on the relative positions and orientations of the donor, acceptor and metal nanostructure, the donor–acceptor distance, and the spectral overlap between SPs and emitters. In addition to FRET between donor and acceptor, energy transfer between plasmonic nanostructure and donor or acceptor also exists. The influence of SPs to energy transfer between donor and acceptor can be quite different in different systems, due to the different energy transfer rate and different energy branching to various decay channels. The energy transfer between donor and acceptor molecules can be accelerated or inhibited.^[205] To fully manipulate the energy transfer process making use of SPs, the coupled system need be precisely controlled.

5.6. Other Effects

Under the weak excitation condition with the excitation power far below the saturation, QEs, such as QDs, can be regarded as single-photon sources due to the low quantum yield of multiexcitons. In the coupled systems of QEs and plasmonic nanostructures, the SPs may not only enhance the spontaneous emission rate of single excitons, but also modify the multiexciton decay dynamics. Due to the nonradiative Auger recombination process, the quantum yield of multiexciton is usually very low. Several experiments have shown that by coupling to plasmonic nanostructures, the ratio of the emission quantum vield of biexciton and exciton is increased.^[214-217] For QDs embedded in PMMA layer on Au film, the biexciton emission was enhanced, and the mean value of the ratio of biexciton and exciton emission quantum yield was found to be about 0.2 with a large spread range due to the different QD positions with respect to the Au film.^[215] By coupling a QD to a silver coated AFM tip, the increase of $g^{(2)}(0)$ was seen as the distance between the tip and the QD was decreased, indicating the increased quantum yield ratio of biexciton and exciton. After retracting the Ag tip, the $g^2(0)$ returned to the original value before the tip approaching.^[216] Similar phenomenon was observed by assembling a QD and a Au nanocube and then separating them through AFM nanomanipulation.^[69] A strong enhancement of the biexcition emission was obtained by controllably positioning a single OD in the near field of a Au nanocone antenna. The radiative decay rates of both excitons and biexcitons are enhanced by about 100-folds at quantum yield of about 60% and 70%, respectively.^[217] For a single QD placed inside the gap between a Au nanopatch and a Au film, the enhanced multiexciton emission was also observed, contributing to the enhancement of the PL brightness.^[129]

The fluorescence blinking (switching between on and off states) occurs widely for colloidal semiconductor QDs, which limits their applications. It is found that the fluorescence blinking can be suppressed when the QDs couple with plasmonic nanostructures. This phenomenon has been demonstrated for QDs coupled with several nanostructures, such as Au films,^[155,156] Au and Ag NPs,^[68,145,146] and Ag nanoprisms.^[110] By using an AFM tip to manipulate a Au NP to get close to a QD, the suppression of blinking was observed in this coupled system compared with the QD before coupling with the Au NP.^[68] By moving the Au NP far away from the QD, the blinking behavior was recovered, confirming the influence of the Au NP. The blinking suppression is because of the modified exciton decay dynamics induced by the metal nanostructures. Based on this effect, non-blinking QDs were synthesized by encapsulating the QDs in a silica shell and then coating them with a Au nanoshell, which show reduced PL lifetime, and enhanced intensity and photostability.^[135]

The coupling of plasmonic nanostructures and multiple QEs can influence the cooperative emission of these QEs. For multiple dipoles near a metal nanostructure with appropriate separation, the cross talk between the dipoles leads to the formation of plasmonic superradiant modes.^[218,219] For two QEs coupled with a metal nanorod, the plasmonic surperradiance can increase the SP generation yield of a single emitter.^[220] For two dipoles coupled with a plasmonic waveguide, the decay rate shows oscillations as a function of the separation of the two dipoles.^[200] Multiple QDs coupled with a plasmonic structure may exhibit photon statistics of a single QD, as demonstrated in the coupled system of a plasmonic gap-bar antenna and a cluster of two or three silica-coated QDs.[221] The entanglement of photons can be preserved in the process of photon-SP-photon conversion.^[222,223] Theoretical studies have shown the quantum entanglement of two QEs mediated by plasmonic NPs and nanowaveguides.^[201,224–229]

6. Plasmonic Waveguide Modified Spontaneous Emission

Plasmonic waveguides enable the propagation of SPs with transverse mode confinement beyond the diffraction limit. Because of the inherent strong field confinement capability, the spontaneous emission of QEs in the proximity of a plasmonic waveguide can be significantly enhanced and a large part of the emission can be captured by the waveguide and converted to guided SPs. The long-range propagation of the SPs on plasmonic nanowaveguides enables the long-distance energy transfer between QEs. Moreover, remote excitation and remote detection of QEs can be achieved by using the propagating SPs and the energy interconversion between SPs and QEs.^[230-232] By utilizing the interference of SPs on plasmonic NW, controllable and selective excitation of single QEs with separation smaller the diffraction limited scale has been realized.^[233] The study of enhanced interaction between QEs and plasmonic waveguides and preferential spontaneous emission into guided SP modes is important for improving our understanding of light-matter interaction at nanoscale and for designing solid-state quantum information devices.

6.1. Theoretical Framework of the Interaction between Quantum Emitters and Plasmonic Waveguides

6.1.1. Plasmonic Nanowire Modified Spontaneous Emission

Chang et al. established a theoretical framework for the plasmonic NW modified spontaneous emission of a QE using the quasistatic approximation.^[234,235] For a conducting cylindrical NW of permittivity ε_2 with radius *R* embedded in a dielectric medium of permittivity ε_1 , there exists one fundamental SP mode with axial symmetry (see TM₀ mode in Figure 1d). The longitudinal component of the wave vector shows a unique $k_{\parallel} \propto 1/R$ behavior, which indicates that the wavelength of this SP mode can become largely reduced relative to the free-space wavelength as *R* approaching zero. The perpendicular component of the wave vector outside the NW is purely imaginary $k_{\perp} \propto i/R$. Therefore, the SP mode is nonradiative and tightly

localized on a scale R around the metal surface, giving rise to a small effective transverse mode area that scales as $A_{\rm eff} \propto R^2$. The SP mode confined well below the diffraction limit leads to a large interaction strength with the nearby QEs. For an oscillating dipole placed at a distance *d* from the center of a metal NW (top sketch in the left panel of Figure 10a), the analytical expressions for the decay rate of the dipole into the fundamental SP mode γ_{SP} , the radiative decay rate into free space $\gamma_{\rm rad,m}$, and the nonradiative decay rate $\gamma_{\rm nrad,m}$ can be obtained. It is noted that these three decay rates correspond to $\gamma_{\rm ET}$, $\gamma'_{\rm rad}$, and $\gamma'_{\rm nrad}$ in Figure 4a, respectively. The $\gamma_{\rm SP}$ is scaled as R^{-3} , due to a reduction in the SP group velocity and the small effective mode area. The $\gamma_{rad,m}$ of the dipole in the vicinity of the NW surface changes slightly from that in uniform dielectric medium. The $\gamma_{\rm nrad.m}$ is of $1/(d-R)^3$ dependence and related to the imaginary part of permittivity.

The coupling between QEs and plasmonic waveguides is usually characterized by the total decay rate enhancement factor (Purcell factor) and the apparent coupling efficiency, which are given by $F_{\rm P} = (\gamma_{\rm SP} + \gamma_{\rm rad,m} + \gamma_{\rm nrad,m})/\gamma_0$ and $\eta_{\rm app} = \gamma_{\rm SP}/(\gamma_{\rm SP} + \gamma_{\rm rad,m})/\gamma_0$ $\gamma_{\rm rad,m}$), respectively. Except for these two parameters, another more meaningful parameter to quantify the energy transfer process is the SP quantum yield which is given by $\eta_{SP} = \gamma_{SP}/(\gamma_{SP} + \gamma_{SP})$ $\gamma_{\rm rad,m}$ + $\gamma_{\rm nrad,m}$). Generally, the SP quantum yield depends on both the NW radius R and the distance d between the NW and the emitter. The position dependence of the decay rates leads to an optimal distance d_0 for which the SP quantum yield is maximized. With the decrease of the NW radius, the probability of decaying into nonplasmon channels is largely decreased. As $R \rightarrow 0$, the optimized probability of emission into SPs (that is, the SP quantum yield) approaches almost unity. For a NW of finite radius, the probability of generating SPs can be increased by coupling the QE with the NW through a nanotip at the NW end (bottom sketch in the left panel of Figure 10a). To decrease the loss caused by SPs, the metal NW can couple with a dielectric waveguide to convert the single SPs to single photons. As shown in the right panel of Figure 10a, higher single photon efficiency is obtained for the NW with a nanotip, with the maximum exceeding 95% for the optimal radius value.^[234] For the NW with radius larger than 10 nm, the values of γ_{SP} and $\eta_{\rm SP}$ calculated by finite element method are significantly larger than that obtained with the quasistatic approximation.^[236]

6.1.2. Surface Plasmons on a Plasmonic Waveguide Interacting with Multiple Quantum Emitters

Single photons emitted from a QE that is strongly coupled with a plasmonic NW can be converted into single SPs with near unit probability and, equivalently, single propagating SPs can interact with a QE with near unit probability. For a single two-level QE strongly coupled with the SP mode of a metal NW, the QE in ground state |g> could reflect the incoming single SPs on resonance with the energy gap between excited state |e> and ground state |g> with reflection coefficient $\approx (1-1/P)^2$ near unit for P >> 1, where $P = \gamma_{SP}/(\gamma_{rad,m} + \gamma_{nrad,m})$.^[238] A similar strategy using a three-level QE with a metastable state |s> decoupled from the SP mode may lead to the realization of a single-photon transistor, in which a single gate photon can control the

SCIENCE NEWS _____ www.advancedsciencenews.com





Figure 10. a) Left-top: A dipole emitter positioned a distance *d* from the center of a NW with radius *R*. Left-bottom: A dipole emitter positioned near the end of a nanotip. Right: Optimized efficiency of single photon generation versus *R*. Solid line: theoretical efficiency using a NW. Dotted line: theoretical efficiency using a nanotip. Solid points: efficiency based on numerical simulations of emission near a nanotip, combined with coupled-mode equations. b) Schematic of the system consisting of two QDs side coupled to a metal NW. The SPs are evanescently coupled to the QDs with coupling strength *g_i* (*i* = 1, 2). The QD_{*i*} is modeled as a two-level system with vacuum state $|0>_i$ and exciton state $|1>_i$. c) Diagram of energy transfer between a donor (emitter) and an acceptor mediated by the SPs on a plasmonic wedge waveguide. (a) Left: Reproduced with permission.^[237] Copyright 2007, American Physical Society. Right: Reproduced with permission.^[237] Copyright 2012, Optical Society of America. (c) Reproduced with permission.^[230] Copyright 2010, American Chemical Society.

propagation of subsequent signal pulses consisting of either individual or multiple photons.^[238]

Two two-level QEs coupled with the same NW can function as two tunable reflectors (Figure 10b). By varying the spatial separation and spectral detuning of the two QEs, the transmission of single SPs on the NW can be controlled.^[239–241] At small spectral detuning, the transmission spectrum shows a Fano-like line shape.^[237] The propagating SPs between the two QEs can be either reflected or transmitted, or can be trapped between the two QEs with entanglement created between them.^[242–244] It was theoretically demonstrated that, for two QEs separated by a distance larger than the operating wavelength, a large degree of entanglement between them can be obtained by coupling with a plasmonic waveguide.^[228]

Because the emission from the QEs can efficiently generate propagating SPs on a nanowaveguide, long-distance energy transfer between donor and acceptor can be achieved by coupling them to the same plasmonic waveguide (Figure 10c, see also Section 5.5). Moreover, the SP assisted energy transfer also reduces the requirement for dipole orientations of donor and acceptor.

6.2. Coupling of Quantum Emitters with Different Plasmonic Waveguides

The efficient coupling between single QEs and plasmonic waveguides opens the potential for efficient single photon/plasmon generation,^[245] single-photon transistor,^[238] entanglement of multiple QEs,^[228] and so on. The experimental realization of exciton–plasmon coupling at single quanta level is one of the major research directions in the field of quantum plasmonics. In the research of exciton–plasmon interaction at the single emitter level, single QDs and single NV centers in nanodiamonds are the most popularly used QEs. New single-photon sources, like defects in 2D materials, have also been incorporated with plasmonic waveguides. This section will focus on the progress of coupling between single QEs and various plasmonic waveguides.

6.2.1. Chemically Synthesized Silver Nanowires

Chemically synthesized crystalline Ag NWs with atomic smoothness can support propagating SPs with low losses in the visible and near-infrared spectral range, which makes them ideal candidates for proof of principle demonstration of the coupling with single QEs. The first demonstration of a single QE coupling with a plasmonic waveguide was realized in the system of a QD and a Ag NW (**Figure 11**a).^[245] The distance between the QD and the NW is controlled by the thickness of spin-coated PMMA layer. The spontaneous emission of the QD into propagating SPs was verified by the high degree of correlation between the time traces of the fluorescence counts from the QD and the end of the NW (bottom panel of Figure 11a). The cross-correlation measurement between the



(a)

30

20

10

C

counts s⁻¹)

ntensity (10³

(e)

 $r_{
m m}$ (ns)

www.advancedsciencenews.com





Figure 11. a) Coupling of a QD to a Ag NW. Top-left: Optical image of a Ag NW. Top-right: Fluorescence image with the excitation laser focused on the QD marked by a red circle. Bottom: Time traces of fluorescence counts from the coupled QD (red curve) and from the end of the NW (blue). b) Top: Fluorescence image of an optically excited NV center in a nanodiamond coupled to a Ag NW. Bottom: Fluorescence emission spectrum of single plasmons coupled out from the right end of the NW (black curve). The red and blue lines show results of simulations taking into account losses during propagation of plasmons on the NW as well as dispersion for NW radius of 29 and 32 nm, respectively. c) Color-coded lifetime data of the NV center in a nanodiamond on AFM tip as a function of height and position perpendicular to a Ag NW. Scale bar is 100 nm. d) Image of the measured QD lifetime near the end of a Ag NW. The color scale is labeled with both lifetime and Purcell factor. The dashed region indicates the location of the NW. e) Distance-dependent properties of the QD-Ag NW coupling system. The measured fluorescence lifetime (i), the decay rate ratio of SP generation channel and free-space radiation channel (ii), the decay rates of different channels (iii), and the SP quantum yield (iv) as a function of Al₂O₃ spacer thickness. f) Left: AFM topography image of two Ag NWs and sketched cross section for a nanodiamond located in the nanogap between two NWs. The black arrow indicates the location of the NV center in the nanodiamond. Right: Fluorescence image of the dual NW structure when the NV center is excited. g) Left: Optical image of SP propagation overlaid on a SEM image of a distributed Bragg reflector resonator fabricated around a Ag NW. Right: Fluorescence spectrum of QDs on the substrate (blue dashed line) and coupled to the plasmon resonator (red line). The transmission spectrum of the device is overlaid (gray line, crosses). (a) Reproduced with permission.^[245] Copyright 2007, Nature Publishing Group. (b) Reproduced with permission.^[246] Copyright 2009, Nature Publishing Group. (c) Reproduced with permission.^[75] Copyright 2014, American Chemical Society. (d) Reproduced with permission.^[45] Copyright 2013, Nature Publishing Group. (e) Reproduced with permission.^[177] Copyright 2015, American Chemical Society. (f) Reproduced with permission.^[247] Copyright 2013, American Chemical Society. (g) Reproduced with permission.^[248] Copyright 2012, American Physical Society.

QD emission and the NW end scattering shows a clear antibunching behavior, which indicates the generation of single quantized SPs on the NW. Later, the coupling between a diamond nanocrystal containing a single NV center and a Ag NW was demonstrated (Figure 11b).^[246] The wave-particle duality of SPs was shown by the observation of strong modulation in the emission spectrum at the NW end (bottom panel of Figure 11b) and the antibunching of the emitted photons.

The NW-QE coupling system can be assembled in more controllable ways. By using an AFM tip, a diamond nanocrystal



containing a single NV center can be moved to approach a nearby Ag NW. The fluorescence lifetime of the NV center was decreased after coupling with Ag NW.[71] By attaching a diamond nanocrystal with a single NV center on an AFM tip, 3D fluorescence lifetime imaging measurement was performed around the Ag NW surface, demonstrating distance and position dependent lifetime (Figure 11c).^[75] Microfluidic flow control provides a method for positioning and moving single QDs around single Ag NWs, as demonstrated by Ropp et al.^[45,249] Combining with the single molecule localization imaging method, they mapped out the distributions of fluorescence intensity and lifetime for the QD at different positions around the Ag NW with a spatial accuracy of about 12 nm. The mapped lifetime near the NW end shows clear oscillations along the direction of the NW (Figure 11d), which is due to the interference of SPs directly launched into the NW and that reflected at the NW end.

For a coupled system of a single QD and a Ag NW, the SP quantum yield, that is the probability of excitons converting to SPs, was experimentally obtained by determining the decay rates of all the exciton recombination channels.^[177] The separation distance between the QD and the NW was controlled by tuning the thickness of Al₂O₃ spacer layer. The QD fluorescence lifetime was decreased with the decrease of the separation distance (Figure 11e (i)), corresponding to the increase of total decay rate. The enhancement factor of total decay rate is 9.8 for the separation of 3 nm. As the Al₂O₃ film thickness decreases from 35 to 3 nm, the decay rate ratio of SP generation channel and farfield radiation channel shows an increase (Figure 11e (ii)), corresponding to the increase of the apparent coupling efficiency. The decay rates of all the three recombination channels are shown in Figure 11e (iii). As can be seen, the decay rates of all the three channels increase as the spacer thickness decreases, but the increasing rates are different. When the QD-NW distance is about 10 nm, the maximum SP quantum yield of 21% is achieved (Figure 11e (iv)), corresponding to the apparent coupling efficiency of 56%. When the QD-NW distance is decreased to about 3 nm, the apparent coupling efficiency is increased to 65%, while the SP quantum yield is decreased to 15.8%.

In addition to QDs and NV centers, the coupling between defect emitters in 2D materials and chemically synthesized Ag NWs was also investigated. 2D TMDCs attract much attention in recent years due to their interesting optical properties, and the directional coupling of valley-dependent fluorescence and Raman emissions with SPs on Ag NWs has been reported.^[250,251] For monolayer TMDCs on metal nanostructures, the strain can induce localized defect emitters, which show single photon emission properties at low temperature. Defects in a hexagonal boron nitride (h-BN) flake provide a new kind of room-temperature single-photon sources. The coupling of Ag NWs with defect emitters in WSe₂ monolayers and h-BN flakes was demonstrated.^[252,253]

The chemically synthesized Ag NW was also used to study the interaction of multiple QEs coupled with the same NW.^[254] The energy transfer between two fluorescent NPs mediated by SPs on a Ag NW was investigated, and the energy transfer efficiency up to 17% was achieved for a donor–acceptor separation of 1.3 μ m.^[198] Energy transfer over longer distance was demonstrated for a single QD donor and a fluorescent nanobead acceptor separated by 8.7 μ m on a Ag NW.^[199] The interaction strength between a single QE and a plasmonic NW is usually modest. Designing plasmonic waveguide with stronger field confinement is desired to enhance the exciton–plasmon coupling strength.^[255] Compared with single NWs, the SP gap mode between two parallel metal NWs possesses larger mode confinement, which can further enhance the spontaneous emission rate.^[256] This was demonstrated in experiment by manipulating a diamond nanocrystal and two Ag NWs with an AFM tip (Figure 11f).^[247] The measured Purcell factor is 8.3, which is 2.2 times higher compared to the single NW case. It is noted that the NV center in their experiment was not placed exactly in the center of the gap, which could influence the performance of two parallel Ag NWs to increase the spontaneous emission rate.

Enhancing the quality factor of the SP mode by introducing a resonator is another strategy to enhance the interaction strength. A plasmonic resonator composed of a Ag NW surrounded by patterned PMMA Bragg reflectors is shown in Figure 11g, where the QDs are randomly distributed in the PMMA.^[248] The highest quality factor at a vacuum wavelength of 638 nm for a NW with diameter of 100 nm is 95, close to the theoretical expectation of 100. For the QDs with emission wavelength at the cavity resonance (right panel of Figure 11g), a Purcell factor of 75 was obtained. The coupling of the plasmonic resonator with a nanodiamoand containing a single NV center was also demonstrated.

6.2.2. Lithographysically Fabricated Plasmonic Waveguides

The advanced lithography techniques facilitate the fabrication of plasmonic waveguides with well-controlled geometries by top-down methods. The coupling structures of colloidal QDs and silver NWs of 100 nm in width and 40 nm in height were fabricated by using a two-step EBL method (**Figure 12a**). A SiO₂ film of 10–15 nm thick was deposited as spacer to prevent quenching of QD emission. The modulation of the fluorescence spectra was observed in this coupled system.^[78,79]

Plasmonic waveguide composed of two metal NWs (two-wire transmission line) supports symmetric and antisymmetric SP modes that can be excited by laser light with polarization parallel and perpendicular to the NW, respectively. Figure 12b shows a two-wire waveguide integrated with an incoupling antenna and a mode detector, which is fabricated by focused ion beam milling on a single-crystalline silver plate.^[257] For a fluorescent nanobead coupled with the waveguide, its spontaneous emission generates propagating SPs, resulting in the emission at the two sides of the mode detector (bottom panel of Figure 12b). For a single molecule in the nanogap of such a waveguide, the fluorescence lifetime is reduced from about 3.6 ns in the uncoupled case to 0.4 ns.^[258] The coupling of strain-induced QEs in monolayer WSe₂ with plasmonic two-wire waveguides is also reported, showing Purcell factor in the range of 2–15.^[259]

Dielectric-loaded plasmonic waveguides that confine SPs laterally by using dielectric stripes patterned on a flat metal film support hybrid plasmonic–photonic modes with longer propagation lengths. Figure 12c shows the coupling of a single NV center in nanodiamond with a dielectric-loaded plasmonic waveguide.^[260] In experiment, the nanodiamond with a single NV center on Ag film was first characterized and its location related to the







Figure 12. a) Left: Optical transmission image of QD-Ag NW coupling structures fabricated by a two-step EBL procedure. Scale bar is 5 µm. The red spot marks one area with QDs. Right: The corresponding fluorescence image. The bright spots at the top are the reference QDs. Light due to SP scattering is seen on the right-side NW ends. b) Top: SEM image of the waveguide structure. Bottom: PL map for exciting the optical antenna with the polarization direction indicated by the orange arrow. c) Left: AFM image of a dielectric loaded plasmonic waveguide. The inset shows the thickness profile across the gray arrow. The red star denotes the position of the NV center coupled to the waveguide. Right: Fluorescence image when the nanodiamond is excited. d) Top-left: AFM image of nanodiamonds positioned in the vicinity of a V-groove waveguide. The solid and dashed circles indicate, respectively, the position of one nanodiamond with a single NV center and the position in the V-groove where it was positioned with an AFM tip. Top-right: AFM image of the nanodiamond inside the V-groove channel. Bottom: Fluorescence image of an assembled structure of NV center and V-groove when the excitation and collection polarizations were both set perpendicular to the groove axis. e) Left: SEM image of a Ag wedge with two block reflectors on the apex. QDs are deposited on the apex of the Ag wedge between the block reflectors. The scale bar is 5 µm. Middle and right: Fluorescence images of three QDs on the apex of a Ag wedge. The scale bars are 1 µm. (a) Reproduced with permission.^[260] Copyright 2012, American Chemical Society. (d) Reproduced with permission.^[263] Copyright 2019, American Chemical Society. (e) Reproduced with permission.^[264] Copyright 2015, Nature Publishing Group. (e) Reproduced with permission.^[264] Copyright 2015, American Chemical Society.

coordinate markers was determined. The dielectric-loaded plasmonic waveguide was then fabricated with nanometer precision around the precharacterized nanodiamond by EBL of hydrogen silsesquioxane resist spin-coated on the Ag surface. A similar system was obtained by coupling a single germanium vacancy (GeV) center in nanodiamond with a dielectric-loaded plasmonic waveguide fabricated on a single-crystalline silver plate.^[261] For branched dielectric-loaded plasmonic waveguides with one nanodiamond containing multiple NV centers on each branch, the nanodiamonds can be selectively excited by using circularly polarized laser light with different handedness.^[262]

V-groove waveguides offer strong confinement of electromagnetic field near the groove bottom, which is easily accessible by solid QEs. As shown in Figure 12d, a NV center in nanodiamond was positioned inside the Au V-groove waveguide with an AFM tip. The emission of the excited NV center was partly coupled to propagating SPs which were out-coupled as photons at the ends of the V-groove, as shown by the dim spots marked with white arrows.^[263]

Wedge waveguides can offer a very small mode size with the electric field tightly confined near the apex. By fabricating two block reflectors on a Ag wedge waveguide, a Fabry–Pérot resonator was formed (left panel of Figure 12e).^[264] When colloidal QDs are placed on the wedge using electrohydrodynamic printing method, their emission can be greatly modified by the plasmonic resonator. For a resonator with 10 μ m length, the emission spectrum of ensemble QDs from one of the reflectors has a linewidth of 3.3 nm at the central peak, corresponding to a quality factor of 191. Comparing with the QDs on glass substrate, the Purcell factor of 12.4 is obtained. The coupling of single QDs with a Ag wedge was also demonstrated. As shown in the middle and right panels of Figure 12e, the emission from one QD on the wedge (QD2) and the emission at the wedge end show correlated blinking.

Table 2 summarizes the Purcell factor of single QEs coupled with different plasmonic waveguides. The chemically synthesized crystalline Ag NWs are the most popularly used plasmonic waveguide for studying the plasmon–exciton coupling, because they are easily attainable, possess relatively low propagation loss, and can be conveniently assembled with single QEs. Comparing with plasmonic NP structures, individual plasmonic waveguides usually provide much lower Purcell factor. To increase the Purcell factor, decreasing the mode volume using plasmonic gap modes and increasing the quality factor using resonators are feasible solutions, as discussed above. Positioning QEs with optimized orientations at exact positions of plasmonic waveguide structures is crucial to increase the coupling strength, and is still very challenging.

7. Strong Coupling

7.1. Principles of Strong Coupling

Strong coupling is a profound concept of cavity quantum electrodynamics.^[27,265,266] When placed in an optical cavity, QEs will decay differently from their counterparts in free space because of the alteration of electromagnetic environment. In weak

www.advancedsciencenews.com

Tab	le 2.	Single	e QEs	coupled	with	various	р	lasmonic	waveguid	es.
-----	-------	--------	-------	---------	------	---------	---	----------	----------	-----

<i>c</i>		
www.afm-	iournal.	de

Waveguides	Size [nm] ^{a)}	QEs	Emission wavelength [nm]	Assembling methods	Separation distance [nm]	Purcell factor	Ref.
Ag NW	$d \approx 102 \pm 24$	QD	655	Spin-coating	≈30	1.7	[245]
Ag NW	<i>d</i> ≈ 70	NV center	550-800	Self-assembly	≈30	2.5	[246]
Ag NW	$d \approx 50-65$	NV center	647–785	AFM manipulation	-	2.9–4.6	[71]
Ag NW	$d \approx 50$	NV center	700	Scanning NV center	-	2.6	[75]
Ag NW	<i>d</i> ≈ 100	QD	630	Flow control	30	2.1	[45]
Ag NW	$d \approx 80$	QD	655	Spin-coating	3	9.75	[177]
Ag NW	<i>d</i> ≈ 115	QD	≈610	Spin-coating	-	≈20	[199]
Ag NW	$w \approx 100, h \approx 50$	QD	780	Two-step EBL	10	≈4	[79]
Ag NW	<i>d</i> ≈ 100	defect in h-BN	600	Stamping	-	1.88	[253]
V-groove waveguide	<i>w</i> ≈ 315, depth 510	NV center	650–750	AFM manipulation	-	2.44	[263]
Dielectric-loaded waveguide	$w \approx 250, h \approx 180$	NV center	550-800	EBL	_	5	[260]
Dielectric-loaded waveguide	$w \approx 250, h \approx 180$	GeV center	602	EBL	-	6	[261]
Two parallel Ag NWs	$w \approx 90, h \approx 80, \text{ gap} \approx 60$	Terrylene diimide molecule	≈667	Spin-coating	-	9	[258]
Two parallel Au NWs	$w \approx 172, h \approx 75, \text{ gap} \approx 96$	Defect in monolayer WSe ₂	740–830	Strain induced	-	2–15	[259]
Two parallel Ag NWs	<i>d</i> ≈ 110	NV center	700	AFM manipulation	-	8.3	[247]

 a^{a} , w, and h represent diameter, width, and height, respectively.

coupling regime, the spontaneous emission of QEs is modified as discussed in Sections 5 and 6. When the coupling strength between QEs and cavity modes is strong enough, namely, in the strong coupling regime, polaritons with mixed states are produced which are part light and part matter.

The coupling strength g can be expressed as

$$g = \frac{\mu \cdot \mathbf{E}}{\hbar} \tag{1}$$

where μ and E are the dipole moment and vacuum electric field at the emitter position, respectively, and \hbar is the reduced Planck constant. The amplitude of the vacuum electric field can be expressed as

$$|\mathbf{E}| = \sqrt{\frac{\hbar\omega}{2\varepsilon V}} \tag{2}$$

where *V* is the mode volume, ε is the permittivity of the material surrounding the emitter, and ω is the angular frequency of the photon. Therefore,

$$g = \mathbf{\mu} \cdot \mathbf{\varepsilon} \sqrt{\frac{\omega}{2\hbar\varepsilon V}}$$
(3)

where $\pmb{\epsilon}$ is the unit vector of the electric field.^[265,267,268]

For simplicity, neglecting the detuning and losses, the Hamiltonian of a single two-level QE interacting with a cavity mode can be defined as

$$\hat{H} = \hbar \omega |e\rangle \langle e| + \hbar \omega \hat{a}^{\dagger} \hat{a} - \hbar g \left(\hat{a} |e\rangle \langle g| + \hat{a}^{\dagger} |g\rangle \langle e| \right)$$
(4)

where $|e\rangle$ and $|g\rangle$ are the excited and ground state of the emitter, respectively, and \hat{a}^{\dagger} and \hat{a} are the creation and annihilation

operator for the photons in the cavity mode, respectively.^[269] Considering Equation (3), the coupling strength can be written as

$$g = \langle g | \hat{\mathbf{p}} | e \rangle \cdot \varepsilon \sqrt{\frac{\omega}{2\hbar\varepsilon V}}$$
(5)

where $\hat{\mathbf{p}}$ is the dipole moment operator.^[44] With this Hamiltonian, we can get the eigenenergy

$$E_{\pm} = \hbar \omega \pm \hbar g \tag{6}$$

For the system of *N* emitters interacting with a cavity mode, $[^{270]}$ as a result of coherence, the eigenenergy of the mixed states is expressed as

$$E_{\pm} = \hbar \omega \pm \sqrt{N} \hbar g \tag{7}$$

Considering the detuning and losses, the system can be described by the coupled oscillator model

$$\begin{pmatrix} \omega_{cav} - i\frac{\kappa}{2} & g \\ g & \omega_0 - i\frac{\gamma}{2} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \omega \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$
(8)

where ω_{cav} (ω_0), κ (γ), and α (β) are the angular frequency, the decay rate, and the Hopfield coefficient of the cavity (emitter), respectively. Thus, we get the eigenvalues of the two polariton branches

$$\omega_{\pm} = \frac{\omega_{\text{cav}} + \omega_0}{2} \pm \frac{1}{2} \sqrt{4g^2 + \left(\delta - i\frac{\kappa - \gamma}{2}\right)^2} - i\frac{\kappa + \gamma}{4}$$
(9)



with the detuning $\delta = \omega_{cav} - \omega_0$. The results obtained on the basis of coupled oscillator model agree well with that of quantum treatment.^[271]

In the case of zero detuning,

ADVANCED SCIENCE NEWS_____ www.advancedsciencenews.com

$$\omega_{\pm} = \omega_0 \pm \frac{1}{2} \sqrt{4g^2 - \left(\frac{\kappa - \gamma}{2}\right)^2} - i\frac{\kappa + \gamma}{4}$$
(10)

representing Lorentz oscillators centered at $\omega_{\pm} = \omega_0 \pm \frac{1}{2} \sqrt{4g^2 - \left(\frac{\kappa - \gamma}{2}\right)^2}$ with the same linewidth $\frac{\kappa + \gamma}{2}$.^[272,273] The vacuum Rabi splitting can be defined as^[274–276]

$$\Omega = \sqrt{4g^2 - \left(\frac{\kappa - \gamma}{2}\right)^2} \tag{11}$$

When the linewidths of the cavity and emitter are much smaller than their resonance energies, we can neglect the damping and get the usually used formula

$$\omega_{\pm} = \frac{\omega_{\text{cav}} + \omega_0}{2} \pm \sqrt{g^2 + \frac{\delta^2}{4}}$$
(12)

It should be noted that not only the strong coupling, cavity/ exciton induced transparency or Fano resonance can also give rise to spectral splitting.^[277–279] The criterion of strong coupling requires that the vacuum Rabi splitting exceeds the mean of the damping rates of the cavity and the emitter,^[265] that is,

$$\Omega = \sqrt{4g^2 - \left(\frac{\kappa - \gamma}{2}\right)^2} \ge \frac{\kappa + \gamma}{2}$$
(13)

7.2. Strong Coupling between Various Emitters and Plasmonic Nanostructures

Equation (3) indicates that smaller mode volume of the cavity benefits strong coupling. The electric field confined far below the diffraction limit in plasmonic nanostructures enables the ultrasmall volume of the SP modes. Therefore, plasmonic nanostructures provide promising platforms for strong coupling. Equation (3) also indicates that the emitters with larger dipole moments result in a stronger coupling strength, which leads to a larger Rabi splitting according to Equation (11). The Rabi splitting is in proportion to the square root of the emitter numbers. Therefore, it is much easier to observe strong coupling phenomena in the systems with plenty of emitters. The square root dependence of the Rabi splitting or coupling strength on the emitter number (the absorbance) was demonstrated in many different systems,^[276,280-289] where the emitter number was controlled by altering the emitter concentration or the thickness of polymer matrix. Early in 1979, Pockrand et al. reported the theoretical study of the interaction between SPs on a silver film and the molecular layer deposited on the silver film by angle and wavelength scans in attenuated total reflection measurements based on the Kretschmann

configuration.^[290] This configuration was employed widely in early experimental studies of strong coupling between metal film and various emitters.^[274,281,283,291,292] Structured metal surfaces and plasmonic NPs provide more possibilities for tuning the SP behaviors. Nanohole arrays in metal film, NP arrays, and 1D grating structures are all used for the strong coupling. Single plasmonic NPs especially nanogaps between nearby NPs can strongly confine electromagnetic field and possess largely reduced mode volume, providing a promising platform for realizing strong coupling at the nanometer scale and at the limit of single QE.^[293,294] The strong coupling is usually experimentally investigated by optical measurements, such as reflection, scattering, transmission, extinction and PL. In addition, electronbased spectroscopies such as electron energy loss spectroscopy and cathodoluminescence can also be used to probe the strong plasmon-exciton coupling,^[295-300] which are particularly useful for the coupling involving dark SP modes and for revealing nanoscale spatial variations. In this section, we briefly review the strong coupling in different systems of emitters and plasmonic structures classified by the emitters used. The emitters used for strong coupling mainly include J-aggregates, dve molecules, QDs, and monolayer or few-layer TMDCs. Besides, quantum wells based on various materials,[301-304] ZnO NW,[295] and CdSe nanoplatelets^[305] were also employed for studying their strong coupling with plasmonic nanostructures.

7.2.1. J-Aggregates

J-aggregates of organic dyes have long been a platform for studying the strong coupling phenomena. Compared with the molecule monomers, the absorption bands of J-aggregates are redshifted with increased sharpness.^[306] The excitons of the J-aggregates, formed by delocalized electrons over many adjacent molecules, have very large transition dipole moments.^[268,287] The low loss and large transition dipole moment make J-aggregates one of the major emitter systems for studying the strong coupling between plasmonic nanostructures and QEs.

Early in 1982, Pockrand et al. reported the observation of strong coupling between J-aggregates and Ag film.^[291] J-aggregates of cyanine dye molecules were deposited onto a Ag film of 55 nm thickness on a quartz substrate. The SPs launched by attenuated total reflection based on a prism in the Kretschmann configuration were strongly coupled to the excitons of J-aggregates. Reflectivity measurements revealed the anticrossing dispersion relation of the plasmon-exciton hybrid states. For the exciton transition dipole moment aligned parallel to the Ag film, two branches of plasmon-exciton polaritons (plexcitons) were observed. When the transition dipole moment has a perpendicular component, three branches of plexcitons were observed. Over two decades later, Bellessa et al. reported the strong coupling in a similar system composed of Ag film and cyanine dye J-aggregates in a PVA matrix.^[292] A Rabi splitting of around 180 meV was achieved in the angle-resolved reflectivity experiments. Moreover, the low energy plexciton branch was also observed in the PL detected through the prism. The lacking of the high energy branch was attributed to the relaxation toward uncoupled excitonic states.

Patterning periodic nanostructures on metal film can generate more SP modes which can be tuned by the periodicity. These SP modes can be excited when the momentum match of SPs and incident light is satisfied by the Bragg diffraction. Dintinger et al. reported the strong coupling between J-aggregates and the (1, 0) SP mode on an array of nanoholes milled in the Ag film of 370 nm thickness by focused ion beam.^[280] The anticrossing behavior was observed in the energy dispersion curves obtained by varying the period of the hole arrays for normal incidence transmission, and the Rabi splitting of about 250 meV was achieved. Angle-resolved transmission experiments showed similar results. The linear relationship between the Rabi splitting and the square root of the J-aggregate absorbance was observed. For nanoholes in 20 nm thin Ag film coated by J-aggregates, Rabi splitting was observed in both extinction and absorption spectra.^[288] For periodic Au nanovoids, it was demonstrated that both the plasmonic-crystallike mode and localized SP mode can strongly couple with the excitons of J-aggregates.^[307] In the hybrid structure consisting of J-aggregate film spin-coated onto a Au nanoslit array, the ultrafast Rabi oscillation was observed,^[308] and the ultrafast manipulation of the Rabi splitting energy was demonstrated.^[308,309] Moreover, optical Stark effect was observed in this strongly coupled system.^[310] Strong coupling between Ag and Al NP arrays and J-aggregates was experimentally demonstrated with Rabi splitting of 450 and 400 meV obtained from the transmission spectra, respectively.^[311,312] It is noted that although NP arrays were fabricated, it is the localized SP mode of single NPs that was involved in these strong coupling systems. NP array on metal film provides another configuration for strong coupling with the J-aggregates sandwiched between the metal film and the NP array.^[313]

For chemically synthesized colloidal metal NPs, their strong coupling with J-aggregates can be characterized by extinction spectra of the mixed solution. Fofang et al. reported the strong coupling of J-aggregates and Au nanoshells in solution.^[314] Spectral splitting was observed when the nanoshell solution was mixed with the solution of J-aggregates. The SP resonance peak can be tuned by controlling the ratio of the inner core radius and the shell radius. The dispersion curves of the plexcitonic states were obtained by tuning the SP resonance energy across the exciton line of J-aggregates. In addition to the dipole mode, the quadrupole mode can be tuned to match the J-aggregate exciton energy by controlling the NP size and ratio of the inner and outer radius. The Rabi splitting is about 120 meV for the dipole mode and about 100 meV for the quadrupole mode. Similar observations were reported in the coupling systems of J-aggregates and Au nanostars,^[315] Ag nanoprisms,^[316,317] Au nanorods,^[318,319] Ag@Au hollow nanoshells,^[320] Au@Ag nanorods,^[321-323] Ag-Au nanorings,^[324] etc. Spectral splitting was observed in both the extinction and PL spectra for the hybrid system of J-aggregates and Au nanorods.^[318] For J-aggregates bound to core-shell Au@Ag nanorods, it was demonstrated that the plexcitons produced by strong coupling show magneto-optical activity.^[321] For chiral J-aggregates coupling with Au@Ag nanorods and for chiral Au@Ag nanorod dimers coupling with J-aggregates, Rabi splitting was observed in both the extinction and circular dichroism spectra.^[323,325]

The strong coupling between single plasmonic nanostructures and many excitons was first reported in the hybrid system of individual lithographically defined Au nanodisk dimers and cyanine dye J-aggregates in PVA matrix.^[326] The SP resonance energy of the Au nanodimers was tuned by keeping the gap size of 15 nm and varying the diameters of the nanodisks from 60 to 115 nm, as shown in Figure 13a (i). The invariable small gap size ensures the extremely confined electromagnetic field in the nanogap. Spectral splitting in the dark-field scattering spectra was observed for polarization parallel to the axis connecting the center of the two nanodisks, as shown in Figure 13a (ii). The dispersion curves in Figure 13a (iii) indicates a Rabi splitting of 230 meV. Strong coupling between dimers of chemically synthesized Au NPs and J-aggregates was also reported. By using DNA origami technique, Au NP dimers can be assembled with a small nanogap of about 5 nm. By tuning the size of the NPs, the SP resonance can be tuned across the exciton energy. From the dark-field scattering spectra of individual dimers, the anticrossing in dispersion was obtained with a Rabi splitting of about 150 meV.[327]

Zengin et al. studied the coupling between chemically synthesized single Ag nanorods and cyanine dye TDBC J-aggregates. Transparency dip was observed in both the darkfield scattering spectra and extinction spectra of single hybrid nanorods.^[328] The average vacuum Rabi splitting of about 100 meV was obtained, approaching the SP damping rate. Later, they reported the strong coupling between individual Ag nanoprisms and TDBC J-aggregates. As shown in Figure 13b, the scattering peak of the Ag nanoprism splits to two peaks for the coupled system, with the dip at the wavelength of J-aggregate absorption peak.^[268] The Rabi splitting of 280 meV exceeds the average damping rate of SP mode and excitons, confirming the realization of strong coupling. In similar systems, spectral splitting in both scattering and PL spectra were observed.^[329]

The strong coupling between a single exciton and a plasmonic nanostructure is highly desired to reach the quantum optics limit. The sharp tips in plasmonic nanostructures can help to decrease the SP mode volume, benefiting the realization of plasmon-exciton strong coupling. Liu et al. chemically coated Au nanorods with Ag shells and obtained Au@Ag nanorods of cuboid shape (Figure 13c (i)).[287] Comparing with the bare Au nanorod, the electric field is more tightly confined around the sharp corners of the cuboid (Figure 13c (ii) and black solid lines in Figure 13c (iii)). Calculations show that mode volume is decreased from \approx 6585 nm³ for the Au nanorod to \approx 71 nm³ for the Au@Ag nanocuboid. The dramatically reduced mode volume leads to the much larger plasmon-exciton coupling coefficient for the cuboid, as shown by the pink dashed lines in Figure 13c (iii). The quick decrease of the coupling coefficient as the emitter gets away from the cuboid corner indicates that a distance of the emitter from the cuboid less than 1 nm is favorable for realizing strong coupling. This small distance can be ensured by the J-aggregate monolayer. By varying the dye concentration, the number of the excitons coupling with single nanocuboids can be controlled. Calculation results show the exciton number ranges from ≈ 0.7 to ≈ 6.1 , corresponding to the vacuum Rabi splitting of ≈72 to 209 meV (Figure 13c (iv)). This indicates the realization of strong coupling at single exciton level for single plasmonic NPs.







Figure 13. a) Strong coupling between single Au nanodisk dimers and DPDC J-aggregates. (i) Left: SEM images of five Au nanodisk dimers with diameters of 60, 70, 85, 100, and 115 nm, respectively. The scale bars correspond to 100 nm. Right: Longitudinally polarized scattering spectra measured for the five bare dimers and the exciton absorption spectrum of the J-aggregates (gray line). (ii) Scattering spectra of hybrid systems of Au nanodimers and J-aggregates with nanodisks ranging from 60 to 115 nm in diameter recorded for longitudinal polarization. (iii) Dispersion curves of the hybrid plexcitonic states. The black and green dashed lines represent the uncoupled exciton and SP energies, respectively. b) Strong coupling between single Ag nanoprisms and TDBC J-aggregates. Top: Extinction spectrum (left) and schematic view (right) of J-aggregates. Middle: Scattering spectrum (left) and schematic view (right) of a Ag nanoprism. Bottom: Scattering spectrum (left) and schematic view (right) of a nanoprism strongly coupled to J-aggregates. c) Strong coupling between single Au@Ag cuboid nanorods and PIC J-aggregates. (i) TEM images of a Au nanorod (top) and a Au@Ag nanorod with cuboid shape (bottom). (ii) Left: Schematic views of the nanorods shown in (i). Right: Simulated electric field distributions of the longitudinal SP mode supported by the Au nanorod and Au@Ag cuboid nanorod. (iii) Normalized electric field and coupling coefficient as functions of the emitter distance from the vertex of the corner along the direction of the maximum electric field [dashed white arrows in (ii)]. The pink dashed lines are the coupling coefficient obtained from different calculation methods. (iv) Statistics of the vacuum Rabi splitting measured for individual hybrid nanocuboids and the corresponding calculated mean exciton number \overline{N}_x for each dye concentration. (a) Reproduced with permission.^[268] Copyright 2013, American Chemical Society. (b) Reproduced with permission.^[268] Copyright 2015, American Physical Society. (c)

7.2.2. Molecules

Molecules usually have a smaller dipole moment, which is adverse to the realization of strong coupling. However, since the damping rates of molecules are usually much larger than the J-aggregates but still lower than SPs, a smaller damping rate difference can be obtained. According to Equation (11), the decay rate matching contributes to the enhancement of Rabi splitting. Hakala et al. reported the strong coupling of rhodamine 6G (R6G) molecules in the matrix of SU-8 resist with the SPs on Ag film of 45 nm thickness launched by prism coupling.^[276] Three polariton branches were detected at both the prism side and the air side for the sample with R6G of high concentration. Vacuum Rabi splitting of 230 and 110 meV were obtained from the air side at the wavelengths corresponding to the absorption maximum and absorption shoulder of R6G molecules, respectively.

The strong coupling between photochromic molecules and nanohole arrays in Ag film was reported by Schwartz et al., and the Rabi splitting as large as 650 meV was obtained.^[275] The photochromic spiropyran (SPI) molecules they used can be photoisomerized to merocyanine (MC) form by UV irradiation and recovered by visible irradiation. The SPI is transparent across the visible range, while the MC shows an absorption peak at 560 nm. The system is weakly coupled for low concentration of MC, and reaches the strong coupling regime when the MC concentration is sufficient. Therefore, reversible switching between weak and strong coupling regime can be achieved by optically controlling the form of molecules. The photoswitchable strong coupling between metal NP arrays and MC molecules was also demonstrated.^[330,331] Moreover, the active tuning of coupling strength was realized by controlling the electrochemical potential in the system of Au nanotriangle array and HITC molecules.^[332]

The surface lattice resonances supported by periodic metal NP arrays possess small linewidth compared with LSPRs of single NPs, and thus provide a good platform for engineering the strong coupling with molecules. The delocalized nature of surface lattice resonances indicates that the molecules near distant NPs are coherently coupled in the strong coupling regime. Rodriguez et al. reported the strong coupling in the hybrid system of a periodic Ag nanorod array covered by a PVA layer doped with R6G molecules.^[333] By increasing the plexciton density through optical pumping, they observed thermalization and cooling of the plexcitons. Väkeväinen et al. measured the extinction spectra of Ag nanodisk arrays coated with R6G of different





concentrations in PMMA, and observed anticrossing behavior involving two surface lattice resonance modes, one localized SP mode, and two molecular transitions.^[284]

Dimers of metal NPs support SPs with the electric field localized in the nanogaps, facilitating the realization of strong coupling. For Ag NP dimers prepared by angle-resolved nanosphere lithography on a glass substrate, their strong coupling with HITC molecules was observed in the extinction spectra.^[286] For single dimers of chemically synthesized Ag NPs coupled with R6G molecules, peak splitting was observed in the dark-field scattering spectra.^[334] The nanogaps between a metal NP and a metal film also support SPs with small mode volume, and strong coupling has been demonstrated in different systems.^[289,335,336] By aligning the transition dipole moment of the molecule in the nanogap, strong coupling at single molecule level was demonstrated. As schematically shown in the left panel of Figure 14a, the methylene blue molecule was encapsulated inside the macrocyclic cucurbit[n]uril molecule, and was located in the nanogap between a gold NP and a gold film with the dipole transition moment perpendicular to the gold mirror.^[335] The ultrasmall mode volume of the plasmonic cavity of about 40 nm³ and the dipole moment orientation aligned with the SP field contribute to the realization of strong coupling even at single molecule level. The right panel of Figure 14a shows the scattering spectra for the coupled system with one, two, and three molecules in the nanogap. The increase of Rabi splitting with the increase of the molecule number can be seen, and the Rabi splitting for a single molecule is about 90 meV. Ojambati et al. studied a single molecule of Atto647 aligned using DNA origami interacting with a gold NP-on-mirror plasmonic cavity.^[336] They observed the peak splitting in both the scattering and PL spectra, and reported Rabi oscillation in power dependent measurement. Moreover, the second-order correlation function of the photon emission statistics reveals the photon bunching and anti-bunching regimes which are dependent on the excitation wavelength.

7.2.3. Quantum Dots

QDs are tiny semiconductor particles (1–100 nm) with the sizes even smaller than the exciton Bohr radii of their bulk counterparts. The small size of the QD leads to discrete energy levels as a result of quantum confinement effect, and the QD can be viewed as an artificial atom. Their optical properties can be easily tuned by controlling their sizes. The wavefunction of the



Figure 14. a) Left: Illustration of a methylene blue molecule in cucurbit[*n*]uril in the NP-on-mirror geometry. Right: Scattering spectra of the NP-on-mirror structures with one, two and three molecules in the nanogaps with fits. b) Scattering spectra of Ag nanobowties with (from top to bottom) one, two and three QDs in the gap with fits. Insets show the SEM images of the corresponding structures. The positions of the QDs are marked by red arrows. Scale bars, 20 nm. c) Measured scattering spectrum (blue) and PL spectrum (green) for a Au NP on a Ag film with QDs linked to the NP (sketched in the inset). d) Left: Illustration of a single QD with a 0.5-nm dielectric capping layer (Al₂O₃) in the plasmonic cavity composed of a tilted Au tip and a Au substrate. Right: PL spectra as the vertical tip-QD distance is varied from 0 to 4 nm. e) Illustration of the plasmonic nanoresonator probe interacting with QDs embedded in a polymer film. Left: The spectrum of a QD changes significantly when coupled to the slit-like plasmonic nanoresonator at the tip apex. Inset: SEM image of a nanoresonator at the apex of a probe tip. Scale bar, 100 nm. (a) Reproduced with permission.^[335] Copyright 2016, Nature Publishing Group. (b) Reproduced with permission.^[67] Copyright 2016, Nature Publishing Group. (c) Reproduced with permission.^[340] Copyright 2018, American Association for the Advancement of Science. (e) Reproduced with permission.^[340] Copyright 2018, American Association for the Advancement of Science.



electron (hole) can extend over thousands of atoms in the QD, leading to a large dipole moment. Compared with molecules, QDs show much higher photostability. These characteristics make QDs favorable for the realization of strong coupling, especially at the single emitter limit.

Gomez et al. reported the strong coupling between a film of CdSe QDs and a silver film with the SPs launched by prism coupling.^[283] The formation of mixed plasmon–exciton polariton states was demonstrated by angle-resolved attenuated total reflection measurements. The vacuum Rabi splitting of 112 and 102 meV were achieved for the QDs of 3.4 and 4.3 nm in diameter, respectively. For QDs coupling with Au nanohole array, Rabi splitting up to 220 meV was obtained from the transmission spectra.^[337] For QDs coupling with Ag NP array, peak splitting of 100 meV in the PL spectrum was observed.^[338]

Several experimental realizations of strong coupling at the single QD level were reported in recent years, with plasmonic nanogaps as the most used cavities. Santhosh et al. successfully put the QDs with the number one to a few into the nanogaps of Ag nanobowties by use of EBL defined PMMA mask and interfacial capillary force of water (see Figure 3g).^[67] One advantage of using QDs is that the number of QDs can be directly determined from the SEM images. Figure 14b shows the scattering spectra and corresponding SEM images of the hybrid nanostructures with one, two, and three QDs in the nanogaps of Ag bowties. As can be seen, spectral splitting is discernible for the structure with one QD, and the splitting becomes larger for the structures with two and three QDs. As the electric field intensity is stronger at the tip of the nanotriangle than that at the center of the nanogap, placing the QDs close to the tip can produce larger Rabi splitting. Analysis to the values of the Rabi splitting and the damping rates of SP mode and exciton indicates that the hybrid system of a silver nanobowtie and a single QD is close to the strong coupling regime.

Strong coupling at the single QD level was also realized by using the nanogap structure formed by gold NP on silver film.^[125] The QDs were linked to gold NPs through their capping molecules, and then the NPs were deposited onto a silver film. For about 1% of the measured samples, splitting was observed in both the scattering and PL spectra, as shown in Figure 14c. The low fraction of strong coupling case for this system is mainly due to the uncertainty of the QDs in the nanogap between the NP and the silver film. It is worth to note that spectral splitting was even observed in the scattering spectra for a gold NP coupled with a single QD.^[70] Similar plasmonic nanogap structure can be formed by replacing the Au NP by a scanning Au tip (left panel of Figure 14d).^[339] The QDs were drop-casted on an Al₂O₃ coated gold film, and were coated by another ultrathin 0.5-nm Al₂O₃ laver. By scanning the tip over the QD, the coupling of a single QD with the plasmonic nanocavity can be well controlled. Peak splitting was observed in the PL spectra when the tip was close to the QD. By controlling the lateral and vertical distance between the tip and the QD, the coupling strength can be tuned. Smaller tip to QD distance results in larger coupling strength (right panel of Figure 14d), with Rabi splitting up to 160 meV obtained.^[339]

The splitting in the PL spectra of single QDs was also detected by coupling a QD to a slit-like plasmonic resonator fabricated on a single-crystalline gold flake that was attached

to the cantilever of contact mode probe.^[340] Colloidal QDs were spin-coated onto the substrate and then covered by PMMA. The single QD was ensured by measuring the second order correlation function of the PL. The precise nanopositioning of the resonator probe enabled precise tuning of the separation between the resonator and the QD, and the transition between weak and strong coupling was observed. As the plasmonic nanoresonator scanned across the QD, its PL spectra showed distance dependent change. Comparing with the QD before the tip approaching, spectral splitting was observed, as shown in Figure 14e. The appearance of four peaks was attributed to that both the neutral and charged states were coupled to the SP mode. To measure the dispersion curves of the hybrid states, the excitation rate was changed to tune the plexciton energy, with the SP energy kept constant as determined by the resonator.

7.2.4. Transition Metal Dichalcogenides

The monolayers of TMDCs with the structure MX_2 are semiconductors of direct bandgap.^[341] The large transition dipole moment of the in-plane exciton and the small linewidth benefit the strong coupling of SPs and excitons in monolayer TMDCs. The 2D layer with atomic thickness facilitates their integration with plasmonic structures and promotes their application in studying strong coupling.

Liu et al. investigated the strong coupling between monolayer MoS₂ and Ag nanodisk array, where five resonances were involved, including A and B excitons of monolayer MoS₂, (+1,0) and (-1,0) diffractive orders of surface lattice resonances, and localized SP mode of the Ag nanodisk.^[342] At low temperature of 77 K, four plexciton branches were observed in the angleresolved reflectance measurements, which were fitted using coupled oscillator model including five oscillators. The coupling strengths between the localized SP mode and both excitons are larger than that between the surface lattice modes and the excitons. The LSPR wavelength can be tuned to match A exciton or B exciton, or tuned to between A and B excitons by changing the diameter of the nanodisks, which leads to the effective control of the coupling strength, plexciton composition, and dispersion. At room temperature, the anticrossing of the dispersions becomes less evident mainly due to the increased damping of excitons, while the spectral splitting for A exciton can still be resolved. The coupling strength between monolayer MoS₂ and Ag nanodisk array can be electrically tuned by varying the gate voltage.^[343] The strong coupling between monolayer WS₂ and nanohole array in Au film was also realized as evidenced by the anticrossing feature in the dispersions obtained by angle-resolved reflection spectra.^[344] Moreover, the lower energy plexciton branch was observed in the angle-resolved PL spectra. For monolayer WS₂ on self-assembled plasmonic crystals consisting of a hexagonally packed layer of silica spheres coated with a silver film and a thin silica layer, strong coupling results in a Rabi splitting of about 160 meV in the transmission spectra, and valley-polarized PL emission was observed.[345]

The strong coupling between monolayer TMDCs and single plasmonic NPs was first demonstrated by Zheng et al. in the coupled system of a single Ag nanorod and monolayer www.advancedsciencenews.com







Figure 15. Strong coupling between monolayer TMDCs and single metal nanostructures. a) (i) Sketch (top) and SEM image (bottom) of a Ag nanorod on WSe2 monolayer coated by Al2O3. (ii) A set of dark-field scattering spectra of the Ag nanorod in (i) with increased Al2O3 thickness. b) (i) Polarization polar plots of scattering intensities of the pristine WS2 exciton (green), high-energy hybrid mode (blue), and low-energy hybrid mode (purple) of the heterostructure. (ii) Purple spheres: ratios of degree of linear polarization between the low-energy hybrid mode and high-energy hybrid mode as a function of detuning. The purple dashed line is a guide for the eye. Solid blue line: dependence of the ratio of the plasmon fraction between the lowenergy hybrid mode and high-energy hybrid mode on the detuning. (iii) Dependence of the $g\sqrt{V}$ on the \sqrt{N} . The insets show the SEM images of the smallest and largest Au nanorods, where the scale bars are 50 nm. c) (i) Sketch of the hybrid structure of a Au nanobowtie and monolayer WSe2. (ii) The PL spectrum of monolayer WSe₂ (top) and the normalized dark-field scattering spectra of various Au nanostructures coupled with monolayer WSe₂ (bottom). Insets show the SEM images of the corresponding coupled nanostructures, and the white arrows indicate the polarization directions. The scale bars are 50 nm. (iii) The extracted peak energies (red circles) of the scattering spectra as a function of detuning for Au nanobowties coupled with monolayer WSe2. The black solid lines are the fitting results with the coupling strength of 93.5 meV, and the black dashed lines indicate the energies of the uncoupled SPs and excitons. The orange areas are between the boundary curves representing the plexciton energies for the minimal (33.2 meV) and maximal (183.0 meV) coupling strengths. (iv) Simulated distribution of the single exciton coupling strength for a Au nanobowtie (with side length of 90 nm and gap size of 10 nm) with the monolayer WSe2 on top. (v) The experimental (red triangles) and simulated (red balls) coupling strength g and simulated $1/\sqrt{V}$ (blue balls) as a function of detuning for strong coupling between the longitudinal SP mode of Au nanobowties and the exciton state of monolayer WSe2. (a) Reproduced with permission.^[346] Copyright 2017, American Chemical Society. (b) Reproduced with permission.^[347] Copyright 2017, American Chemical Society. (c) Reproduced with permission.^[348] Copyright 2020, Royal Society of Chemistry.

 WSe_2 .^[346] Mechanically exfoliated WSe_2 monolayers were placed on a SiO₂/Si substrate, and then chemically synthesized Ag nanorods were drop-casted onto the sample surface (**Figure 15**a (i)). The third order longitudinal SP mode with

narrower linewidth was selected for the strong coupling. For the same single nanorod, the SP energy was tuned by gradually depositing Al_2O_3 of different thickness to scan across the exciton energy, and spectral splitting for different detuning was



clearly seen in the dark-field scattering spectra, as shown in Figure 15a (ii). Strong coupling in a similar system of a single Au nanorod on monolayer WS₂ was reported by Wen et al.^[347] The scattering light of two plexciton states is linearly polarized (Figure 15b (i)), which is different from the scattering properties of the pristine WS₂ exciton but follows the longitudinal dipolar SP mode of the Au nanorod. The ratio of the degree of linear polarization between the lower energy plexciton and higher energy plexciton is decreased as the detuning varies from the minus values to the positive values (purple dots in Figure 15b (ii)), and follows similar trend as the ratio of the plasmon fraction between these two branches (blue line in Figure 15b (ii)). Nanorods of different sizes but with the same SP resonance energy that matches the exciton energy were coupled with the monolayer WS₂. As the mode volume is decreased with the decrease of the nanorod size, less excitons are involved in the strong coupling for smaller nanorod (Figure 15b (iii)). The minimum number of excitons coupled with the nanorod was estimated to be about 5 for the smallest nanorod (about 50 nm in length and 20 nm in width), corresponding to Rabi splitting of about 91 meV. In addition, the active control of strong plasmon-exciton coupling was demonstrated by varying temperature or applying gate voltage to tune the excitons.

Later, the strong coupling phenomena between various single plasmonic nanocavities and monolayer or multilayer TMDCs were demonstrated, for example, Au nanorod on monolayer WSe2,[349] Ag nanoprism on monolayer/multilayer WS₂,^[296,350,351] Au bi-pyramids on monolayer/multiplayer WSe₂ and monolayer MoS₂,^[352,353] Au nanodisks on monolayer/ multilayer WS2,[354] Au@Ag core-shell nanocuboid on monolayer MoS₂ and WS₂,^[355] and monolayer/multilayer TMDCs in the nanogaps of NP-on-mirror structures.^[98,356-358] While chemically synthesized metal NPs are widely used for strong coupling with TMDCs, metal NPs made by lithography methods are highly desired since they are compatible with on-chip integration and their SP resonance properties can be readily engineered by varying the dimensions and geometries. Yan et al. studied the plasmon-exciton strong coupling in the coupled system of lithographically fabricated single gold nanostructures and monolayer WSe₂, as schematically shown in Figure 15c (i).^[348] Peak splitting was observed in all the dark-field scattering spectra for a gold nanobowtie and monomers of nanotriangle, nanodisk and nanorod coated by monolayer WSe₂ (Figure 15c (ii)). The SP resonance wavelength of the gold nanobowtie was tuned by changing the side lengths of the nanotriangles while keeping the nanogaps to be about 10 nm. Figure 15c (iii) shows the energies of the two plexciton branches as a function of the energy detuning between the longitudinal SP mode and the exciton. A Rabi splitting of 187 meV is achieved at zero detuning. Simulation result shows that the single exciton coupling strength shares the same distribution as the in-plane electric field, and the excitons at the nanogap contribute dominantly to the total coupling strength (Figure 15c (iv)). The coupling strength is larger for smaller nanobowties, which agrees with the trend of the mode volume (Figure 15c (v)).

For a clear grasp of the results reported in the literatures, **Table 3** summarizes the key information of various strong coupling systems, including the emitter and cavity types, whether single emitter and single plasmonic nanocavity, the types of



measured spectra, the resonance energy $\hbar\omega_0$, the spectral linewidth of emitter $\hbar\gamma$ and cavity $\hbar\kappa$; and the Rabi splitting $\hbar\Omega$ (for simplicity, \hbar was omitted in Table 3). Among the four kinds of QEs discussed above, J-aggregates and monolayer/few-layer TMDCs show narrow spectral linewidths, and are most intensively used in plasmon–exciton strong coupling experiments. Compared with J-aggregates, the Rabi splitting for TMDCs is generally smaller. QDs are preferable candidate for experiments aiming at the quantum optics limit, because the number of QDs can be clearly resolved by microscopy techniques and a single QD can be further confirmed by measuring the second order correlation function of the emitted photons. The different kinds of plasmonic structures enable nanoscale manipulation of optical fields, providing versatile platforms for engineering plasmon–exciton strong coupling.

7.3. Spatial Coherence and Temporal Response

7.3.1. Spatial Coherence

The square root dependence of the Rabi splitting on the emitter number implies the collective nature of strong coupling. The plasmon-exciton polariton states can inherit the collective property of the SP modes, resulting in the coherent emission of the far separated emitters. The coherence of spatially remote emitters caused by strong coupling with SPs was experimentally demonstrated by Guebrou et al.^[359] The strong coupling system consists of TDBC J-aggregates on a silver film of 45 nm thickness on a glass cover slip. To study the spatial coherence of the emission from this hybrid system, Young-type interferometric experiments were performed. Two slits were added to the intermediate image plane of the sample, which selected the emission from two regions on both sides of the excitation spot with a separation distance of 2.8 µm. The strong coupling generated plexcitons with the radiation propagating upward and downward (left panel of Figure 16a (i)), reaching the two regions selected by the two slits. The radiation propagating along these two paths interfered on the entrance slit of the spectrometer, resulting in the inference fringes in the wavelength range of 610-640 nm, as shown in the right panel of Figure 16a (i). By inserting a beam block in the Fourier plane of the sample to select the wave vector components corresponding to the propagation in the upper half-space, interference fringes were still visible (Figure 16a (ii)). In the case of weak coupling, no fringes were observed in both configurations. These results clearly demonstrate the spatial coherence of the plexcitonic states. By enlarging the laser spot to cover both interfering regions on the sample, interference fringes were also observed. The visibility of the fringes is decreased with the increase of the distance between two interfering regions, as shown in Figure 16a (iii). The comparison for two wavelengths of 610 and 630 nm shows that the coherence length is reduced when the wavelength becomes closer to the bare exciton emission at 600 nm.

Spatial coherence was also reported in the strongly coupled system of periodic silver nanorod arrays covered by fluorescent molecules doped in PMMA.^[285] The evolution of the spatial coherence was observed when transiting from the weak to the strong coupling regime by increasing the concentration

www.advancedsciencenews.com

www.afm-journal.de

Table 3. Strong coupling between QEs and different plasmonic nanostructures.

QEs	Plasmonic nanostructures	Single QE/ single NP ^{a)}	Spectral type ^{b)}	<i>ω</i> ₀ [eV] ^{c)}	γ [meV]	к[meV]	$\Omega [\text{meV}]^{d-f)}$	Ref.
TDBC J-aggregates in PVA	Ag film	X/X	Ref PL	2.104	47	70	180	[292]
TDBC J-aggregates	Ag film	X/X	Ref	2.1	49	-	300	[281]
TDBC J-aggregates in PVA	Ag film	X/X	Ref	2.09	51	33085	*40–150	[274]
TDBC J-aggregates	Ag film	X / X	Ref PL	2.07	-	-	300	[359]
TDBC J-aggregates	Ag film Corrugated Ag film	×/×	Ref PL	2.1	-	-	310	[302]
TDBC J-aggregates	Corrugated Ag film	×/×	Ref PL	2.07	-	-	180 —	[360]
S2275 J-aggregates in PVA	Thin Ag film between PVA layers	×/×	Ref PL	1.91	41	4.4	26	[361]
DPDC J-aggregates in PVA	Ag nanohole array	X/X	Tran	1.78	-	-	250	[280]
TDBC J- aggregates	Ag nanohole array	X/X	Ext Abs	2.1	80	757	**313 **304	[288]
Porphyrin J-aggregates	Square Ag nanohole array Hexagonal Ag nanohole array	X/X	Tran	2.53	*149	190 510	300 420	[362]
Thia J-aggregates in PVA	Au nanohole array	X/X	Tran	1.99	-	-	99–245	[363]
Thia J-aggregates in PVA	Au nanohole array	X/X	Tran	1.99	-	-	260	[364]
Cyanine dye J-aggregates	Spherical Au nanovoid array	X/X	Ref	1.85	-	-	230	[307]
Cyanine dye J-aggregates	Au nanoslit array	X/X	Ref	1.78	-	-	*110	[309]
Cyanine dye J-aggregates	Au nanoslit array	X/X	Ref	1.789	-	-	110	[308]
Cyanine dye J-aggregates	Au nanoslit array	X/X	Ref	1.79	-	-	110	[310]
TDBC J-aggregates	Ag nanodisk array	X/X	Tran	2.11	52	180	450	[311]
TDBC J-aggregates	Ag nanodisk array	X/X	Ext	2.07	32	*257–683	*380–460	[365]
TDBC J-aggregates	Al nanodisk array Al nanorod array	X / X	Tran	2.1	66	-	400 400	[312]
Porphyrin J-aggregates	Vertically oriented Au nanorods	X / X	Ref PL	1.84	-	-	125	[366]
J-aggregates	Vertically oriented Au nanorods	X/X	Ext	1.99	66	-	310##	[367]
J-aggregates	Au nanopyramid array on Au film	X/X	Ref	1.44	50	56	200	[313]
DPDC J-aggregates	Au nanoshells in solution	X/X	Ext	1.79	52	-	120	[314]
JC1 J-aggregates	Au nanostars in solution	X/X	Ext	2.08	-	-	**260#	[315]
TDBC J-aggregates	Ag nanoprisms in solution	X/X	Ext	2.09	51	-	>400	[316]
TDBC J-aggregates	Ag nanoprisms in solution	X/X	Ext	2.11	-	-	*200–400	[317]
PIC J-aggregates	Ag nanoplatelets in solution	X/X	Ext	2.156	21	-	207	[368]
PIC J-aggregates	Au hollow nanoprisms in solution	X/X	Ext	2.16	21	408	**198	[369]
Cyanine dye J-aggregates	Ag@Au hollow nanoshells in solution	X/X	Ext	2.16	17.9	404	225	[320]
JC1 J-aggregates	Au nanorods in solution	X/X	Ext PL	2.09	*28	-	200	[318]
JC1 J-aggregates	Au nanorods in solution	X/X	Ext	2.09	*28	215	233#	[319]
JC1 J-aggregates	Au@Ag nanorods in solution	X/X	Ext	2.10	36	-	175	[321]
TDBC J-aggregates	Au@Ag nanorods in solution	X/X	Ext	2.11	28	160	194	[322]
TCC J-aggregates	Au bipyramids in solution	X/X	Ext	*1.78	-	-	120	[370]
PIC J-aggregates	Au nanocubes in solution	X/X	Ext	2.14	25	253	**100	[371]
TDBC J-aggregates	Ag nanodisks in solution	X/X	Ext	2.11	32	-	>300	[372]

www.advancedsciencenews.com

Table 3. Continued.

CdSe/ZnS QDs

CdSe/ZnS QDs

QEs	Plasmonic nanostructures	Single QE/ single NP ^{a)}	Spectral type ^{b)}	<i>ω</i> ₀ [eV] ^{c)}	γ [meV]	κ[meV]	$\Omega \left[\text{meV}\right]^{\text{d-f})}$	Ref.
TDBC J-aggregates	Ag-Au nanorings in solution	×/×	Ext	2.11	32	_	>300	[324]
TDBC J-aggregates	Dimers of Au@Ag nanorods in solution	X/X	CD	2.12	50	*290	205 (left-handed) 199 (right-handed)	[325]
Chiral TDBC J-aggregates	Au@Ag nanocuboids in solution	×/×	CD Ext	2.12	46	296	136 214	[323]
TDBC J-aggregates	Ag nanorods	×/√	Scat Ext	2.11	50	*115	100	[328]
TDBC J-aggregates	Ag nanoprisms	X/V	Scat	2.11	100	*200	280##	[268]
TDBC J-aggregates	Ag nanoprisms	×/√	Scat PL	2.11	100	150	400 *100	[329]
TDBC J-aggregates	Ag nanoprisms	×/√	Scat PL	2.11	50	150–200	200–250	[373]
TDBC J-aggregates	Ag nanoprisms	X/V	Scat	-	-	-	200#	[374]
PIC J-aggregates	Au@Ag cuboid nanorods	<i>\</i> <i>\</i>	Scat	2.16	25	135	78–220	[287]
TDBC J-aggregates	Au@Ag nanorings Au@Ag nanocuboids	×/√	Scat	2.116	25	221	200 156	[375]
DPDC J-aggregates in PVA	Au nanodisk dimers	X/V	Scat	1.79	52	372	230–400	[326]
Cyanine dye J-aggregates	Au NP dimers	X/V	Scat	2.14	30	240	150	[327]
J-aggregates	Au nanocubes on Au film	X/V	Scat	1.91	59	187	170	[376]
R6G molecules in SU-8	Ag film	X/X	Ref PL	2.29, 2.45	-	-	**200, 100 **230, 110	[276]
R6G molecules	Thin Ag film with irregular nanostructures	X/X	Ext	2.23, 2.42	_	-	380	[282]
MC molecules in PMMA	Ag nanohole array	X/X	Tran	2.2	-	-	650	[275]
H ₂ TPPS ₄ molecules in PVA	Ag nanohole array	X/X	Tran	2.9	-	-	210#	[377]
R6G molecules in PVA	Ag nanorod array	X/X	Ext PL	2.27	*200	*20	250	[333]
DiD molecules	Ag nanorod array	X/X	Tran	1.85	-	-	*290	[285]
Rylene dye molecules in PMMA	Ag nanorod array	X/X	Ext	2.24, 2.41	-	-	220	[378]
Rylene dye molecules in PMMA	Ag nanorod array	X/X	Ext PL	2.24, 2.41	_	-	200	[379]
Rylene dye molecules in PMMA	Ag nanorod array	X/X	Ext PL	2.24, 2.41	_	-	200	[380]
MC molecules in PMMA	Ag NP array	X/X	Ext	*2.18	-	-	294##	[330]
MC molecules in PMMA	Al nanodisk array	X/X	Tran	2.18	497	141	572	[331]
Heptamethine cyanine dye molecules	Ag nanodisk array	X/X	Ext	1.52	*38	200	*356–550	[381]
IR-792 molecules in solution	Au nanodisk array	X/X	Ref PL	1.53	150	10	164	[382]
HITC molecules	Au nanotriangle array	X/X	Ext	1.69	90	210	*200–540	[332]
HITC molecules	Tip-to-side triangular Ag NP dimer array	X/X	Ext	1.65	50	140	390	[286]
Atto 532 molecules	Ag nanocubes on Ag film	X/X	Ref	2.33	65	215	152	[289]
Methylene blue molecules	Au NPs on Au film	<i>\</i> <i>\</i>	Scat	1.86	85	*122	90	[335]
Atto 647 molecules	Au NPs on Au film	√/√	Scat PL	1.92	-	-	 *60	[336]
CdSe QD film	Ag film	X/X	Ref	2.175 *2.08	100 187	-	112 102	[283]
CdSe QD film	Au nanohole array	X/X	Tran	2.05	_	_	220	[337]

X/X

X/X

PL

ΡL

2.01

2.07

65.82

70

_

45

Ag NP array

Ag NP array

[338]

[383]

100#

100#



www.advancedsciencenews.com

ADVANCED FUNCTIONAL MATERIALS www.afm-journal.de

Table 3. Continued.

QEs	Plasmonic nanostructures	Single QE/ single NP ^{a)}	Spectral type ^{b)}	$\omega_0 [eV]^{c)}$	γ [meV]	κ[meV]	$\Omega [\text{meV}]^{\text{d-f})}$	Ref.
CdZnS/ZnS QDs	Al-QDs-Al nanodisks	X/✓	CL	2.83	190	_	1200	[300]
CdSe/ZnS QDs	Ag nanobowties	<i>\</i> <i>\</i>	Scat	1.8	130	385	**176#	[67]
CdSe/ZnS QDs	Ag nanobowties	×/√	EELS	1.8 2.0	110–130	350–395	**200 [#] **160 [#]	[297]
CdSe/CdS QDs	Au NP dimer	X/✓	Scat, PL	2.09	*95	*240	*370 [#]	[384]
CdSeTe/ZnS QDs in PMMA	Slit-like Au nanoresonator at tip apex	<i>\</i> <i>\</i>	PL	1.55	-	78	110	[340]
CdSe/CdS QDs	Au NPs on Ag film	√/√	Scat PL	1.92	40–100	100	230#	[125]
CdSe/ZnS QDs	Au tip above Au substrate	\checkmark / \checkmark	PL	1.870	65	176	163##	[339]
Carbon QDs	Au NPs on Au film	×/√	Scat	1.82	100	*160	140	[385]
Monolayer WS ₂	Au nanohole array	X/X	Tran PL	2.016	28	36	60 —	[344]
Monolayer WS ₂	Chirped Ag nanogroove array	X/X	Ref	2.028	40	240	**54	[386]
Monolayer MoS ₂	Au nanogroove array	X/X	Ref	1.84	-	-	**65	[154]
Monolayer WS ₂	Ag coated monolayer of silica spheres	X/X	Tran PL	2.03	_	-	160	[345]
Monolayer WS ₂ 2-layer WS ₂ 4-layer WS ₂ 16-layer WS ₂	Ag nanorod array	X/X	Ref	2.023	28, 25 59 62 60	54, 60 55 61 67	47, 52 58 78 100	[387]
Monolayer WSe ₂	Ag nanorods	×/√	Scat	1.659	43	98	**49.5	[346]
Monolayer WS ₂	Au nanorods	×/√	Scat	1.950	57	149	91–133	[347]
Small pieces of monolayer WS_2	Au nanorods	×/√	Scat PL	1.960	50	130	**41 **39	[388]
Monolayer WSe ₂	Au nanorods	X/✓	Scat	1.67	47	82	98	[349]
Monolayer MoS ₂ Monolayer WS ₂	Au@Ag nanocuboid	×/√	Scat	1.881–1.806 2.021–1.962	59–75 65–95	197–212	**62.4–36.2 [#] **72.4–82 [#]	[355]
Monolayer WSe ₂ 2-layer WSe ₂ 3-layer WSe ₂ 4-layer WSe ₂ 8-layer WSe ₂	Au bi-pyramids	X/√	Scat	1.67	44 66 56 68 63	110	83.1 *89 *96 *102 *101	[352]
Monolayer MoS ₂	Au bi-pyramids	X/✓	Scat	1.88–1.90	50	105	80	[353]
Monolayer WS ₂	Au nanotriangles on glass in water	×/√	Scat	2.02	100 86	148 278	339.20 [#] 198.51 [#]	[389]
Monolayer WS ₂ 7-layer WS ₂	Au nanodisks	×/√	Scat	1.963 1.942	28 44	170	108 175	[354]
6-layer WS ₂	Ag truncated nanopyramids	×/√	EELS Scat	2.03	70	210	**130 _	[296]
Monolayer WS ₂	Ag nanoprisms	X/✓	Scat	2.012	20	190	120	[350]
Monolayer WS ₂	Ag nanoprisms	X/✓	Scat	2.05	23	120	96	[351]
				2.01	43		**76	
Monolayer WSe ₂	Au nanobowties Au nanodisks Au nanoprisms Au nanorods	×/ <i>√</i>	Scat	1.673	55	204 *452 *279 *190	187 **223 **159 **121	[348]
12-layer WSe ₂	Au NPs on Au film	×/√	Scat PL	1.63	70	-	137	[356]
Monolayer WSe ₂	Ag nanocubes on Ag film	×/√	Scat	1.66	45	130	**36.7	[98]
Monolayer WS ₂	Ag nanocubes on Ag film	×/√	Scat	2.02	50	220	145	[357]

www.advancedsciencenews.com

Table 3. Continued.



QEs	Plasmonic nanostructures	Single QE/ single NP ^{a)}	Spectral type ^{b)}	$\omega_0 [{ m eV}]^{ m c)}$	γ [meV]	к[meV]	$\Omega \ [\text{meV}]^{\text{d-f})}$	Ref.
Monolayer WS ₂	Au nanoprisms on Au film	X/√	Scat PL	1.99	50	180	163	[358]
Monolayer MoS ₂	Ag nanocubes on Au film	×/√	Scat	1.86	50	280	190	[390]
Monolayer MoS ₂	Au nanospheres on Au film	×/√	Scat PL	1.865	30	45	130	[391]
Monolayer WS ₂	Ga NPs on Au film	X/√	Scat	2.02	33	258	122.5	[392]

^{a)} X and \checkmark represent no and yes, respectively; ^{b)}spectral type Ref, Tran, Scat, Abs, Ext, CD, EELS, and CL represent reflection, transmission, scattering, absorption, extinction, circular dichroism, electron energy loss spectroscopy, and cathodoluminescence, respectively; ^{c)}* marks the data estimated according to the literatures; ^{d)}** marks the data which do not strictly satisfy the criterion of strong coupling; ^{e)#} indicates that the data for anticrossing in dispersion relation are not provided; ^{f)##} marks the value which is not the Rabi splitting at zero detuning.

of molecules. It was found that the spatial coherence length increased with the increase of the weight of the plasmonic component in the mixed state, and high degree of spatial coherence was observed even when the mode was very exciton-like. In a similar system, the long-range spatial coherence of nonlinear emission was demonstrated.^[378]

7.3.2. Temporal Response

In the strong coupling regime, the energy can transfer back and forth between the emitter and the SPs, known as Rabi oscillation, with the period $T_{\rm R} \approx 2\pi/\Omega$. While the Rabi oscillation with time and Rabi splitting in spectra are two aspects



Figure 16. a) Spatial coherence property for the strong coupling sample of J-aggregates on a silver film. (i) Left: Sketch of the propagation mechanism. Right: Interference pattern recorded without selection on the wave vector. (ii) Interference pattern recorded with only the upward propagation. The intensity profile measured along the white dotted line is drawn on the right side of the figure. (iii) Visibility of the fringes as a function of the interslit distance for two detection wavelengths (610 and 630 nm). b) Temporal response for the strong coupling sample of J-aggregates on a gold nanoslit array. (i) Schematic of coherent ultrafast spectroscopy on a hybrid nanostructure consisting of a 50-nm-thick film of J-aggregate molecules in a polymer matrix coated onto a gold nanoslit array. Strongly localized SP fields (in red) exist in and near the slits. Incident and reflected laser pulses and J-aggregate excitons are shown schematically. (ii) Time evolution of the $\Delta R/R$ signal near the lower plexciton resonance measured at two different incidence angles θ , exhibiting pronounced sub-40 fs Rabi oscillations. The shorter oscillation period for $\theta = 39^{\circ}$ reflects the increased exciton–SP detuning. Simulated dynamics for $\theta = 39^{\circ}$ is shown as a dashed line (shifted vertically by -0.025). (iii) Experimental (open symbols) and calculated (solid lines) oscillation periods and plexciton energies as a function of θ . (a) Reproduced with permission.^[309] Copyright 2012, American Physical Society. (b) Reproduced with permission.^[309]

of the same physical phenomenon, nearly all studies reported the spectral response, which can be more easily obtained. As shown in Table 3, the Rabi splitting for the coupled plasmonic structures and emitters is usually at the level of about 100 meV, corresponding to the Rabi oscillation period of about tens of femtoseconds, which requires ultrafast optical techniques to be detected in experiments.

DVANCED

IENCE NEWS

Vasa et al. studied the ultrafast Rabi oscillation in the hybrid system of J-aggregates and gold nanoslit array (Figure 16b (i)).^[308] The strong coupling was demonstrated by angle-resolved reflectivity measurements with the Rabi splitting of about 110 meV for a grating with period of 430 nm. To resolve the ultrafast dynamic process, angle-resolved pump-probe spectroscopy was performed on the strong coupling system. Nearly collinearly propagating, p-polarized pump and probe pulses with sub-15 fs duration and centered at 1.8 eV were weakly focused onto the sample at variable incidence angle. The plexciton dynamics was probed by monitoring the differential reflectivity spectrum $\Delta R/R$ as a function of probe frequency and time delay between pump and probe pulses.

For incidence angle of 39°, the differential reflectivity signal near the lower plexciton resonance (1.65 eV) shows clear signatures of Rabi oscillations with a period of about 27 fs (red line in Figure 16b (ii)). The simulations reproduce the oscillatory lower plexciton dynamics (black dashed line in Figure 16b (ii)). When decreasing the detuning between the SP and exciton by changing the incidence angle to 31°, the oscillation period increases to about 37 fs. Experimental results of Rabi period for several values of the detuning are consistent with the simulation results (Figure 16b (iii)). At high pump fluence and for small detuning, much stronger dispersive nonlinearities of lower plexcitons were observed with clear signatures of Rabi oscillations, and the Rabi period decreases progressively with increasing delay. Out-of-phase Rabi oscillations on the upper plexciton branch was also observed. The plasmon-exciton population transfer induces the transient oscillations in exciton density, which gives rise to a periodic modulation of Rabi splitting and thus optical nonlinearity. The coherent manipulation of the coupling energy by pump light on a timescale of tens of femtoseconds provides a route toward all-optical ultrafast nanophotonic devices.

8. Applications

8.1. Plasmon Modified Spontaneous Emission

The plasmon modified spontaneous emission can be used in various applications, such as sensing, imaging, light harvesting, anticounterfeiting, light emitting devices, single-photon sources, and various other plasmonic devices. Based on Purcell effect, an emitter will undergo drastic increase in its decay rate when approaching a plasmonic nanostructure, and the decay rate is sensitive to their relative distance. This provides a method for sensing the LDOS (related with the PL lifetime) and the distance between the emitter and plasmonic structure. The LDOS sensing can be accomplished by attaching the emitter to a scanning probe. By scanning the emitter around the plasmonic nanostructure, the lifetime mapping can be obtained. Fluorescence lifetime imaging was demonstrated by scanning a fluorescent nanobead and a NV center across gold or silver NWs.^[74,75] Spatial oscillations of QD lifetime close to a silver NW was observed by controlling the QD position using a microfluidic device.^[45]

The plasmon-enhanced fluorescence can be used to probe the electric field distribution of hot spots. Cang et al. demonstrated the imaging of fluorescence enhancement profile of single hot spots as small as 15 nm with an accuracy down to 1.2 nm.^[393] As a result of the Brownian motion, single molecules will adsorb randomly on the surface of the sample (Al thin films and Ag NP clusters), and produce bright fluorescence when coming to the hot spots. By using a maximum likelihood single molecule localization method, the position of the molecule can be determined with single-nanometer accuracy. With hundreds of frames of images recorded, the positions of molecules and corresponding fluorescence intensity were obtained, producing the fluorescence enhancement profile around the hot spots. It is noted that the result in this study is the profile of fluorescence enhancement instead of electromagnetic field enhancement, since both the absorption enhancement and emission modification contribute to fluorescence enhancement. To eliminate the influence of emission enhancement, Mack et al. used fluorescent molecules with the absorption maximum matching the plasmon resonance and the fluorescence emission wavelength far away from the plasmon wavelength.^[394] This widefield method provides a high-throughput way to reconstruct the interaction maps of single molecules and plasmonic nanostructures by highly parallelized ensemble-level single molecule detection.[395]

The enhanced fluorescence also enables super-resolution imaging methods by combining with scanning probe microscopy. By attaching a single gold NP to the tip of the scanning probe, super-resolution imaging of single molecules was achieved with the full width at half maximum (FWHM) of the fluorescence image about 65 nm.^[5,6] A plasmonic antenna can also be fabricated on the tip to image fluorescent molecules. By using an Al nanoantenna sculpted with a focused ion beam at the end face of an aperture near-field fiber probe, small single molecule fluorescence spot with FWHM \approx 30 nm was obtained.^[176] Akin to the plasmonic antenna attached to a scanning probe, a metal tip can play the similar role.^[396]

The plasmonic nanostructures can be used to improve the performance of solid state light sources, such as light emitting diodes (LEDs).^[397] The efficiency of a LED is the product of excitation efficiency, quantum yield (also called internal quantum efficiency), and extraction efficiency which is the fraction of light radiated into free space. The quantum yield improvement of InGaN guantum well was demonstrated by depositing Ag film or fabricating Ag grating structures on the quantum well with a spacer between them.^[398] For the emitters with high quantum yield, the enhancement of emission intensity can be achieved by enhanced excitation efficiency and extraction efficiency.^[399] By using plasmonic structures, the radiation direction of the emitters can be tailored without the need of secondary optical components, providing a practicable way for miniaturization and integration. The spectral resonance properties also make it possible to selectively enhance the emission at certain spectral range, providing more possibilities for





designing high performance white light and colored LEDs. Moreover, it is reported that plasmonic nanostructures can enhance the stability of organic LED.^[400]

The plasmon modified spontaneous emission provides valuable ways to tailor the properties of single-photon sources based on single QEs. As discussed in Section 5, the brightness, emission direction, and polarization can all be modified by plasmonic nanostructures. Coupling single QEs with plasmonic waveguides provides fundamental building blocks for constructing quantum nanophotonic circuits, as discussed in Section 6.

8.2. Strong Coupling

In the strong coupling regime, the polariton states of part light and part matter provide new opportunities for various potential applications. The typical effective mass of polariton is only around 10⁻⁴–10⁻⁵ times the free electron mass,^[401,402] resulting in a large de Broglie wavelength even at room temperature. As the bosons can undergo Bose-Einstein condensation (BEC) when their de Broglie wavelength becomes comparable to their average separation,^[401] the polaritons provide a platform to realize BEC at room temperature.^[403,404] In the hybrid system of silver nanorod array and R6G molecules, thermalization and cooling of plasmon-exciton polaritons were observed.^[333] In a similar system composed of silver nanorod array and rylene dye molecules, the formation of a nonequilibrium room temperature plexciton condensate was demonstrated.^[380] Time-resolved experiments revealed the picosecond dynamics and a 2.5 meV energy blueshift of the condensate. A spatial coherence length longer than 100 µm was observed, well over the excitation spot size. The condensation was also realized in a system consisting of an array of gold NPs overlaid with a solution of dye molecules. It occurred only for pump pulse durations below a critical value of 100-250 fs, showing the ultrafast character of the thermalization and condensate formation.^[382]

Similar with BEC, due to the bosonic nature of exciton polaritons, lasing without population inversion can occur in strong coupling systems.^[405–407] Based on an array of metal NPs and organic emitters, plasmon–exciton polariton laser was demonstrated.^[379] The rylene dye molecules in PMMA matrix were spin-coated on a silver nanorod array. The dark plasmon mode of the array with low loss contributes to the accumulation of the plexciton population, leading to lasing with very low threshold power.

In addition, the plasmon–exciton strong coupling can be exploited for coherent emission,^[285,359,378,408] nonlinearities,^[409–411] quantum entanglement,^[412,413] single-photon sources,^[414] and sensing.^[415] Other than the applications in optics, strong coupling can alter the material properties. It is reported that photobleaching of organic chromophores can be suppressed by strong coupling.^[374] For the organic molecules of TDBC J-aggregates strongly coupled with a silver nanoprism, a 100-fold stabilization of the J-aggregates was found for red-detuned plasmon mode, which was attributed to the suppressed population transfer from the excited singlet state to the long-lived triplet state because of the very short lifetime of plexcitons (\approx 10 fs).

9. Conclusions and Outlook

We have reviewed the main fundamental aspects of plasmon modified spontaneous emission of QEs, the coupling of plasmonic waveguides and QEs, and the plasmon-exciton strong coupling. Plasmonic nanostructures function as optical nanoantennas to concentrate electromagnetic field into nanoscale spaces, enhance the local electromagnetic field and LDOS, and thus enhance the fluorescence intensity and shorten the lifetime. Especially, plasmonic nanogaps provide nanocavities with extremely large field enhancement and small mode volume, leading to most significant modification to spontaneous emission. The spectral profiles of SP resonances lead to the specific spectral shapes of the fluorescence. The emission direction can be well controlled by proper design of the plasmonic nanostructure, which can benefit the efficient collection of fluorescence. The plasmonic antennas also influence the polarization of fluorescence emission by plasmon-exciton coupling with high efficiency. The interaction between SPs and excitons can mediate the energy transfer processes between QEs, enabling energy transfer over longer distances. Moreover, SPs can also modify the multiexciton processes in QEs, suppress fluorescence blinking, and mediate the cooperative emission and entanglement of multiple QEs.

Plasmonic nanowaveguides can not only function as optical nanoantennas to modify the spontaneous emission of QEs, but also guide the electromagnetic signals over long distances with the field confinement beyond the diffraction limit. Therefore, the coupling of QEs and nanowaveguides provides more possibilities to manipulate and utilize the spontaneous emission of QEs. We have reviewed the coupling of QEs, especially single QEs, with various plasmonic waveguides, among which chemically synthesized Ag NWs are mostly used. Due to the single photon emission properties, single QEs coupling with plasmonic waveguides provide a fundamental building block for quantum plasmonic nanocircuits.

The strong coupling of plasmons and excitons leads to the formation of light–matter mixed plexciton states. The small mode volume of SPs leads to stronger vacuum electric field and thus larger coupling strength, in favor of the realization of strong coupling. We have reviewed the strong coupling of J-aggregates, molecules, QDs, and 2D TMDCs with various plasmonic nanostructures, mainly including metal films, metal nanohole/NP arrays, and single plasmonic nanocavities. Strong coupling at single exciton level has been demonstrated in experiments for molecules, J-aggregates, and QDs. Monolayer TMDCs with large transition dipole moment and other particular properties, such as the locked spin and valley degrees of freedom and atomic thickness, have attracted much attention and been widely used in the study of plasmon–exciton strong coupling.

The coupling strength between QEs and plasmonic nanostructures sensitively depends on many factors, such as their separation distance, orientation and strength of exciton dipole, plasmon mode profile and volume, and spectral matching. Therefore, realizing precisely controlled coupling systems is highly desired, and advanced techniques to assemble or fabricate such systems need be developed. Moreover, the development of exciton materials less susceptible to photodamage will help to develop nanophotonic devices with longer durability.



In the weak coupling regime, designing and realizing systems with multiple outstanding properties such as high brightness, large decay rates, high quantum yield, and narrow emission angle range will be very attractive. The improvement of emission performances can also promote their applications in various devices. Largely hindered by the difficulties of precisely preparing coupled systems, the experimental study of interaction between QEs mediated by SPs is guite limited, and the progress in this direction may be promoted with the development of advanced technologies. Plasmonic nanostructures provide a versatile platform to realize plasmon-exciton strong coupling at ambient conditions at nanoscale. In addition to pushing the strong coupling to the limit of single exciton and single plasmonic nanocavity, other aspects of and the rich phenomena related to strong coupling, such as those mentioned in Sections 7.3 and 8.2, need further investigation. With optimized structure designs and improved material properties, larger Rabi splitting can be expected, which may lead to the regime of ultrastrong coupling. The study of plasmon-exciton interactions can help to reveal the fundamental quantum optics and cavity quantum electrodynamics phenomena at nanoscale, and advance the developments of burgeoning quantum technology and various nanophotonic applications. With the progress of nanotechnologies and advanced materials, new developments of plasmon-exciton interactions and corresponding applications will be seen.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 11774413, 12074421, and 91850207), and the Strategic Priority Research Program of Chinese Academy of Sciences (Grant No. XDB33000000). Figure 2 and minor typographical errors were corrected on December 16, 2021 after initial online publication.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

nanocavities, optical antennas, quantum emitters, Rabi splitting, singlephoton sources, surface plasmons, surface-enhanced fluorescence

- Received: January 27, 2021
- Revised: August 24, 2021
- Published online: September 12, 2021
- H. X. Xu, E. J. Bjerneld, M. Kall, L. Borjesson, Phys. Rev. Lett. 1999, 83, 4357.
- [2] H. X. Xu, J. Aizpurua, M. Kall, P. Apell, Phys. Rev. E 2000, 62, 4318.
- [3] J. J. Baumberg, J. Aizpurua, M. H. Mikkelsen, D. R. Smith, Nat. Mater. 2019, 18, 668.
- [4] H. Wei, H. X. Xu, Nanoscale **2013**, *5*, 10794.
- [5] S. Kuhn, U. Hakanson, L. Rogobete, V. Sandoghdar, Phys. Rev. Lett. 2006, 97, 017402.
- [6] P. Anger, P. Bharadwaj, L. Novotny, Phys. Rev. Lett. 2006, 96, 113002.



- [7] J. F. Li, C. Y. Li, R. F. Aroca, Chem. Soc. Rev. 2017, 46, 3962.
- [8] H. X. Xu, M. Kall, Phys. Rev. Lett. 2002, 89, 246802.
- [9] M. L. Juan, M. Righini, R. Quidant, Nat. Photonics 2011, 5, 349.
- [10] R. M. Ma, R. F. Oulton, Nat. Nanotechnol. 2019, 14, 12.
- [11] H. Wu, Y. X. Gao, P. Z. Xu, X. Guo, P. Wang, D. X. Dai, L. M. Tong, Adv. Opt. Mater. 2019, 7, 1900334.
- [12] P. Muhlschlegel, H. J. Eisler, O. J. F. Martin, B. Hecht, D. W. Pohl, *Science* 2005, 308, 1607.
- [13] S. Kim, J. H. Jin, Y. J. Kim, I. Y. Park, Y. Kim, S. W. Kim, Nature 2008, 453, 757.
- [14] M. Kauranen, A. V. Zayats, Nat. Photonics 2012, 6, 737.
- [15] K. M. Mayer, J. H. Hafner, Chem. Rev. 2011, 111, 3828.
- [16] H. Wei, D. Pan, S. P. Zhang, Z. P. Li, Q. Li, N. Liu, W. H. Wang, H. X. Xu, Chem. Rev. 2018, 118, 2882.
- [17] T. J. Davis, D. E. Gomez, A. Roberts, Nanophotonics 2017, 6, 543.
- [18] A. B. Taylor, P. Zijlstra, ACS Sens. 2017, 2, 1103.
- [19] R. Bardhan, S. Lal, A. Joshi, N. J. Halas, Acc. Chem. Res. 2011, 44, 936
- [20] M. Kim, M. Lin, J. Son, H. X. Xu, J. M. Nam, Adv. Opt. Mater. 2017, 5 1700004
- [21] H. K. Choi, K. S. Lee, H. H. Shin, J. J. Koo, G. J. Yeon, Z. H. Kim, Acc. Chem. Res. 2019, 52, 3008.
- [22] Z. L. Zhang, C. Y. Zhang, H. R. Zheng, H. X. Xu, Acc. Chem. Res. 2019, 52, 2506.
- [23] Y. H. Jang, Y. J. Jang, S. Kim, L. N. Quan, K. Chung, D. H. Kim, *Chem. Rev.* 2016, 116, 14982.
- [24] E. M. Purcell, Phys. Rev. 1946, 69, 681.
- [25] M. Pelton, Nat. Photonics 2015, 9, 427.
- [26] A. Huck, U. L. Andersen, Nanophotonics 2016, 5, 483.
- [27] P. Torma, W. L. Barnes, Rep. Prog. Phys. 2015, 78, 013901.
- [28] M. Pelton, S. D. Storm, H. X. Leng, Nanoscale 2019, 11, 14540.
- [29] H. J. Chen, L. Shao, Q. Li, J. F. Wang, Chem. Soc. Rev. 2013, 42, 2679.
- [30] H. Wei, A. Reyes-Coronado, P. Nordlander, J. Aizpurua, H. X. Xu, ACS Nano 2010, 4, 2649.
- [31] P. Nordlander, C. Oubre, E. Prodan, K. Li, M. I. Stockman, Nano Lett. 2004, 4, 899.
- [32] H. X. Xu, J. Quantum Spectrosc. Radiat. Transfer 2004, 87, 53.
- [33] H. X. Xu, M. Kall, ChemPhysChem 2003, 4, 1001.
- [34] C. Ciraci, R. T. Hill, J. J. Mock, Y. Urzhumov, A. I. Fernandez-Dominguez, S. A. Maier, J. B. Pendry, A. Chilkoti, D. R. Smith, *Science* 2012, 337, 1072.
- [35] W. Chen, S. P. Zhang, M. Kang, W. K. Liu, Z. W. Ou, Y. Li, Y. X. Zhang, Z. Q. Guan, H. X. Xu, *Light: Sci. Appl.* **2018**, *7*, 56.
- [36] L. Mao, Z. P. Li, B. Wu, H. X. Xu, Appl. Phys. Lett. 2009, 94, 243102.
- [37] J. Zuloaga, E. Prodan, P. Nordlander, Nano Lett. 2009, 9, 887.
- [38] R. Esteban, A. G. Borisov, P. Nordlander, J. Aizpurua, Nat. Commun. 2012, 3, 825.
- [39] D. Pan, H. Wei, Z. L. Jia, H. X. Xu, Sci. Rep. 2014, 4, 4993.
- [40] H. Wei, Z. P. Li, X. R. Tian, Z. X. Wang, F. Z. Cong, N. Liu, S. P. Zhang, P. Nordlander, N. J. Halas, H. X. Xu, *Nano Lett.* 2011, *11*, 471.
- [41] S. P. Zhang, H. Wei, K. Bao, U. Hakanson, N. J. Halas, P. Nordlander, H. X. Xu, Phys. Rev. Lett. 2011, 107, 096801.
- [42] C. Chakraborty, N. Vamivakas, D. Englund, Nanophotonics 2019, 8, 2017.
- [43] X. W. He, N. F. Hartmann, X. D. Ma, Y. Kim, R. Ihly, J. L. Blackburn, W. L. Gao, J. Kono, Y. Yomogida, A. Hirano, T. Tanaka, H. Kataura, H. Htoon, S. K. Doorn, *Nat. Photonics* **2017**, *11*, 577.
- [44] L. Novotny, B. Hecht, Principles of Nano-Optics., Cambridge University Press, Cambridge 2012.
- [45] C. Ropp, Z. Cummins, S. Nah, J. T. Fourkas, B. Shapiro, E. Waks, *Nat. Commun.* 2013, 4, 1447.
- [46] C. U. Hail, C. Holler, K. Matsuzaki, P. Rohner, J. Renger, V. Sandoghdar, D. Poulikakos, H. Eghlidi, *Nat. Commun.* 2019, 10, 1880.

www.advancedsciencenews.com

- [47] D. D. Ge, S. Marguet, A. Issa, S. Jradi, T. H. Nguyen, M. Nahra, J. Beal, R. Deturche, H. S. Chen, S. Blaize, J. Plain, C. Fiorini, L. Douillard, O. Soppera, X. Q. Dinh, C. Dang, X. Y. Yang, T. Xu, B. Wei, X. W. Sun, C. Couteau, R. Bachelot, *Nat. Commun.* 2020, *11*, 3414.
- [48] F. Li, D. P. Josephson, A. Stein, Angew. Chem., Int. Ed. 2011, 50, 360.
- [49] D. Nepal, L. F. Drummy, S. Biswas, K. Park, R. A. Vaia, ACS Nano 2013, 7, 9064.
- [50] C. Strelow, T. S. Theuerholz, C. Schmidtke, M. Richter, J. P. Merkl, H. Kloust, Z. L. Ye, H. Weller, T. F. Heinz, A. Knorr, H. Lange, *Nano Lett.* 2016, *16*, 4811.
- [51] X. Li, J. Qian, L. Jiang, S. L. He, Appl. Phys. Lett. 2009, 94, 063111.
- [52] A. H. Fu, C. M. Micheel, J. Cha, H. Chang, H. Yang, A. P. Alivisatos, J. Am. Chem. Soc. 2004, 126, 10832.
- [53] E. Cohen-Hoshen, G. W. Bryant, I. Pinkas, J. Sperling, I. Bar-Joseph, Nano Lett. 2012, 12, 4260.
- [54] F. Nicoli, T. Zhang, K. Hubner, B. Y. Jin, F. Selbach, G. Acuna, C. Argyropoulos, T. Liedl, M. Pilo-Pais, *Small* **2019**, *15*, 1804418.
- [55] G. P. Acuna, F. M. Moller, P. Holzmeister, S. Beater, B. Lalkens, P. Tinnefeld, *Science* 2012, 338, 506.
- [56] C. Vietz, I. Kaminska, M. S. Paz, P. Tinnefeld, G. P. Acuna, ACS Nano 2017, 11, 4969.
- [57] L. Xin, M. Lu, S. Both, M. Pfeiffer, M. J. Urban, C. Zhou, H. Yan, T. Weiss, N. Liu, K. Lindfors, ACS Photonics 2019, 6, 985.
- [58] H. H. Zhang, M. X. Li, K. W. Wang, Y. Tian, J. S. Chen, K. T. Fountaine, D. DiMarzio, M. Z. Liu, M. Cotlet, O. Gang, ACS *Nano* **2020**, *14*, 1369.
- [59] B. P. Khanal, A. Pandey, H. Li, Q. L. Lin, W. K. Bae, H. M. Luo, V. I. Klimov, J. M. Pietryga, ACS Nano 2012, 6, 3832.
- [60] H. Naiki, A. Masuhara, S. Masuo, T. Onodera, H. Kasai, H. Oikawa, J. Phys. Chem. C 2013, 117, 2455.
- [61] N. S. Abadeer, M. R. Brennan, W. L. Wilson, C. J. Murphy, ACS Nano 2014, 8, 8392.
- [62] X. D. Ma, K. Fletcher, T. Kipp, M. P. Grzelczak, Z. Wang, A. Guerrero-Martinez, I. Pastoriza-Santos, A. Kornowski, L. M. Liz-Marzan, A. Mews, J. Phys. Chem. Lett. 2011, 2, 2466.
- [63] I. Gorelikov, N. Matsuura, Nano Lett. 2008, 8, 369.
- [64] T. Ming, L. Zhao, Z. Yang, H. J. Chen, L. D. Sun, J. F. Wang, C. H. Yan, Nano Lett. 2009, 9, 3896.
- [65] H. M. Su, Y. C. Zhong, T. Ming, J. F. Wang, K. S. Wong, J. Phys. Chem. C 2012, 116, 9259.
- [66] H. M. Shen, R. Y. Chou, Y. Y. Hui, Y. B. He, Y. Q. Cheng, H. C. Chang, L. M. Tong, Q. H. Gong, G. W. Lu, *Laser Photonics Rev.* 2016, *10*, 647.
- [67] K. Santhosh, O. Bitton, L. Chuntonov, G. Haran, Nat. Commun. 2016, 7, 11823.
- [68] D. Ratchford, F. Shafiei, S. Kim, S. K. Gray, X. Q. Li, Nano Lett. 2011, 11, 1049.
- [69] S. Masuo, K. Kanetaka, R. Sato, T. Teranishi, ACS Photonics 2016, 3, 109.
- [70] T. Hartsfield, W. S. Chang, S. C. Yang, T. Ma, J. W. Shi, L. Y. Sun, G. Shvets, S. Link, X. Q. Li, *Proc. Natl. Acad. Sci. U. S. A.* 2015, *112*, 12288.
- [71] A. Huck, S. Kumar, A. Shakoor, U. L. Anderson, Phys. Rev. Lett. 2011, 106, 096801.
- [72] S. Schietinger, M. Barth, T. Alchele, O. Benson, Nano Lett. 2009, 9, 1694.
- [73] J. Tang, J. Xia, M. Fang, F. Bao, G. Cao, J. Shen, J. Evans, S. He, *Nat. Commun.* 2018, 9, 1705.
- [74] M. Frimmer, Y. T. Chen, A. F. Koenderink, Phys. Rev. Lett. 2011, 107, 123602.
- [75] A. W. Schell, P. Engel, J. F. M. Werra, C. Wolff, K. Busch, O. Benson, *Nano Lett.* 2014, 14, 2623.
- [76] N. Nikolay, N. Sadzak, A. Dohms, B. Lubotzky, H. Abudayyeh, R. Rapaport, O. Benson, Appl. Phys. Lett. 2018, 113, 113107.

- [78] C. Gruber, P. Kusar, A. Hohenau, J. R. Krenn, Appl. Phys. Lett. 2012, 100, 231102.
- [79] C. Gruber, A. Trugler, A. Hohenau, U. Hohenester, J. R. Krenn, Nano Lett. 2013, 13, 4257.
- [80] Y. Meng, G. Cheng, Z. Q. Man, Y. Xu, S. Zhou, J. Bian, Z. D. Lu, W. H. Zhang, *Adv. Mater.* **2020**, *32*, 2005979.
- [81] A. G. Curto, G. Volpe, T. H. Taminiau, M. P. Kreuzer, R. Quidant, N. F. van Hulst, *Science* **2010**, *329*, 930.
- [82] A. G. Curto, T. H. Taminiau, G. Volpe, M. P. Kreuzer, R. Quidant, N. F. van Hulst, *Nat. Commun.* 2013, *4*, 1750.
- [83] E. B. Urena, M. P. Kreuzer, S. Itzhakov, H. Rigneault, R. Quidant, D. Oron, J. Wenger, *Adv. Mater.* **2012**, *24*, OP314.
- [84] S. I. Bozhevolnyi, J. B. Khurgin, Optica 2016, 3, 1418.
- [85] H. F. Yuan, S. Khatua, P. Zijlstra, M. Yorulmaz, M. Orrit, Angew. Chem., Int. Ed. 2013, 52, 1217.
- [86] S. Khatua, P. M. R. Paulo, H. F. Yuan, A. Gupta, P. Zijlstra, M. Orrit, ACS Nano 2014, 8, 4440.
- [87] Y. Chen, K. Munechika, I. Jen-La Plante, A. M. Munro, S. E. Skrabalak, Y. Xia, D. S. Ginger, *Appl. Phys. Lett.* **2008**, *93*, 053106.
- [88] A. Kinkhabwala, Z. F. Yu, S. H. Fan, Y. Avlasevich, K. Mullen, W. E. Moerner, Nat. Photonics 2009, 3, 654.
- [89] D. Punj, M. Mivelle, S. B. Moparthi, T. S. van Zanten, H. Rigneault, N. F. van Hulst, M. F. Garcia-Parajo, J. Wenger, *Nat. Nanotechnol.* 2013, *8*, 512.
- [90] S. K. H. Andersen, S. Kumar, S. I. Bozhevolnyi, Nano Lett. 2017, 17, 3889.
- [91] G. C. Li, Q. Zhang, S. A. Maier, D. Lei, Nanophotonics 2018, 7, 1865.
- [92] W. Chen, S. P. Zhang, Q. Deng, H. X. Xu, Nat. Commun. 2018, 9, 801.
- [93] T. B. Hoang, G. M. Akselrod, M. H. Mikkelsen, Nano Lett. 2016, 16, 270.
- [94] A. Rose, T. B. Hoang, F. McGuire, J. J. Mock, C. Ciraci, D. R. Smith, M. H. Mikkelsen, *Nano Lett.* 2014, 14, 4797.
- [95] G. M. Akselrod, C. Argyropoulos, T. B. Hoang, C. Ciraci, C. Fang, J. N. Huang, D. R. Smith, M. H. Mikkelsen, *Nat. Photonics* 2014, 8, 835.
- [96] S. I. Bogdanov, M. Y. Shalaginov, A. S. Lagutchev, C. C. Chiang, D. Shah, A. S. Baburin, I. A. Ryzhikov, I. A. Rodionov, A. V. Kildishev, A. Boltasseva, V. M. Shalaev, *Nano Lett.* **2018**, *18*, 4837.
- [97] S. I. Bogdanov, O. A. Makarova, X. H. Xu, Z. O. Martin, A. S. Lagutchev, M. Olinde, D. Shah, S. N. Chowdhury, A. R. Gabidullin, I. A. Ryzhikov, I. A. Rodionov, A. V. Kildishev, S. I. Bozhevolnyi, A. Boltasseva, V. M. Shalaev, J. B. Khurgin, *Optica* **2020**, *7*, 463.
- [98] J. W. Sun, H. T. Hu, D. Zheng, D. X. Zhang, Q. Deng, S. P. Zhang, H. X. Xu, ACS Nano 2018, 12, 10393.
- [99] Y. X. Zhang, W. Chen, T. Fu, J. W. Sun, D. X. Zhang, Y. Li, S. P. Zhang, H. X. Xu, *Nano Lett.* **2019**, *19*, 6284.
- [100] Y. Luo, G. D. Shepard, J. V. Ardelean, D. A. Rhodes, B. Kim, K. Barmak, J. C. Hone, S. Strauf, *Nat. Nanotechnol.* **2018**, *13*, 1137.
- [101] Y. M. Wu, J. H. Xu, E. T. Poh, L. L. Liang, H. L. Liu, J. K. W. Yang, C. W. Qiu, R. A. L. Vallee, X. G. Liu, *Nat. Nanotechnol.* **2019**, *14*, 1110.
- [102] K. J. Russell, T. L. Liu, S. Y. Cui, E. L. Hu, Nat. Photonics 2012, 6, 459.
- [103] E. Dulkeith, A. C. Morteani, T. Niedereichholz, T. A. Klar, J. Feldmann, S. A. Levi, F. van Veggel, D. N. Reinhoudt, M. Moller, D. I. Gittins, *Phys. Rev. Lett.* **2002**, *89*, 203002.
- [104] G. P. Acuna, M. Bucher, I. H. Stein, C. Steinhauer, A. Kuzyk, P. Holzmeister, R. Schreiber, A. Moroz, F. D. Stefani, T. Liedl, F. C. Simmel, P. Tinnefeld, ACS Nano 2012, 6, 3189.



www.advancedsciencenews.com

- [105] C. Liang, J. Y. Luan, Z. Y. Wang, Q. S. Jiang, R. Gupta, S. S. Cao, K. K. Liu, J. J. Morrissey, E. D. Kharasch, R. R. Naik, S. Singamaneni, ACS Appl. Mater. Interfaces 2021, 13, 11414.
- [106] A. Singh, P. M. de Roque, G. Calbris, J. T. Hugall, N. F. van Hulst, *Nano Lett.* 2018, 18, 2538.
- [107] J. H. Hwang, S. Park, J. Son, J. W. Park, J. M. Nam, Nano Lett. 2021, 21, 2132.
- [108] Y. Chen, K. Munechika, D. S. Ginger, Nano Lett. 2007, 7, 690.
- [109] K. Munechika, Y. Chen, A. F. Tillack, A. P. Kulkarni, I. J. L. Plante, A. M. Munro, D. S. Ginger, *Nano Lett.* **2010**, *10*, 2598.
- [110] C. T. Yuan, P. Yu, H. C. Ko, J. Huang, J. Tang, ACS Nano 2009, 3, 3051.
- [111] K. Aslan, M. Wu, J. R. Lakowicz, C. D. Geddes, J. Am. Chem. Soc. 2007, 129, 1524.
- [112] S. Y. Liu, L. Huang, J. F. Li, C. Wang, Q. Li, H. X. Xu, H. L. Guo, Z. M. Meng, Z. Shi, Z. Y. Li, *J. Phys. Chem. C* 2013, *117*, 10636.
- [113] A. Puchkova, C. Vietz, E. Pibiri, B. Wunsch, M. S. Paz, G. P. Acuna, P. Tinnefeld, *Nano Lett.* **2015**, *15*, 8354.
- [114] K. Hubner, M. Pilo-Pais, F. Selbach, T. Liedl, P. Tinnefeld, F. D. Stefani, G. P. Acuna, *Nano Lett.* **2019**, *19*, 6629.
- [115] J. Schedlbauer, P. Wilhelm, L. Grabenhorst, M. E. Federl, B. Lalkens, F. Hinderer, U. Scherf, S. Hoger, P. Tinnefeld, S. Bange, J. Vogelsang, J. M. Lupton, *Nano Lett.* **2020**, *20*, 1074.
- [116] D. Punj, R. Regmi, A. Devilez, R. Plauchu, S. B. Moparthi, B. Stout, N. Bonod, H. Rigneault, J. Wenger, ACS Photonics 2015, 2, 1099.
- [117] B. X. Song, Z. H. Jiang, Z. R. Liu, Y. X. Wang, F. X. Liu, S. B. Cronin, H. Yang, D. M. Meng, B. Y. Chen, P. Hu, A. M. Schwartzberg, S. Cabrini, S. Haas, W. Wu, ACS Nano **2020**, *14*, 14769.
- [118] J. Zhang, Y. Fu, M. H. Chowdhury, J. R. Lakowicz, Nano Lett. 2007, 7, 2101.
- [119] A. Bek, R. Jansen, M. Ringler, S. Mayilo, T. A. Klar, J. Feldmann, Nano Lett. 2008, 8, 485.
- [120] T. S. Zhang, N. Y. Gao, S. Li, M. J. Lang, Q. H. Xu, J. Phys. Chem. Lett. 2015, 6, 2043.
- [121] K. Trofymchuk, V. Glembockyte, L. Grabenhorst, F. Steiner, C. Vietz, C. Close, M. Pfeiffer, L. Richter, M. L. Schutte, F. Selbach, R. Yaadav, J. Zahringer, Q. S. Wei, A. Ozcan, B. Lalkens, G. P. Acuna, P. Tinnefeld, *Nat. Commun.* **2021**, *12*, 950.
- [122] W. Q. Zhao, X. C. R. Tian, Z. N. Fang, S. Y. Xiao, M. Qiu, Q. He, W. Feng, F. Y. Li, Y. B. Zhang, L. Zhou, Y. W. Tan, *Light: Sci. Appl.* 2021, 10, 79.
- [123] T. B. Hoang, G. M. Akselrod, C. Argyropoulos, J. N. Huang, D. R. Smith, M. H. Mikkelsen, *Nat. Commun.* 2015, *6*, 7788.
- [124] X. Z. Qi, T. W. Lo, D. Liu, L. T. Feng, Y. Chen, Y. K. Wu, H. L. Ren, G. C. Guo, D. Y. Lei, X. F. Ren, *Nanophotonics* **2020**, *9*, 2097.
- [125] H. X. Leng, B. Szychowski, M. C. Daniel, M. Pelton, Nat. Commun. 2018, 9, 4012.
- [126] Y. Luo, X. W. He, Y. Kim, J. L. Blackburn, S. K. Doorn, H. Htoon, S. Strauf, Nano Lett. 2019, 19, 9037.
- [127] G. C. Yang, Q. X. Shen, Y. J. Niu, H. Wei, B. F. Bai, M. H. Mikkelsen, H. B. Sun, *Laser Photonics Rev.* 2020, 14, 1900213.
- [128] H. Y. Wang, Y. Lin, P. Z. Ma, Y. Zhong, H. T. Liu, J. Mater. Chem. C 2019, 7, 13526.
- [129] A. R. Dhawan, C. Belacel, J. U. Esparza-Villa, M. Nasilowski, Z. M. Wang, C. Schwob, J. P. Hugonin, L. Coolen, B. Dubertret, P. Senellart, A. Maitre, *Light: Sci. Appl.* **2020**, *9*, 33.
- [130] C. Belacel, B. Habert, F. Bigourdan, F. Marquier, J. P. Hugonin, S. M. de Vasconcellos, X. Lafosse, L. Coolen, C. Schwob, C. Javaux, B. Dubertret, J. J. Greffet, P. Senellart, A. Maitre, *Nano Lett.* 2013, 13, 1516.
- [131] G. R. Zhang, Y. Gu, Q. H. Gong, J. J. Chen, Nanophotonics 2020, 9, 3557.
- [132] G. C. Yang, Y. J. Niu, H. Wei, B. F. Bai, H. B. Sun, Nanophotonics 2019, 8, 2313.
- [133] Y. Luo, E. D. Ahmadi, K. Shayan, Y. C. Ma, K. S. Mistry, C. J. Zhang, J. Hone, J. L. Blackburn, S. Strauf, *Nat. Commun.* 2017, *8*, 1413.

- [134] S. Y. Cao, L. P. Hou, Q. F. Wang, C. Y. Li, W. X. Yu, X. T. Gan, K. H. Liu, M. Premaratne, F. J. Xiao, J. L. Zhao, *Photonics Res.* **2021**, *9*, 501.
- [135] B. T. Ji, E. Giovanelli, B. Habert, P. Spinicelli, M. Nasilowski, X. Z. Xu, N. Lequeux, J. P. Hugonin, F. Marquier, J. J. Greffet, B. Dubertret, *Nat. Nanotechnol.* **2015**, *10*, 170.
- [136] B. Demory, T. A. Hill, C. H. Teng, L. Zhang, H. Deng, P. C. Ku, ACS Photonics 2015, 2, 1065.
- [137] H. Rigneault, J. Capoulade, J. Dintinger, J. Wenger, N. Bonod, E. Popov, T. W. Ebbesen, P. F. Lenne, *Phys. Rev. Lett.* 2005, 95, 117401.
- [138] H. Aouani, O. Mahboub, N. Bonod, E. Devaux, E. Popov, H. Rigneault, T. W. Ebbesen, J. Wenger, *Nano Lett.* 2011, *11*, 637.
- [139] H. Aouani, O. Mahboub, E. Devaux, H. Rigneault, T. W. Ebbesen, J. Wenger, *Nano Lett.* 2011, *11*, 2400.
- [140] F. Werschler, B. Lindner, C. Hinz, F. Conradt, P. Gumbsheimer, Y. Behovits, C. Negele, T. de Roo, O. Tzang, S. Mecking, A. Leitenstorfer, D. V. Seletskiy, *Nano Lett.* **2018**, *18*, 5396.
- [141] J. T. Choy, I. Bulu, B. J. M. Hausmann, E. Janitz, I. C. Huang, M. Loncar, Appl. Phys. Lett. 2013, 103, 161101.
- [142] T. Cai, J. H. Kim, Z. L. Yang, S. Dutta, S. Aghaeimeibodi, E. Waks, ACS Photonics 2018, 5, 3466.
- [143] T. T. Tran, D. Q. Wang, Z. Q. Xu, A. K. Yang, M. Toth, T. W. Odom, I. Aharonovich, *Nano Lett.* **2017**, *17*, 2634.
- [144] A. R. Rashed, M. Habib, N. Das, E. Ozbay, H. Caglayan, New J. Phys. 2020, 22, 093033.
- [145] X. D. Ma, H. Tan, T. Kipp, A. Mews, Nano Lett. 2010, 10, 4166.
- [146] Y. Matsumoto, R. Kanemoto, T. Itoh, S. Nakanishi, M. Ishikawa, V. Biju, J. Phys. Chem. C 2008, 112, 1345.
- [147] H. M. Li, F. T. He, C. K. Ji, W. W. Zhu, Y. Q. Xu, W. K. Zhang, X. R. Meng, X. M. Fang, T. Ding, J. Phys. Chem. C 2019, 123, 25359.
- [148] F. Tam, G. P. Goodrich, B. R. Johnson, N. J. Halas, Nano Lett. 2007, 7, 496.
- [149] B. Peng, Z. P. Li, E. Mutlugun, P. L. H. Martinez, D. H. Li, Q. Zhang, Y. Gao, H. V. Demir, Q. H. Xiong, *Nanoscale* **2014**, *6*, 5592.
- [150] Z. Eftekhari, A. Ghobadi, M. C. Soydan, D. U. Yildirim, N. Cinel, E. Ozbay, Opt. Lett. 2021, 46, 1664.
- [151] L. Langguth, D. Punj, J. Wenger, A. F. Koenderink, ACS Nano 2013, 7, 8840.
- [152] H. H. Su, S. Wu, Y. H. Yang, Q. Leng, L. Huang, J. Q. Fu, Q. J. Wang, H. Liu, L. Zhou, *Nanophotonics* **2020**, *10*, 975.
- [153] Z. Wang, Z. G. Dong, Y. H. Gu, Y. H. Chang, L. Zhang, L. J. Li, W. J. Zhao, G. Eda, W. J. Zhang, G. Grinblat, S. A. Maier, J. K. W. Yang, C. W. Qiu, A. T. S. Wee, *Nat. Commun.* **2016**, *7*, 11283.
- [154] M. W. Yu, S. Ishii, S. S. Li, J. R. Ku, J. H. Yang, K. L. Su, T. Taniguchi, T. Nagao, K. P. Chen, *npj 2D Mater. Appl.* **2021**, *5*, 47.
- [155] K. T. Shimizu, W. K. Woo, B. R. Fisher, H. J. Eisler, M. G. Bawendi, *Phys. Rev. Lett.* **2002**, *89*, 117401.
- [156] Y. Ito, K. Matsuda, Y. Kanemitsu, Phys. Rev. B 2007, 75, 033309.
- [157] Y. Z. Chi, G. X. Chen, F. Jelezko, E. Wu, H. P. Zeng, *IEEE Photonics Technol. Lett.* 2011, 23, 374.
- [158] M. Mivelle, T. S. van Zanten, L. Neumann, N. F. van Hulst, M. F. Garcia-Parajo, *Nano Lett.* **2012**, *12*, 5972.
- [159] S. Kumar, H. Park, H. Cho, R. H. Siddique, V. Narasimhan, D. Yang, H. Choo, *Nat. Commun.* **2020**, *11*, 2930.
- [160] K. Munechika, Y. C. Chen, A. F. Tillack, A. P. Kulkarni, I. Jen-La Plante, A. M. Munro, D. S. Ginger, *Nano Lett.* 2011, *11*, 2725.
- [161] H. X. Xu, X. H. Wang, M. P. Persson, H. Q. Xu, M. Kall, P. Johansson, *Phys. Rev. Lett.* **2004**, *93*, 243002.
- [162] E. C. Le Ru, P. G. Etchegoin, J. Grand, N. Felidj, J. Aubard, G. Levi, J. Phys. Chem. C 2007, 111, 16076.
- [163] M. Ringler, A. Schwemer, M. Wunderlich, A. Nichtl, K. Kurzinger, T. A. Klar, J. Feldmann, Phys. Rev. Lett. 2008, 100, 203002.
- [164] L. Zhao, T. Ming, H. J. Chen, Y. Liang, J. F. Wang, Nanoscale 2011, 3, 3849.
- [165] J. R. Lakowicz, Anal. Biochem. 2004, 324, 153.



www.advancedsciencenews.com



- [167] M. Ramezani, A. Casadei, G. Grzela, F. Matteini, G. Tutuncuoglu, D. Ruffer, A. F. I. Morral, J. G. Rivas, *Nano Lett.* **2015**, *15*, 4889.
- [168] Y. C. Jun, K. C. Y. Huang, M. L. Brongersma, Nat. Commun. 2011, 2, 283.
- [169] M. G. Harats, N. Livneh, G. Zaiats, S. Yochelis, Y. Paltiel, E. Lifshitz, R. Rapaport, Nano Lett. 2014, 14, 5766.
- [170] N. Livneh, M. G. Harats, S. Yochelis, Y. Paltiel, R. Rapaport, ACS Photonics 2015, 2, 1669.
- [171] N. Livneh, M. G. Harats, D. Istrati, H. S. Eisenberg, R. Rapaport, *Nano Lett.* **2016**, *16*, 2527.
- [172] S. K. H. Andersen, S. Bogdanov, O. Makarova, Y. Xuan, M. Y. Shalaginov, A. Boltasseva, S. I. Bozhevolnyi, V. M. Shalaev, ACS Photonics 2018, 5, 692.
- [173] H. Abudayyeh, B. Lubotzky, A. Blake, J. Wang, S. Majumder, Z. Hu, Y. Kim, H. Htoon, R. Bose, A. V. Malko, J. A. Hollingsworth, R. Rapaport, APL Photonics **2021**, 6, 036109.
- [174] I. M. Hancu, A. G. Curto, M. Castro-Lopez, M. Kuttge, N. F. van Hulst, *Nano Lett.* 2014, 14, 166.
- [175] D. Vercruysse, X. Z. Zheng, Y. Sonnefraud, N. Verellen, G. Di Martino, L. Lagae, G. A. E. Vandenbosch, V. V. Moshchalkov, S. A. Maier, P. Van Dorpe, ACS Nano 2014, 8, 8232.
- [176] T. H. Taminiau, F. D. Stefani, F. B. Segerink, N. F. Van Hulst, Nat. Photonics 2008, 2, 234.
- [177] Q. Li, H. Wei, H. X. Xu, Nano Lett. 2015, 15, 8181.
- [178] Y. L. Wang, C. Li, G. Y. Duan, L. L. Wang, L. Yu, Adv. Opt. Mater. 2019, 7, 1801362.
- [179] X. W. Wang, Y. Y. Li, R. Toufanian, L. C. Kogos, A. M. Dennis, R. Paiella, Adv. Opt. Mater. 2020, 8, 1901951.
- [180] H. J. Lezec, A. Degiron, E. Devaux, R. A. Linke, L. Martin-Moreno, F. J. Garcia-Vidal, T. W. Ebbesen, *Science* 2002, 297, 820.
- [181] T. Ming, L. Zhao, H. J. Chen, K. C. Woo, J. F. Wang, H. Q. Lin, *Nano Lett.* **2011**, *11*, 2296.
- [182] T. C. Zuo, H. J. Goldwyn, B. P. Isaacoff, D. J. Masiello, J. S. Biteen, J. Phys. Chem. Lett. 2019, 10, 5047.
- [183] T. Shegai, Z. P. Li, T. Dadosh, Z. Y. Zhang, H. X. Xu, G. Haran, Proc. Natl. Acad. Sci. U. S. A. 2008, 105, 16448.
- [184] Z. P. Li, T. Shegai, G. Haran, H. X. Xu, ACS Nano 2009, 3, 637.
- [185] S. S. Kruk, M. Decker, I. Staude, S. Schlecht, M. Greppmair, D. N. Neshev, Y. S. Kivshar, ACS Photonics 2014, 1, 1218.
- [186] A. Ghimire, E. Shafran, J. M. Gerton, Sci. Rep. 2014, 4, 6456.
- [187] C. R. Han, J. T. Ye, Nat. Commun. 2020, 11, 713.
- [188] Z. W. Li, C. X. Liu, X. Rong, Y. Luo, H. T. Cheng, L. H. Zheng, F. Lin, B. Shen, Y. J. Gong, S. Zhang, Z. Y. Fang, *Adv. Mater.* 2018, *30*, 1801908.
- [189] J. W. Sun, H. T. Hu, D. Pan, S. P. Zhang, H. X. Xu, Nano Lett. 2020, 20, 4953.
- [190] Z. L. Wu, J. G. Li, X. T. Zhang, J. M. Redwing, Y. B. Zheng, Adv. Mater. 2019, 31, 1904132.
- [191] T. Wen, W. D. Zhang, S. Liu, A. Q. Hu, J. Y. Zhao, Y. Ye, Y. Chen, C. W. Qiu, Q. H. Gong, G. W. Lu, *Sci. Adv.* **2020**, *6*, eaao0019.
- [192] P. Andrew, W. L. Barnes, Science 2004, 306, 1002.
- [193] M. Lunz, V. A. Gerard, Y. K. Gun'ko, V. Lesnyak, N. Gaponik, A. S. Susha, A. L. Rogach, A. L. Bradley, *Nano Lett.* **2011**, *11*, 3341.
- [194] X. Zhang, C. A. Marocico, M. Lunz, V. A. Gerard, Y. K. Gun'ko, V. Lesnyak, N. Gaponik, A. S. Susha, A. L. Rogach, A. L. Bradley, ACS Nano 2014, 8, 1273.
- [195] D. Bouchet, D. Cao, R. Carminati, Y. De Wilde, V. Krachmalnicoff, Phys. Rev. Lett. 2016, 116, 037401.
- [196] Z. K. Zhou, M. Li, Z. J. Yang, X. N. Peng, X. R. Su, Z. S. Zhang, J. B. Li, N. C. Kim, X. F. Yu, L. Zhou, Z. H. Hao, Q. Q. Wang, ACS *Nano* **2010**, *4*, 5003.
- [197] Y. C. Yu, J. M. Liu, C. J. Jin, X. H. Wang, Nanoscale Res. Lett. 2013, 8, 209.

- [198] J. de Torres, P. Ferrand, G. C. des Francs, J. Wenger, ACS Nano 2016, 10, 3968.
- [199] D. Bouchet, E. Lhuillier, S. Ithurria, A. Gulinatti, I. Rech, R. Carminati, Y. De Wilde, V. Krachmalnicoff, *Phys. Rev. A* 2017, 95, 033828.
- [200] D. Martin-Cano, L. Martin-Moreno, F. J. Garcia-Vidal, E. Moreno, Nano Lett. 2010, 10, 3129.
- [201] Y. Li, A. Nemilentsau, C. Argyropoulos, Nanoscale 2019, 11, 14635.
- [202] J. R. Lakowicz, J. Kusba, Y. B. Shen, J. Malicka, S. D'Auria, Z. Gryczynski, I. Gryczynski, J. Fluoresc. 2003, 13, 69.
- [203] T. Ozel, P. L. Hernandez-Martinez, E. Mutlugun, O. Akin, S. Nizamoglu, I. O. Ozel, Q. Zhang, Q. H. Xiong, H. V. Demir, *Nano Lett.* 2013, 13, 3065.
- [204] F. Reil, U. Hohenester, J. R. Krenn, A. Leitner, Nano Lett. 2008, 8, 4128.
- [205] K. S. Kim, J. H. Kim, H. Kim, F. Laquai, E. Arifin, J. K. Lee, S. I. Yoo, B. H. Sohn, ACS Nano 2012, 6, 5051.
- [206] L. Zhao, T. Ming, L. Shao, H. J. Chen, J. F. Wang, J. Phys. Chem. C 2012, 116, 8287.
- [207] L. Bujak, T. Ishii, D. K. Sharma, S. Hirata, M. Vacha, Nanoscale 2017, 9, 1511.
- [208] P. Ghenuche, M. Mivelle, J. de Torres, S. B. Moparthi, H. Rigneault, N. F. Van Hulst, M. F. Garcia-Parajo, J. Wenger, *Nano Lett.* 2015, 15, 6193.
- [209] V. Faessler, C. Hrelescu, A. A. Lutich, L. Osinkina, S. Mayilo, F. Jackel, J. Feldmann, Chem. Phys. Lett. 2011, 508, 67.
- [210] M. Lessard-Viger, M. Rioux, L. Rainville, D. Boudreau, Nano Lett. 2009, 9, 3066.
- [211] C. Blum, N. Zijlstra, A. Lagendijk, M. Wubs, A. P. Mosk, V. Subramaniam, W. L. Vos, *Phys. Rev. Lett.* **2012**, *109*, 203601.
- [212] P. Ghenuche, J. de Torres, S. B. Moparthi, V. Grigoriev, J. Wenger, Nano Lett. 2014, 14, 4707.
- [213] A. O. Hamza, F. N. Viscomi, J. S. G. Bouillard, A. M. Adawi, J. Phys. Chem. Lett. 2021, 12, 1507.
- [214] Y. S. Park, Y. Ghosh, Y. Chen, A. Piryatinski, P. Xu, N. H. Mack, H. L. Wang, V. I. Klimov, J. A. Hollingsworth, H. Htoon, *Phys. Rev. Lett.* **2013**, *110*, 117401.
- [215] S. J. LeBlanc, M. R. McClanahan, M. Jones, P. J. Moyer, Nano Lett. 2013, 13, 1662.
- [216] H. Takata, H. Naiki, L. Wang, H. Fujiwara, K. Sasak, N. Tamai, S. Masuo, *Nano Lett.* **2016**, *16*, 5770.
- [217] K. Matsuzaki, S. Vassant, H. W. Liu, A. Dutschke, B. Hoffmann,
 X. W. Chen, S. Christiansen, M. R. Buck, J. A. Hollingsworth,
 S. Gotzinger, V. Sandoghdar, *Sci. Rep.* 2017, *7*, 42307.
- [218] V. N. Pustovit, T. V. Shahbazyan, Phys. Rev. Lett. 2009, 102, 077401.
- [219] V. N. Pustovit, T. V. Shahbazyan, Phys. Rev. B 2010, 82, 075429.
- [220] I. E. Protsenko, A. V. Uskov, X. W. Chen, H. X. Xu, J. Phys. D: Appl. Phys. 2017, 50, 254003.
- [221] F. Wang, N. S. Karan, H. M. Nguyen, B. D. Mangum, Y. Ghosh, C. J. Sheehan, J. A. Hollingsworth, H. Htoon, *Small* **2015**, *11*, 5028.
- [222] E. Altewischer, M. P. van Exter, J. P. Woerdman, Nature 2002, 418, 304.
- [223] S. Fasel, F. Robin, E. Moreno, D. Emi, N. Gisin, H. Zbinden, *Phys. Rev. Lett.* 2005, *94*, 110501.
- [224] R. C. Ge, S. Hughes, Phys. Rev. B 2015, 92, 205420.
- [225] M. Otten, R. A. Shah, N. F. Scherer, M. S. Min, M. Pelton, S. K. Gray, Phys. Rev. B 2015, 92, 125432.
- [226] J. Hakami, M. S. Zubairy, Phys. Rev. A 2016, 93, 022320.
- [227] G. Y. Chen, Y. N. Chen, D. S. Chun, Opt. Lett. 2008, 33, 2212.
- [228] A. Gonzalez-Tudela, D. Martin-Cano, E. Moreno, L. Martin-Moreno, C. Tejedor, F. J. Garcia-Vidal, *Phys. Rev. Lett.* 2011, 106, 020501.
- [229] F. Bello, N. Kongsuwan, J. F. Donegan, O. Hess, Nano Lett. 2020, 20, 5830.
- [230] Y. R. Fang, H. Wei, F. Hao, P. Nordlander, H. X. Xu, Nano Lett. 2009, 9, 2049.

FUNCTIONAL

www.advancedsciencenews.com



- [231] H. Wei, D. Ratchford, X. Q. Li, H. X. Xu, C. K. Shih, Nano Lett. 2009, 9, 4168.
- [232] Q. Li, H. Wei, H. X. Xu, Chin. Phys. B 2014, 23, 097302.
- [233] Q. Li, D. Pan, H. Wei, H. X. Xu, Nano Lett. 2018, 18, 2009.
- [234] D. E. Chang, A. S. Sorensen, P. R. Hemmer, M. D. Lukin, Phys. Rev. Lett. 2006, 97, 053002.
- [235] D. E. Chang, A. S. Sorensen, P. R. Hemmer, M. D. Lukin, *Phys. Rev. B* 2007, 76, 035420.
- [236] Y. T. Chen, T. R. Nielsen, N. Gregersen, P. Lodahl, J. Mork, *Phys. Rev. B* 2010, *81*, 125431.
- [237] M. T. Cheng, Y. Y. Song, Opt. Lett. 2012, 37, 978.
- [238] D. E. Chang, A. S. Sorensen, E. A. Demler, M. D. Lukin, Nat. Phys. 2007, 3, 807.
- [239] N. C. Kim, J. B. Li, Z. J. Yang, Z. H. Hao, Q. Q. Wang, Appl. Phys. Lett. 2010, 97, 061110.
- [240] W. Chen, G. Y. Chen, Y. N. Chen, Opt. Express 2010, 18, 10360.
- [241] J. B. Li, M. D. He, X. J. Wang, X. F. Peng, L. Q. Chen, Chin. Phys. B 2014, 23, 067302.
- [242] G. Y. Chen, N. Lambert, C. H. Chou, Y. N. Chen, F. Nori, *Phys. Rev. B* 2011, 84, 045310.
- [243] G. Y. Chen, Y. N. Chen, Opt. Lett. 2012, 37, 4023.
- [244] D. Martin-Cano, A. Gonzalez-Tudela, L. Martin-Moreno, F. J. Garcia-Vidal, C. Tejedor, E. Moreno, *Phys. Rev. B* 2011, *84*, 235306.
- [245] A. V. Akimov, A. Mukherjee, C. L. Yu, D. E. Chang, A. S. Zibrov,
 P. R. Hemmer, H. Park, M. D. Lukin, *Nature* 2007, *450*, 402.
- [246] R. Kolesov, B. Grotz, G. Balasubramanian, R. J. Stohr, A. A. L. Nicolet, P. R. Hemmer, F. Jelezko, J. Wrachtrup, *Nat. Phys.* 2009, 5, 470.
- [247] S. Kumar, A. Huck, U. L. Andersen, Nano Lett. 2013, 13, 1221.
- [248] N. P. de Leon, B. J. Shields, C. L. Yu, D. E. Englund, A. V. Akimov,
 M. D. Lukin, H. Park, *Phys. Rev. Lett.* 2012, *108*, 226803.
- [249] C. Ropp, Z. Cummins, S. Nah, J. T. Fourkas, B. Shapiro, E. Waks, *Nat. Commun.* 2015, 6, 6558.
- [250] S.-H. Gong, F. Alpeggiani, B. Sciacca, E. C. Garnett, L. Kuipers, *Science* 2018, 359, 443.
- [251] Q. Guo, T. Fu, J. Tang, D. Pan, S. Zhang, H. Xu, Phys. Rev. Lett. 2019, 123, 183903.
- [252] T. Cai, S. Dutta, S. Aghaeimeibodi, Z. Yang, S. Nah, J. T. Fourkas, E. Waks, *Nano Lett.* **2017**, *17*, 6564.
- [253] K. Y. Jeong, S. W. Lee, J. H. Choi, J. P. So, H. G. Park, Nanomaterials 2020, 10, 1663.
- [254] Q. Li, H. Wei, H. X. Xu, Nano Lett. 2014, 14, 3358.
- [255] J. J. Ren, Y. Gu, D. X. Zhao, F. Zhang, T. C. Zhang, Q. H. Gong, *Phys. Rev. Lett.* **2017**, 118, 073604.
- [256] S. D. Liu, M. T. Cheng, Z. J. Yang, Q. Q. Wang, Opt. Lett. 2008, 33, 851.
- [257] C. Schorner, S. Adhikari, M. Lippitz, Nano Lett. 2019, 19, 3238.
- [258] C. Schorner, M. Lippitz, Nano Lett. 2020, 20, 2152.
- [259] M. Blauth, M. Jurgensen, G. Vest, O. Hartwig, M. Prechtl, J. Cerne, J. J. Finley, M. Kaniber, Nano Lett. 2018, 18, 6812.
- [260] H. Siampour, S. Kumar, S. I. Bozhevolnyi, ACS Photonics 2017, 4, 1879.
- [261] H. Siampour, S. Kumar, V. A. Davydov, L. F. Kulikova, V. N. Agafonov, S. I. Bozhevolnyi, *Light: Sci. Appl.* **2018**, 7, 61.
- [262] Y. H. Kan, S. Kumar, F. Ding, C. Y. Zhao, S. I. Bozhevolnyi, Adv. Opt. Mater. 2020, 8, 2000854.
- [263] E. Bermudez-Urena, C. Gonzalez-Ballestero, M. Geiselmann, R. Marty, I. P. Radko, T. Holmgaard, Y. Alaverdyan, E. Moreno, F. J. Garcia-Vidal, S. I. Bozhevolnyi, R. Quidant, *Nat. Commun.* 2015, *6*, 7883.
- [264] S. J. P. Kress, F. V. Antolinez, P. Richner, S. V. Jayanti, D. K. Kim, F. Prins, A. Riedinger, M. P. C. Fischer, S. Meyer, K. M. McPeak, D. Poulikakos, D. J. Norris, *Nano Lett.* **2015**, *15*, 6267.
- [265] G. Khitrova, H. M. Gibbs, M. Kira, S. W. Koch, A. Scherer, Nat. Phys. 2006, 2, 81.

- [266] P. Lodahl, S. Mahmoodian, S. Stobbe, Rev. Mod. Phys. 2015, 87, 347.
- [267] T. Yoshie, A. Scherer, J. Hendrickson, G. Khitrova, H. M. Gibbs, G. Rupper, C. Ell, O. B. Shchekin, D. G. Deppe, *Nature* 2004, 432, 200.
- [268] G. Zengin, M. Wersall, S. Nilsson, T. J. Antosiewicz, M. Kall, T. Shegai, Phys. Rev. Lett. 2015, 114, 157401.
- [269] M. O. Scully, M. S. Zubairy, *Quantum Optics.*, Cambridge University Press, Cambridge 1997.
- [270] G. S. Agarwal, Phys. Rev. Lett. 1984, 53, 1732.
- [271] S. Rudin, T. L. Reinecke, Phys. Rev. B 1999, 59, 10227.
- [272] J. P. Reithmaier, G. Sek, A. Loffler, C. Hofmann, S. Kuhn, S. Reitzenstein, L. V. Keldysh, V. D. Kulakovskii, T. L. Reinecke, A. Forchel, *Nature* **2004**, *432*, 197.
- [273] L. C. Andreani, G. Panzarini, J. M. Gerard, Phys. Rev. B 1999, 60, 13276.
- [274] S. Balci, C. Kocabas, S. Ates, E. Karademir, O. Salihoglu, A. Aydinli, *Phys. Rev. B* 2012, *86*, 235402.
- [275] T. Schwartz, J. A. Hutchison, C. Genet, T. W. Ebbesen, Phys. Rev. Lett. 2011, 106, 196405.
- [276] T. K. Hakala, J. J. Toppari, A. Kuzyk, M. Pettersson, H. Tikkanen, H. Kunttu, P. Torma, *Phys. Rev. Lett.* **2009**, *103*, 053602.
- [277] P. R. Rice, R. J. Brecha, Opt. Commun. 1996, 126, 230.
- [278] U. Fano, Phys. Rev. 1961, 124, 1866.
- [279] T. J. Antosiewicz, S. P. Apell, T. Shegai, ACS Photonics 2014, 1, 454.
- [280] J. Dintinger, S. Klein, F. Bustos, W. L. Barnes, T. W. Ebbesen, *Phys. Rev. B* 2005, 71, 035424.
- [281] C. Bonnand, J. Bellessa, J. C. Plenet, Phys. Rev. B 2006, 73, 245330.
- [282] N. I. Cade, T. Ritman-Meer, D. Richards, Phys. Rev. B 2009, 79, 241404(R).
- [283] D. E. Gomez, K. C. Vernon, P. Mulvaney, T. J. Davis, Nano Lett. 2010, 10, 274.
- [284] A. I. Vakevainen, R. J. Moerland, H. T. Rekola, A. P. Eskelinen, J. P. Martikainen, D. H. Kim, P. Torma, *Nano Lett.* **2014**, *14*, 1721.
- [285] L. Shi, T. K. Hakala, H. T. Rekola, J. P. Martikainen, R. J. Moerland, P. Torma, *Phys. Rev. Lett.* **2014**, *112*, 153002.
- [286] F. Nagasawa, M. Takase, K. Murakoshi, J. Phys. Chem. Lett. 2014, 5, 14.
- [287] R. M. Liu, Z. K. Zhou, Y. C. Yu, T. W. Zhang, H. Wang, G. H. Liu, Y. M. Wei, H. J. Chen, X. H. Wang, *Phys. Rev. Lett.* **2017**, *118*, 237401.
- [288] E. S. H. Kang, S. Z. Chen, S. Sardar, D. Tordera, N. Armakavicius, V. Darakchieva, T. Shegai, M. P. Jonsson, ACS Photonics 2018, 5, 4046.
- [289] J. N. Huang, A. J. Traverso, G. C. Yang, M. H. Mikkelsen, ACS Photonics 2019, 6, 838.
- [290] I. Pockrand, J. D. Swalen, J. G. Gordon, M. R. Philpott, J. Chem. Phys. 1979, 70, 3401.
- [291] I. Pockrand, A. Brillante, D. Mobius, J. Chem. Phys. 1982, 77, 6289.
- [292] J. Bellessa, C. Bonnand, J. C. Plenet, J. Mugnier, Phys. Rev. Lett. 2004, 93, 036404.
- [293] S. Savasta, R. Saija, A. Ridolfo, O. Di Stefano, P. Denti, F. Borghese, ACS Nano 2010, 4, 6369.
- [294] A. Manjavacas, F. J. G. de Abajo, P. Nordlander, *Nano Lett.* 2011, *11*, 2318.
- [295] J. K. Wei, N. Jiang, J. Xu, X. D. Bai, J. Y. Liu, Nano Lett. 2015, 15, 5926.
- [296] A. B. Yankovich, B. Munkhbat, D. G. Baranov, J. Cuadra, E. Olsen,
 H. Lourenco-Martins, L. H. G. Tizei, M. Kociak, E. Olsson,
 T. Shegai, *Nano Lett.* 2019, *19*, 8171.
- [297] O. Bitton, S. N. Gupta, L. Houben, M. Kvapil, V. Krapek, T. Sikola, G. Haran, Nat. Commun. 2020, 11, 487.
- [298] A. Crai, A. Demetriadou, O. Hess, ACS Photonics 2020, 7, 401.
- [299] G. P. Zouros, G. D. Kolezas, N. A. Mortensen, C. Tserkezis, *Phys. Rev. B* 2020, 101, 085416.
- [300] L. Li, L. Wang, C. Du, Z. Y. Guan, Y. X. Xiang, W. Wu, M. X. Ren, X. Z. Zhang, A. W. Tang, W. Cai, J. J. Xu, *Nanoscale* **2020**, *12*, 3112.

www.advancedsciencenews.com



- [301] C. Symonds, J. Bellessa, J. C. Plenet, A. Brehier, R. Parashkov, J. S. Lauret, E. Deleporte, *Appl. Phys. Lett.* 2007, 90, 091107.
- [302] C. Symonds, C. Bonnand, J. C. Plenet, A. Brehier, R. Parashkov, J. S. Lauret, E. Deleporte, J. Bellessa, *New J. Phys.* 2008, 10, 065017.
- [303] J. Bellessa, C. Symonds, C. Meynaud, J. C. Plenet, E. Cambril, A. Miard, L. Ferlazzo, A. Lemaitre, *Phys. Rev. B* 2008, 78, 205326.
- [304] P. Vasa, R. Pomraenke, S. Schwieger, Y. I. Mazur, V. Kunets, P. Srinivasan, E. Johnson, J. E. Kihm, D. S. Kim, E. Runge, G. Salamo, C. Lienau, *Phys. Rev. Lett.* **2008**, *101*, 116801.
- [305] J. M. Winkler, F. T. Rabouw, A. A. Rossinelli, S. V. Jayanti, K. M. McPeak, D. K. Kim, B. le Feber, F. Prins, D. J. Norris, *Nano Lett.* **2019**, *19*, 108.
- [306] F. Wurthner, T. E. Kaiser, C. R. Saha-Moller, Angew. Chem., Int. Ed. 2011, 50, 3376.
- [307] Y. Sugawara, T. A. Kelf, J. J. Baumberg, M. E. Abdelsalam, P. N. Bartlett, Phys. Rev. Lett. 2006, 97, 266808.
- [308] P. Vasa, W. Wang, R. Pomraenke, M. Lammers, M. Maiuri, C. Manzoni, G. Cerullo, C. Lienau, Nat. Photonics 2013, 7, 128.
- [309] P. Vasa, R. Pomraenke, G. Cirmi, E. De Re, W. Wang, S. Schwieger, D. Leipold, E. Runge, G. Cerullo, C. Lienau, ACS Nano 2010, 4, 7559.
- [310] P. Vasa, W. Wang, R. Pomraenke, M. Maiuri, C. Manzoni, G. Cerullo, C. Lienau, *Phys. Rev. Lett.* **2015**, *114*, 036802.
- [311] J. Bellessa, C. Symonds, K. Vynck, A. Lemaitre, A. Brioude, L. Beaur, J. C. Plenet, P. Viste, D. Felbacq, E. Cambril, P. Valvin, *Phys. Rev. B* 2009, *80*, 033303.
- [312] E. Eizner, O. Avayu, R. Ditcovski, T. Ellenbogen, Nano Lett. 2015, 15, 6215.
- [313] P. Zheng, S. Kasani, N. Q. Wu, Nanoscale Horiz. 2019, 4, 516.
- [314] N. T. Fofang, T. H. Park, O. Neumann, N. A. Mirin, P. Nordlander, N. J. Halas, *Nano Lett.* **2008**, *8*, 3481.
- [315] D. Melnikau, D. Savateeva, A. Susha, A. L. Rogach, Y. P. Rakovich, Nanoscale Res. Lett. 2013, 8, 134.
- [316] S. Balci, Opt. Lett. 2013, 38, 4498.
- [317] S. Balci, B. Kucukoz, O. Balci, A. Karatay, C. Kocabas, G. Yaglioglu, ACS Photonics 2016, 3, 2010.
- [318] D. Melnikau, R. Esteban, D. Savateeva, A. S. Iglesias, M. Grzelczak, M. K. Schmidt, L. M. Liz-Marzan, J. Aizpurua, Y. P. Rakovich, J. Phys. Chem. Lett. 2016, 7, 354.
- [319] T. Hendel, V. Krivenkov, A. Sanchez-Iglesias, M. Grzelczak, Y. P. Rakovich, *Nanoscale* 2020, 12, 16875.
- [320] L. C. Sun, Z. Li, J. S. He, P. J. Wang, Nanophotonics 2019, 8, 1835.
- [321] D. Melnikau, A. A. Govyadinov, A. Sanchez-Iglesias, M. Grzelczak,
 L. M. Liz-Marzan, Y. P. Rakovich, *Nano Lett.* 2017, 17, 1808.
- [322] K. Liang, J. Q. Guo, Y. M. Huang, L. Yu, Nanoscale 2020, 12, 23069.
- [323] F. Wu, J. Q. Guo, Y. M. Huang, K. Liang, L. Jin, J. Q. Li, X. Y. Deng, R. Z. Jiao, Y. M. Liu, J. S. Zhang, W. Zhang, L. Yu, ACS Nano 2021, 15, 2292.
- [324] C. M. Guvenc, F. M. Balci, S. Sarisozen, N. Polat, S. Balci, J. Phys. Chem. C 2020, 124, 8334.
- [325] J. J. Zhu, F. Wu, Z. H. Han, Y. X. Shang, F. S. Liu, H. Y. Yu, L. Yu, N. Li, B. Q. Ding, *Nano Lett.* **2021**, *21*, 3573.
- [326] A. E. Schlather, N. Large, A. S. Urban, P. Nordlander, N. J. Halas, *Nano Lett.* 2013, 13, 3281.
- [327] E. M. Roller, C. Argyropoulos, A. Hogele, T. Liedl, M. Pilo-Pais, Nano Lett. 2016, 16, 5962.
- [328] G. Zengin, G. Johansson, P. Johansson, T. J. Antosiewicz, M. Kall, T. Shegai, *Sci. Rep.* 2013, 3, 3074.
- [329] M. Wersall, J. Cuadra, T. J. Antosiewicz, S. Balci, T. Shegai, Nano Lett. 2017, 17, 551.
- [330] A. L. Baudrion, A. Perron, A. Veltri, A. Bouhelier, P. M. Adam, R. Bachelot, Nano Lett. 2013, 13, 282.
- [331] L. H. Lin, M. S. Wang, X. L. Wei, X. L. Peng, C. Xie, Y. B. Zheng, *Nano Lett.* **2016**, *16*, 7655.

- [332] F. Kato, H. Minamimoto, F. Nagasawa, Y. S. Yamamoto, T. Itoh, K. Murakoshi, ACS Photonics 2018, 5, 788.
- [333] S. R. K. Rodriguez, J. Feist, M. A. Verschuuren, F. J. Garcia Vidal, J. G. Rivas, *Phys. Rev. Lett.* **2013**, *111*, 166802.
- [334] T. Itoh, Y. S. Yamamoto, H. Tamaru, V. Biju, S. Wakida, Y. Ozaki, *Phys. Rev. B* 2014, *89*, 195436.
- [335] R. Chikkaraddy, B. de Nijs, F. Benz, S. J. Barrow, O. A. Scherman, E. Rosta, A. Demetriadou, P. Fox, O. Hess, J. J. Baumberg, *Nature* 2016, *535*, 127.
- [336] O. S. Ojambati, R. Chikkaraddy, W. D. Deacon, M. Horton, D. Kos, V. A. Turek, U. F. Keyser, J. J. Baumberg, *Nat. Commun.* 2019, 10, 1049.
- [337] H. Wang, H. Y. Wang, A. Toma, T. Yano, Q. D. Chen, H. L. Xu, H. B. Sun, R. P. Zaccaria, J. Phys. Chem. Lett. 2016, 7, 4648.
- [338] R. K. Yadav, M. R. Bourgeois, C. Cherqui, X. G. Juarez, W. J. Wang, T. W. Odom, G. C. Schatz, J. K. Basu, ACS Nano 2020, 14, 7347.
- [339] K. D. Park, M. A. May, H. X. Leng, J. R. Wang, J. A. Kropp, T. Gougousi, M. Pelton, M. B. Raschke, *Sci. Adv.* 2019, *5*, eaav5931.
- [340] H. Gross, J. M. Hamm, T. Tufarelli, O. Hess, B. Hecht, Sci. Adv. 2018, 4, eaar4906.
- [341] K. F. Mak, J. Shan, Nat. Photonics 2016, 10, 216.
- [342] W. J. Liu, B. Lee, C. H. Naylor, H. S. Ee, J. Park, A. T. C. Johnson, R. Agarwal, *Nano Lett.* **2016**, *16*, 1262.
- [343] B. Lee, W. J. Liu, C. H. Naylor, J. Park, S. C. Malek, J. S. Berger, A. T. C. Johnson, R. Agarwal, *Nano Lett.* 2017, *17*, 4541.
- [344] S. J. Wang, S. L. Li, T. Chervy, A. Shalabney, S. Azzini, E. Orgiu, J. A. Hutchison, C. Genet, P. Samori, T. W. Ebbesen, *Nano Lett.* 2016, 16, 4368.
- [345] B. Y. Ding, Z. P. Zhang, Y. H. Chen, Y. F. Zhang, R. J. Blaikie, M. Qiu, ACS Nano 2019, 13, 1333.
- [346] D. Zheng, S. P. Zhang, Q. Deng, M. Kang, P. Nordlander, H. X. Xu, Nano Lett. 2017, 17, 3809.
- [347] J. X. Wen, H. Wang, W. L. Wang, Z. X. Deng, C. Zhuang, Y. Zhang, F. Liu, J. C. She, J. Chen, H. J. Chen, S. Z. Deng, N. S. Xu, *Nano Lett.* 2017, 17, 4689.
- [348] X. H. Yan, H. Wei, Nanoscale 2020, 12, 9708.
- [349] J. X. Wen, H. Wang, H. J. Chen, S. Z. Deng, N. S. Xu, Chin. Phys. B 2018, 27, 096101.
- [350] J. Cuadra, D. G. Baranov, M. Wersall, R. Verre, T. J. Antosiewicz, T. Shegai, *Nano Lett.* **2018**, *18*, 1777.
- [351] B. Munkhbat, D. G. Baranov, A. Bisht, M. A. Hogue, B. Karpiak, S. P. Dash, T. Shegai, ACS Nano 2020, 14, 1196.
- [352] M. Stuhrenberg, B. Munkhbat, D. G. Baranov, J. Cuadra, A. B. Yankovich, T. J. Antosiewicz, E. Olsson, T. Shegai, *Nano Lett.* 2018, 18, 5938.
- [353] J. Lawless, C. Hrelescu, C. Elliott, L. Peters, N. McEvoy, A. L. Bradley, ACS Appl. Mater. Interfaces 2020, 12, 46406.
- [354] M. Geisler, X. M. Cui, J. F. Wang, T. Rindzevicius, L. Gammelgaard, B. S. Jessen, P. A. D. Goncalves, F. Todisco, P. Boggild, A. Boisen, M. Wubs, N. A. Mortensen, S. S. Xiao, N. Stenger, ACS Photonics 2019, 6, 994.
- [355] T. W. Lo, Q. Zhang, M. Qiu, X. Y. Guo, Y. J. Meng, Y. Zhu, J. J. Xiao,
 W. Jin, C. W. Leung, D. Y. Lei, ACS Photonics 2019, 6, 411.
- [356] M. E. Kleemann, R. Chikkaraddy, E. M. Alexeev, D. Kos, C. Carnegie,
 W. Deacon, A. C. de Pury, C. Grosse, B. de Nijs, J. Mertens,
 A. I. Tartakovskii, J. J. Baumberg, *Nat. Commun.* 2017, *8*, 1296.
- [357] X. B. Han, K. Wang, X. Y. Xing, M. Y. Wang, P. X. Lu, ACS Photonics 2018, 5, 3970.
- [358] J. Qin, Y. H. Chen, Z. P. Zhang, Y. F. Zhang, R. J. Blaikie, B. Y. Ding, M. Qiu, *Phys. Rev. Lett.* **2020**, 124, 063902.
- [359] S. A. Guebrou, C. Symonds, E. Homeyer, J. C. Plenet, Y. N. Gartstein, V. M. Agranovich, J. Bellessa, *Phys. Rev. Lett.* 2012, 108, 066401.
- [360] C. Bonnand, J. Bellessa, C. Symonds, J. C. Plenet, Appl. Phys. Lett. 2006, 89, 231119.

www.advancedsciencenews.com



- [362] A. Salomon, S. J. Wang, J. A. Hutchison, C. Genet, T. W. Ebbesen, *ChemPhysChem* **2013**, *14*, 1882.
- [363] H. Wang, A. Toma, H. Y. Wang, A. Bozzola, E. Miele, A. Haddadpour, G. Veronis, F. De Angelis, L. Wang, Q. D. Chen, H. L. Xu, H. B. Sun, R. P. Zaccaria, *Nanoscale* **2016**, *8*, 13445.
- [364] H. Wang, H.-Y. Wang, A. Bozzola, A. Toma, S. Panaro, W. Raja, A. Alabastri, L. Wang, Q.-D. Chen, H.-L. Xu, F. De Angelis, H.-B. Sun, R. P. Zaccaria, *Adv. Funct. Mater.* **2016**, *26*, 6198.
- [365] F. Todisco, S. D'Agostino, M. Esposito, A. I. Fernandez-Dominguez, M. De Giorgi, D. Ballarini, L. Dominici, L. Tarantini, M. Cuscuna, F. Della Sala, G. Gigli, D. Sanvitto, ACS Nano 2015, 9, 9691.
- [366] S. Fedele, M. Hakami, A. Murphy, R. Pollard, J. Rice, Appl. Phys. Lett. 2016, 108, 053102.
- [367] G. A. Wurtz, P. R. Evans, W. Hendren, R. Atkinson, W. Dickson, R. J. Pollard, A. V. Zayats, W. Harrison, C. Bower, *Nano Lett.* 2007, 7, 1297.
- [368] B. G. DeLacy, O. D. Miller, C. W. Hsu, Z. Zander, S. Lacey, R. Yagloski, A. W. Fountain, E. Valdes, E. Anquillare, M. Soljacic, S. G. Johnson, J. D. Joannopoulos, *Nano Lett.* **2015**, *15*, 2588.
- [369] K. Das, B. Hazra, M. Chandra, Phys. Chem. Chem. Phys. 2017, 19, 27997.
- [370] M. S. Kirschner, W. D. Ding, Y. X. Li, C. T. Chapman, A. W. Lei, X. M. Lin, L. X. Chen, G. C. Schatz, R. D. Schaller, *Nano Lett.* 2018, 18, 442.
- [371] T. T. Song, Z. X. Chen, W. B. Zhang, L. M. Lin, Y. J. Bao, L. Wu, Z. K. Zhou, Nanomaterials 2019, 9, 564.
- [372] F. M. Balci, S. Sarisozen, N. Polat, S. Balci, J. Phys. Chem. C 2019, 123, 26571.
- [373] M. Wersall, B. Munkhbat, D. G. Baranov, F. Herrera, J. S. Cao, T. J. Antosiewicz, T. Shegai, ACS Photonics 2019, 6, 2570.
- [374] B. Munkhbat, M. Wersall, D. G. Baranov, T. J. Antosiewicz, T. Shegai, Sci. Adv. 2018, 4, eaas9552.
- [375] N. Li, Z. H. Han, Y. M. Huang, K. Liang, X. F. Wang, F. Wu, X. Y. Qi, Y. X. Shang, L. Yu, B. Q. Ding, J. Mater. Chem. C 2020, 8, 7672.
- [376] X. X. Chen, Y. H. Chen, J. Qin, D. Zhao, B. Y. Ding, R. J. Blaikie, M. Qiu, *Nano Lett.* **2017**, *17*, 3246.
- [377] L. Efremushkin, M. Sukharev, A. Salomon, J. Phys. Chem. C 2017, 121, 14819.
- [378] M. Ramezani, Q. Le-Van, A. Halpin, J. G. Rivas, Phys. Rev. Lett. 2018, 121, 243904.
- [379] M. Ramezani, A. Halpin, A. I. Fernandez-Dominguez, J. Feist, S. R. K. Rodriguez, F. J. Garcia-Vidal, J. G. Rivas, *Optica* 2017, 4, 31.
- [380] M. De Giorgi, M. Ramezani, F. Todisco, A. Halpin, D. Caputo, A. Fieramosca, J. Gomez-Rivas, D. Sanvitto, ACS Photonics 2018, 5, 3666.
- [381] F. Todisco, M. De Giorgi, M. Esposito, L. De Marco, A. Zizzari, M. Bianco, L. Dominici, D. Ballarini, V. Arima, G. Gigli, D. Sanvittot, ACS Photonics 2018, 5, 143.
- [382] A. I. Vakevainen, A. J. Moilanen, M. Necada, T. K. Hakala, K. S. Daskalakis, P. Torma, *Nat. Commun.* 2020, *11*, 3139.
- [383] R. K. Yadav, M. Otten, W. J. Wang, C. L. Cortes, D. J. Gosztola, G. P. Wiederrecht, S. K. Gray, T. W. Odom, J. K. Basu, *Nano Lett.* 2020, 20, 5043.
- [384] Y. Luo, Y. C. Wang, M. Q. Liu, H. Zhu, O. Chen, S. L. Zou, J. Zhao, J. Phys. Chem. Lett. 2020, 11, 2449.
- [385] J. M. Katzen, C. Tserkezis, Q. R. Cai, L. H. Li, J. M. Kim, G. Lee, G. A. Yi, W. R. Hendren, E. J. G. Santos, R. M. Bowman, F. M. Huang, ACS Appl. Mater. Interfaces 2020, 12, 19866.
- [386] Y. G. Sang, C. Y. Wang, S. S. Raja, C. W. Cheng, C. T. Huang, C. A. Chen, X. Q. Zhang, H. Ahn, C. K. Shih, Y. H. Lee, J. W. Shi, S. Gwo, *Nano Lett.* **2021**, *21*, 2596.

- [387] S. J. Wang, L. V. Quynh, F. Vaianella, B. Maes, S. E. Barker, R. H. Godiksen, A. G. Curto, J. G. Rivas, ACS Photonics 2019, 6, 286.
- [388] Y. Z. Jiang, H. Wang, S. Y. Wen, H. J. Chen, S. Z. Deng, ACS Nano 2020, 14, 13841.
- [389] M. S. Wang, A. Krasnok, T. Y. Zhang, L. Scarabelli, H. Liu, Z. L. Wu, L. M. Liz-Marzan, M. Terrones, A. Alu, Y. B. Zheng, *Adv. Mater.* 2018, *30*, 1705779.
- [390] S. Y. Hou, L. Y. M. Tobing, X. L. Wang, Z. W. Xie, J. H. Yu, J. Zhou, D. H. Zhang, C. Dang, P. Coquet, B. K. Tay, M. D. Birowosuto, E. H. T. Teo, H. Wang, *Adv. Opt. Mater.* **2019**, *7*, 1900857.
- [391] X. Z. Liu, J. Yi, S. Yang, E. C. Lin, Y. J. Zhang, P. Y. Zhang, J. F. Li, Y. Wang, Y. H. Lee, Z. Q. Tian, X. Zhang, *Nat. Mater.* **2021**, *20*, 1210.
- [392] F. Deng, H. F. Liu, L. Xu, S. Lan, A. E. Miroshnichenko, Laser Photonics Rev. 2020, 14, 1900420.
- [393] H. Cang, A. Labno, C. G. Lu, X. B. Yin, M. Liu, C. Gladden, Y. M. Liu, X. Zhang, *Nature* 2011, 469, 385.
- [394] D. L. Mack, E. Cortes, V. Giannini, P. Torok, T. Roschuk, S. A. Maier, *Nat. Commun.* 2017, 8, 14513.
- [395] L. Saemisch, M. Liebel, N. F. van Hulst, Nanoscale 2020, 12, 3723.
- [396] E. J. Sanchez, L. Novotny, X. S. Xie, Phys. Rev. Lett. 1999, 82, 4014.
- [397] G. Lozano, S. R. K. Rodriguez, M. A. Verschuuren, J. G. Rivas, Light: Sci. Appl. 2016, 5, e16080.
- [398] K. Okamoto, I. Niki, A. Shvartser, Y. Narukawa, T. Mukai, A. Scherer, Nat. Mater. 2004, 3, 601.
- [399] G. Lozano, D. J. Louwers, S. R. K. Rodriguez, S. Murai, O. T. A. Jansen, M. A. Verschuuren, J. G. Rivas, *Light: Sci. Appl.* 2013, 2, e66.
- [400] M. A. Fusella, R. Saramak, R. Bushati, V. M. Menon, M. S. Weaver, N. J. Thompson, J. J. Brown, *Nature* **2020**, *585*, 379.
- [401] J. Kasprzak, M. Richard, S. Kundermann, A. Baas, P. Jeambrun, J. M. J. Keeling, F. M. Marchetti, M. H. Szymanska, R. Andre, J. L. Staehli, V. Savona, P. B. Littlewood, B. Deveaud, L. S. Dang, *Nature* 2006, 443, 409.
- [402] H. Deng, H. Haug, Y. Yamamoto, Rev. Mod. Phys. 2010, 82, 1489.
- [403] J. D. Plumhof, T. Stoferle, L. J. Mai, U. Scherf, R. F. Mahrt, Nat. Mater. 2014, 13, 247.
- [404] G. Lerario, A. Fieramosca, F. Barachati, D. Ballarini, K. S. Daskalakis, L. Dominici, M. De Giorgi, S. A. Maier, G. Gigli, S. Kena-Cohen, D. Sanvitto, *Nat. Phys.* **2017**, *13*, 837.
- [405] A. Imamoglu, R. J. Ram, S. Pau, Y. Yamamoto, Phys. Rev. A 1996, 53, 4250.
- [406] S. Christopoulos, G. B. H. von Hogersthal, A. J. D. Grundy, P. G. Lagoudakis, A. V. Kavokin, J. J. Baumberg, G. Christmann, R. Butte, E. Feltin, J. F. Carlin, N. Grandjean, *Phys. Rev. Lett.* 2007, 98, 126405.
- [407] S. Kena-Cohen, S. R. Forrest, Nat. Photonics 2010, 4, 371.
- [408] J. Yuen-Zhou, S. K. Saikin, V. M. Menon, J. Phys. Chem. Lett. 2018, 9, 6511.
- [409] B. Rousseaux, D. G. Baranov, M. Kall, T. Shegai, G. Johansson, *Phys. Rev. B* 2018, 98, 045435.
- [410] F. Nan, Y. F. Zhang, X. G. Li, X. T. Zhang, H. Li, X. H. Zhang,
 R. B. Jiang, J. F. Wang, W. Zhang, L. Zhou, J. H. Wang, Q. Q. Wang,
 Z. Y. Zhang, *Nano Lett.* **2015**, *15*, 2705.
- [411] N. T. Fofang, N. K. Grady, Z. Y. Fan, A. O. Govorov, N. J. Halas, Nano Lett. 2011, 11, 1556.
- [412] M. Hensen, T. Heilpern, S. K. Gray, W. Pfeiffer, ACS Photonics 2018, 5, 240.
- [413] X. Xiong, J. B. You, P. Bai, C. E. Png, Z. K. Zhou, L. Wu, Nanophotonics 2020, 9, 257.
- [414] J. B. You, X. Xiong, P. Bai, Z. K. Zhou, R. M. Ma, W. L. Yang, Y. K. Lu, Y. F. Xiao, C. E. Png, F. J. Garcia-Vidal, C. W. Qiu, L. Wu, *Nano Lett.* **2020**, *20*, 4645.
- [415] N. Kongsuwan, X. Xiong, P. Bai, J. B. You, C. E. Png, L. Wu, O. Hess, Nano Lett. 2019, 19, 5853.









Hong Wei is a professor at Institute of Physics, Chinese Academy of Sciences. She received her B.S. in physics from Shandong University in 2004, and her Ph.D. in condensed matter physics from Institute of Physics, Chinese Academy of Sciences, in 2009. Her current research interests include interactions of surface plasmons and excitons, plasmonic waveguides and circuits, surfaceenhanced spectroscopy, and nanophotonic devices.



Xiaohong Yan is currently a Ph.D. candidate in condensed matter physics at Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, China. He received his bachelor degree in applied physics from Changchun University of Science and Technology in 2015. His research focuses on the interactions between surface plasmons and excitons.



Yijie Niu is currently a Ph.D. candidate in School of Physics and Technology, Wuhan University and Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences. He received his B.S. in physics from Zhengzhou University in 2015. His research focuses on the weak and strong coupling between surface plasmons and excitons.



Qiang Li received his B.S. in physics from Hebei Normal University in 2008, his M.S. in optics from South China Normal University in 2011, and his Ph.D. in condensed matter physics from Institute of Physics, Chinese Academy of Science, in 2014. His doctoral work focused on the exciton– plasmon interaction between single quantum dots and silver nanowires. He became a postdoctoral fellow at the Department of Physics, Hong Kong University of Science and Technology in 2015, where he studied the exciton–plasmon coupling using broadband ultrafast pump-probe spectroscopy. Since 2017, he has been a lecturer at South China Normal University. His current research is related to the exciton–plasmon interaction at single molecule level.







Zhili Jia is currently an associate professor in Center for Advanced Measurement Science, National Institute of Metrology, China. He received his B.S. degree from Hunan University in 2008, M.S. degree from Hunan University in 2011, and Ph.D. degree from University of Chinese Academy of Sciences in 2017. During the period from August 2017 to October 2019, he was working in The National Center for Nanoscience and Technology, as a postdoctor. His current research is focused on surface plasmons, 2D materials, and metrology of materials.



Hongxing Xu is a professor of physics and dean of School of Microelectronics at Wuhan University. He is a member of Chinese Academy of Sciences. He received his B.S. from Peking University in 1992 and his Ph.D. from Chalmers University of Technology in 2002, both in physics. From 2002 to 2004, he was an assistant professor in the Division of Solid State Physics at Lund University. From 2005 to 2014, he was a professor at Institute of Physics, Chinese Academy of Sciences. His research interests include plasmonics, nanophotonics, surface-/tip-enhanced spectroscopy, and single molecule spectroscopy.