Controlling plexcitonic strong coupling via multidimensional hotspot nanoengineering

Xiao Xiong,*†,‡ Yiming Lai,†‡,¶,∥ Daniel Clarke,†‡,¶ Nuttawut Kongsuwan,¶,§,||
Zhaogang Dong,¶ Ping Bai,† Ching Eng Png,† Ortwin Hess,*‡,¶ and Lin Wu,*#,†

† Institute of High Performance Computing, A*STAR (Agency for Science, Technology and Research), 1 Fusionopolis Way, #16-16 Connexis, Singapore 138632, Singapore.
‡ School of Physics and CRANN Institute, Trinity College Dublin, Dublin 2, Ireland.
¶ The Blackett Laboratory, Imperial College London, Prince Consort Road, London SW7 2AZ, United Kingdom.
§ Quantum Technology Foundation (Thailand), 98 Soi Ari, Bangkok, 10110, Thailand.
|| Thailand Center of Excellence in Physics, Ministry of Higher Education, Science, Research and Innovation, Bangkok 10400, Thailand.
¶ Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), 2 Fusionopolis Way, #08-03 Innovis, 138634 Singapore.
# Science, Mathematics and Technology (SMT), Singapore University of Technology and Design (SUTD), 8 Somapah Road, Singapore 487372.

@ These authors contribute equally.

E-mail: xiong_xiao@ihpc.a-star.edu.sg; ortwin.hess@tcd.ie; lin_wu@sutd.edu.sg

Abstract

Plexcitonic strong coupling has ushered in an era of room-temperature quantum electrodynamics that is achievable at the nanoscale, with potential applications ranging from high-precision single-molecule spectroscopy to quantum technologies functional
under ambient conditions. Realizing these applications on an industrial scale requires scalable and mass-producible plasmonic cavities that provide ease of access and control for quantum emitters. Via a rational selection of substrates and the canonical gold bowtie nanoantenna, we propose a novel design strategy for multidimensional engineering of nanocavity antenna-mode hotspots, which facilitates their elevation to the top of the nanobowtie gap and provides a field enhancement of \( \sim 500 \) fold (a 1.6-fold increase compared to a conventional nanobowtie-on-glass cavity at the bottom of the nanobowtie gap). We discuss the formation mechanism for such antenna modes using different material substrates from the perspective of charge carrier motion, and analyze their sensitivity to the geometrical parameters of the device. The advantages of these antenna modes, particularly in view of their dominantly in-plane polarized near-fields, are further elaborated in a spatiotemporal study of plexcitonic strong coupling involving single emitters and layered ensembles thereof, which reveals ultrafast quantum dynamics dependent on both the substrate and nanobowtie geometry, as well as the potential for applications related to 2D materials whose excitonic dipoles are typically oriented in-plane. The conceptual discovery of this substrate-enabled antenna-mode nanoengineering could readily be extended to tailor hotspots in other plasmonic platforms, and we anticipate that this work could inspire a wide range of novel research directions from photoluminescence spectroscopy and sensing to the design of quantum logic gates and systems for long-range energy transfer.

I. Introduction

Realizing strong light-matter interaction with a single quantum emitter has been an essential ingredient of many quantum technologies\(^1\) including optoelectronics,\(^2\) polariton chemistry,\(^3\) and ultrafast spectroscopy.\(^4\) Although this phenomenon was previously exclusive to experiments at cryogenic temperatures, recent advances in plasmonics have brought light-matter interaction to the era of room-temperature single-emitter strong coupling.\(^5\) The intense electromagnetic field confinement provided by plasmonic nanocavities compensates
for the severe Ohmic loss in metals and enables rapid energy exchange between plasmon polaritons and matter excitons, giving rise to hybrid plasmon-excitons or plexcitons.\textsuperscript{5–10} Strongly-coupled plexcitonic systems allow for a wide range of applications including ultrafast single-photon emission\textsuperscript{11} single-qubit coherent control,\textsuperscript{12} charge transport,\textsuperscript{13} long-range energy transfer,\textsuperscript{14,15} and universal quantum logic gates\textsuperscript{16} which provide fundamental building blocks for optical communication and quantum information processing. In the context of polariton chemistry, plexcitonic systems can efficiently trigger many-molecule reactions\textsuperscript{17} and alter photochemical processes.\textsuperscript{18} These applications have also spurred the development of fundamental theories on plexcitonic systems,\textsuperscript{19,20} bringing new vigor and vitality into the field of plasmonics.

In practice, achieving plexcitonic strong coupling with individual nanoantennas and arrays thereof demands a careful system design with an ultralow mode volume, extreme near-field enhancement, and an emitter whose transition dipole moment is precisely aligned with the maximum field direction. Among the various plasmonic nanocavity systems that have been investigated to date,\textsuperscript{10} the so-called nanoparticle-on-mirror\textsuperscript{21–23} (NPoM) configuration has emerged as one of the most successful, in which strong coupling at the single-molecule limit is enabled by the use of an extremely small (< 0.9 nm) metal-insulator-metal gap, in conjunction with supramolecular guest-host chemistry to accommodate a single dye molecule.\textsuperscript{5,24–26} However, the use of such nanogap systems poses a number of technical challenges. First, individual dye molecules generally present small dipole moments, and aligning the molecule within the nanogap often relies on a probabilistic approach.\textsuperscript{5} Second, such nanogaps cannot readily accommodate more sizeable quantum emitters or their ensembles, including quantum dots or aggregates of large dye molecules. Fortunately, two-dimensional (2D) materials, such as semiconducting transition-metal dichalcogenides (TMDCs) in monolayer form,\textsuperscript{27,28} have emerged as promising candidate quantum matter for plexcitonic strong coupling in plasmonic nanogaps, by virtue of their atomic-scale thickness (∼ 3 Å) together with the room-temperature stability and large dipole moments of their excitons. However,
even if such ultrathin materials can be accommodated in a nanogap, their coupling to the cavity is still inefficient due to the misalignment of their in-plane excitonic dipole moments with respect to the direction of the dominant cavity field.\textsuperscript{29} As a result, one may be compelled to compromise the field enhancement of the cavity by increasing the gap size,\textsuperscript{29–31} such that an in-plane electric field component is allowed, or to harness the interlayer excitons supported by, for instance, heterostructures with type II band alignment, which often have only low oscillator strengths.\textsuperscript{32–34} Moreover, the NPoM and other contemporary cavity designs such as the cuboid Au@Ag nanorod\textsuperscript{6} are usually fabricated via chemical assembly, which poses a significant challenge to produce devices on an industrial scale. Notably, recent experiments on plexcitonic strong coupling have emerged based on nanostructures fabricated via top-down lithography.\textsuperscript{35–40} Such a technique allows for deterministic control of plasmonic nanosystems and may enable large-scale fabrication of plexcitonic chips, thus opening a route to practical applications of strong coupling. Towards the ultimate realization of plexcitonic quantum technologies and with a view to the potential of top-down fabrication approaches, we are motivated to explore plasmonic nanocavities with the following features: (1) hotspots that are open to excitonic matter; (2) plasmon-enhanced near-fields that are strongly aligned with excitonic dipoles; and (3) a design that is scalable and conducive to mass production.

In this work, we propose a novel concept based on a gold bowtie nanoantenna for plasmonic nanocavity design where plasmonic hotspots can be engineered via substrates. Here, we consider a bowtie placed on gold (Au), silicon (Si), and glass substrates, in comparison with a bare bowtie without substrate (\textit{i.e.}, suspended in air). Numerical simulations demonstrate that the hotspot in the gap region can be strongly enhanced and, more importantly, elevated to the upper surface of the bowtie by using Au and Si substrates, in stark contrast to the extensively studied bowtie-on-glass cavity. Such hotspots are more exposed and thus more readily accessible to quantum emitters. Our proposed scheme is particularly favorable for achieving a strong dipole coupling with 2D materials, since the dominant electric field is directed along the longitudinal axis of the bowtie (\textit{i.e.}, aligned with the in-plane ex-
tonic dipoles in 2D materials). The studied plasmonic modes are also radiative with a good out-coupling efficiency to free space. Using a single bowtie placed on either a Au or Si substrate, we demonstrate strong coupling between their plasmonic modes and quantum matter comprising a single emitter or an ensemble thereof. The bowtie-on-Au and bowtie-on-Si cavities provide hotspots localized to the upper surface of the structure, and can potentially be fabricated via a top-down etching approach.

II. Substrate-dependent Plasmonic Response of the Bowtie Cavity

To elucidate the substrate-dependent optical response of the Au bowtie nanocavity, we solve Maxwell’s equations numerically by the finite-element method, as described in the Supporting Information (see Sec. S1). The Au bowtie is characterized by a set of geometrical parameters: bowtie width $w$, height $h$, gap distance $d$, apex angle $\alpha$, and radius of curvature $r$ at the corners, as illustrated in Fig. 1(a). In the following discussion, we fix the bowtie geometry with $w = 100 \text{ nm}$, $h = 30 \text{ nm}$, $d = 2 \text{ nm}$, $\alpha = 60^\circ$, and $r = 5 \text{ nm}$, for simplicity. The detailed dependence of the optical response on the bowtie geometry can be found in the Supporting Information (see Sec. S2). The calculated spectral absorption rates for the Au bowtie are shown in Figs. 1(a)iii-1(d)iii, with each exhibiting a multipeak structure that is sensitive to the choice of substrate. Note that, for the bowtie-on-Si cavity, there is a structured plateau feature around 700 nm, which has been discussed in the Supporting Information (see Sec. S1).

For each substrate and incident wavelength, we analyzed the electric near-field distribution around the nanobowtie, and found the maximum field enhancement at the wavelengths designated by the arrows. The corresponding normalized near-field profiles in the gap region are displayed in Figs. 1(a)ii-1(d)ii. Note that, unless explicitly stated otherwise, the electric field data (both $|E|$ and the individual field components) are normalized by the amplitude of the incident light field, $|E_0| = 1 \text{ V/m}$, and are thus unitless. It can be seen that the
hotspots for the nanobowtie-on-Au and nanobowtie-on-Si cavities are lifted to the top of the gap, with the normalized $|\mathbf{E}|$ (i.e., field enhancement) for the Au substrate slightly larger. For the bowtie-on-glass cavity [Fig. 1(c)ii], the hotspot is located close to the substrate due to the higher refractive index of glass compared to the background air, while for the bare nanobowtie [Fig. 1(d)ii], the field enhancement is spatially uniform due to the symmetric environment. Compared to the glass substrate, the Au and Si substrates facilitate the elevation of the hotspot and, more importantly, enable a higher field enhancement of $\sim$
1.6 times ($|E|_{\text{max}} \sim 482$ for bowtie-on-Au, $|E|_{\text{max}} \sim 468$ for bowtie-on-Si, and $|E|_{\text{max}} \sim 306$ for bowtie-on-glass). Both features are extremely desirable in the practical pursuit of room-temperature, plexcitonic strong coupling.

We have also calculated the radiative ($\Gamma_{\text{rad}}$), non-radiative ($\Gamma_{\text{nr}}$), and total ($\Gamma_{\text{tot}}$) decay rates for a classical dipole, aligned along the $x$-axis and located at the center of the gap along the bowtie upper surface. As shown in Figs. 1(a)iv-1(d)iv, each configuration supports a radiative mode (highlighted with star symbols), whose wavelength is in good agreement with a peak in the corresponding absorption spectrum. This indicates that these modes not only possess an optimal field enhancement, but also couple efficiently to free space, thus allowing for far-field manipulations. Specifically, $\Gamma_{\text{rad}}^{\text{Au}} > \Gamma_{\text{rad}}^{\text{air}} > \Gamma_{\text{rad}}^{\text{glass}} > \Gamma_{\text{rad}}^{\text{Si}}$. Although the radiative yield $\Gamma_{\text{rad}}^{\text{Si}}$ is the lowest, it is still comparable ($\sim 10^5$) to $\Gamma_{\text{rad}}^{\text{Au}}$ for the bowtie-on-Au cavity. With a Lorentzian fitting, the decay rates of the plasmon modes (half-width at half-maximum) are found to be $\kappa_c^{\text{Au}} = 42.08$ meV for the bowtie-on-Au cavity and $\kappa_c^{\text{Si}} = 57.58$ meV for the bowtie-on-Si cavity, respectively. It should be noted that in the absorption spectra there are also other resonant peaks representing higher-order modes. As an example, we provide the details of the non-radiative mode at 570 nm for the bowtie-on-Au cavity in the Supporting Information (see Sec. S3).

III. Physical Origins of the Hotspot Elevation

We performed in-depth studies of the corresponding radiative modes to better understand the physical origins of their substrate-dependent optical properties. Firstly, we extracted their three-dimensional normalized near-field profiles (color maps), as displayed in Figs. 2(a)i-2(d)i. The field profiles show the locations of the hotspots: at the top of the gap for the bowtie-on-Au and bowtie-on-Si cavities, at the bottom of the gap for the bowtie-on-glass cavity, and uniform along the gap for the bare bowtie, which are consistent with the cross-sectional plots in Fig. 1. The normalized electric field distributions inside the
Figure 2: **Analysis of the substrate-dependent hotspot distributions.** Details of the radiative modes supported by different substrates: (a) gold, (b) silicon, and (c) glass; in comparison with (d) a bare bowtie in air. (i) Three-dimensional normalized electric near-field profiles of the bowties (color map), with superimposed vectorial electric field distributions (purple arrows) inside the devices. The arrow direction indicates that of the electric field, while its length is proportional to the magnitude of the electric field in a logarithmic scale. (ii) The near-field distributions for the normalized $E_z$ component in the gap region (side views), with bold, gradient arrows indicating the charge flow and dashed black lines indicating the geometric boundaries of the bowtie. (iii) Near-field distributions for the normalized electric field magnitude and components at the upper surface of the bowties (top views), with superimposed charge distribution polarities. The field profiles show that $E_x$ is the dominant component. The bowtie geometry is identical throughout with $w = 100$ nm, $h = 30$ nm, $d = 2$ nm, $\alpha = 60^\circ$, and $r = 5$ nm.

Bowtie structures are also presented as vectors (purple arrows), where the orientations and lengths of the arrows indicate the directions and magnitudes of the normalized electric field respectively. The charge flows (arrows) for the bowtie-on-Au and bowtie-on-Si cavities have a similar appearance, as do those for the bowtie-on-glass cavity and bare bowtie. For the former pair, the normalized electric field distributions suggest a dominantly vertical migration and accumulation of charge towards the upper tips of the nanoprisms, resulting in a stronger field enhancement (hotspot) at the upper surface of each structure. In contrast, for the latter pair, the charge motion has a largely horizontal character that leads to their accumulation along each of the opposing metal-dielectric interfaces, giving rise to a more spatially homogeneous field enhancement in the gap.
The same observation can also be made from the cross-sectional distributions for the \( z \)-component of the normalized electric field, \( E_z \), as shown in Figs. 2(a)ii-2(d)ii. These unambiguously demonstrate that the electric field bears a significant vertical component for the bowtie-on-Au and bowtie-on-Si cavities (note the reddish and bluish coloration in the metal regions), implying a strongly vertical charge flow towards the upper vertices of the nanoprisms, as given by the bold, gradient arrows. It should be emphasized that the charge flows are not identical for the Au and Si substrates [Figs. 2(a)i-2(b)i]. For the bowtie-on-Si cavity, the internal electric field and thus the electronic charge motion bear some horizontal character away from the gap region, as indicated by an additional pair of bold, gradient arrows with such orientation in Fig. 2(b)ii. As for the bowtie-on-glass and bare bowtie structures [Figs. 2(c)ii-2(d)ii], the normalized \( E_z \) component is much less significant in the metal regions (as indicated by the gray color), thus the bold, gradient arrows are all horizontal.

Additionally, Figs. 2(a)iii-2(d)iii present the normalized near-field distributions at the upper surface of the bowtie structures for all electric field components. We note that the normalized field-component distributions in Fig. 2(c)iii for the glass substrate are qualitatively similar to those at the lower (contact) surface, but with a magnitude that is smaller by almost a factor of 2 (\(|E|_{\text{max}} \sim 180 \) at the upper surface and \(|E|_{\text{max}} \sim 306 \) at the lower surface). In the same figures, we also designate the polarity of the induced charge distributions according to the positive/negative signs of each component. Our findings suggest that the charge distributions for both the bowtie-on-Au and bowtie-on-Si cavities are strongly localized to the gap region, while some accumulation of charge along the exterior corners must also be present for the bowtie-on-glass cavity and bare bowtie. On this basis, we conclude that the radiative modes supported by the bowtie-on-glass cavity and bare bowtie are simply the conventional, bonding dimer plasmon modes that originate from the coupling between adjacent metal nanoprisms.\[1\] In contrast, for the bowtie-on-Au and bowtie-on-Si cavities, the radiative modes bear strong contributions from the coupling between the sub-
strate and nanoprisms, and are thus of a fundamentally different nature. Further discussion and characterization of the latter modes, including the origins of their elevated hotspots, can be found in the Supporting Information (see Sec. S4). Finally, it is worth highlighting that in all cases, the $E_x$ component is the dominant one, which is decisively favored for a strong dipole interaction with 2D materials, whose excitonic dipoles are typically oriented in-plane. However, among our investigated device configurations, the bowtie-on-Au and bowtie-on-Si cavities would enable the most efficient coupling compared to the bowtie-on-glass and bare bowtie, due to the $\sim 2.22$ times larger field enhancement at the upper surface.

IV. Antenna Mode for Strong Coupling

Figure 3: Strong coupling of the bowtie-on-Au and bowtie-on-Si cavity antenna modes with a sheet of quantum emitters. (a) The scattering spectra of the plexcitonic system for the bowtie-on-Au cavity (schematic in the inset) with the emitter resonance swept from 675 nm to 825 nm. The dashed lines trace the peaks in the scattering spectra, indicating the anticrossing behavior and Rabi splitting. (b) The scattering spectra of the plexcitonic system for the bowtie-on-Si cavity (schematic in the inset) with the emitter resonance swept from 580 nm to 700 nm. (c) The temporal dynamics of the normalized polarization $|P|/\varepsilon_0|E_0|$ for a single emitter placed in the nanogap hotspot of the bowtie-on-Au (top) and bowtie-on-Si (bottom) cavities. The dashed lines outline the envelope of $|P|/\varepsilon_0|E_0|$, where the oscillatory feature indicates a coherent exchange of energy between the cavity antenna mode and the quantum emitter. The bowtie geometry is identical throughout with $w = 100$ nm, $h = 30$ nm, $d = 2$ nm, $\alpha = 60^\circ$, and $r = 5$ nm, while the emitters have a fixed transition dipole moment of magnitude 5 D.
In view of the dominantly in-plane polarized near-fields of the antenna mode and its potential for achieving strong light-matter interaction with 2D excitonic materials, such as semiconducting TMDCs and doped graphene, we next explore the performance of the bowtie-on-Au and bowtie-on-Si cavities in coupling active quantum media via their plasmonic hotspots. More specifically, we solve numerically the Maxwell-Bloch equations\textsuperscript{[12]} adopted for nanoplasmonic materials and cavities,\textsuperscript{[43–45]} for a thin sheet of uniformly distributed, two-level quantum emitters placed across the upper surface of each bowtie structure. Details concerning the Maxwell-Bloch treatment and calculation parameters can be found in the Supporting Information (see Sec. S5). The emitters are identical and characterized by their transition wavelength $\lambda_e$, decay rate $\Gamma_e$ (half-width at half-maximum), and dipole moment $\mu$. We first fix the decay rate $\Gamma_e = 6.5$ meV (i.e., $10^{13}$ rad/s) and dipole moment $\mu = 5$ D oriented along the $x$-axis, and study the scattering response of each coupled system as the emitter transition wavelength $\lambda_e$ is swept across the cavity mode of interest.

As shown in Figs. 3(a) and 3(b), the scattering spectra with swept $\lambda_e$ exhibit a splitting feature for both the bowtie-on-Au and bowtie-on-Si cavities, as traced by the black dashed lines. The minimal splittings denoted $\Omega$ therein are obtained as $\Omega^{\text{Au}} = 82.78$ meV (at $\lambda_e = 747$ nm) and $\Omega^{\text{Si}} = 92.76$ meV (at $\lambda_e = 650$ nm). Although such splitting is a well-known manifestation of strong coupling in the single- or many-emitter regimes, it could also originate from a coherent Fano interference effect under intermediate coupling conditions.\textsuperscript{[16]} To provide firm evidence that our bowtie-on-Au and bowtie-on-Si cavities are capable of supporting light-matter strong coupling, we also investigate the interaction of the antenna mode with a single, two-level emitter positioned in the elevated hotspot of each cavity and subject to identical excitation conditions. The corresponding scattering spectra in the single-emitter regime are shown in Fig. S6 of the Supporting Information, where a dual-peak structure with an anticrossing behaviour is observed as the cavity resonance and emitter transition are progressively detuned. To gain a deeper insight, we further examine the temporal dynamics of the normalized polarization for the emitter in each coupled system.
As shown in Fig. 3(c), the polarization fluctuations in each case have a period of $\sim 1.2$ fs, corresponding to the transition frequency of the emitter, and conform to an exponentially decaying envelope (dashed lines). Crucially, this envelope is accompanied by an oscillatory modulation, which signifies a coherent energy cycling characteristic of plexciton formation in each system. For the bowtie-on-Au cavity, the oscillation period is $\sim 115$ fs, corresponding to an energy exchange rate of 8.69 THz. In contrast, the oscillation is less pronounced for the bowtie-on-Si cavity, where only one round of energy exchange is observed. This is attributable to the multiplicity of resonant modes [particularly at longer wavelengths, see Fig. 3(b)] supported by the bowtie-on-Si cavity, which provide additional channels by which energy dissipates from the cavity antenna mode. As energy is transferred from the emitter to the antenna mode, it may quickly dissipate via other resonant modes that are spectrally or spatially overlapping with the antenna mode. The presence of Rabi oscillations constitutes an unambiguous signature of the plexcitonic regime in the case of a single quantum emitter, and we can thus identify the dual-peak features in Figs. S6(a) and S6(b) as polaritonic splittings. Invoking a phenomenological, dissipative Jaynes-Cummmings treatment, the latter can be related to the single-emitter coupling strength $g_0$ via $\Omega = \sqrt{4g^2_0 - (\Gamma_e - \kappa_c)^2}$, where $\Gamma_e$ is the emitter decay rate defined above and $\kappa_c$ is the decay rate of the cavity mode. The single-emitter coupling strengths are thereby deduced as $g_{0\text{Au}} = 31.28$ meV for the bowtie-on-Au cavity, and $g_{0\text{Si}} = 33.81$ meV for the bowtie-on-Si cavity, respectively (see Sec. S6).

The ability of these plasmonic cavities to support strong coupling in the single-emitter regime suggests that the spectral splittings observed for an ensemble of many such emitters in Figs. 3(a) and 3(b) could also originate from a strong coupling behaviour, mediated by one or perhaps a collection of emitters interacting with the same antenna mode of each bowtie-on-substrate cavity. In the absence of intrinsic cavity or emitter dissipative effects, the Tavis-Cummings model yields the well-known prediction that the separation of the dressed states in such a scenario is given by $\Omega = 2g_{\text{eff}}$, with an effective coupling strength
$g_{\text{eff}} = \sqrt{N}g_0$ enhanced relative to the single-emitter one $g_0$ according to the number $N$ of quantum emitters that collectively participate in the strong coupling. Given the complexity of treating dissipation in the many-emitter case, we shall adopt these simple relations in the present analysis to provide effective estimates for the strength and collectivity of light-matter interaction, albeit retaining the renormalizing effect of decay in the calculation of $g_0$ (as above). From the splittings observed in Figs. 3(a) and 3(b), the effective coupling strengths are deduced as $g_{\text{eff}}^{\text{Au}} = 41.39 \text{ meV}$ and $g_{\text{eff}}^{\text{Si}} = 46.38 \text{ meV}$, and the effective number of emitters can be estimated as $N^{\text{Au}} \approx 2$ and $N^{\text{Si}} \approx 2$.

According to the above analysis, the bowtie-on-Au and bowtie-on-Si cavities result in a similar coupling strength with the same quantum emitters, albeit at different emitter transition wavelengths $\lambda_e$. They can therefore be used to achieve strong light-matter interaction in different spectral ranges and match with different quantum emitters. From an experimental perspective, the evaporation of a Au film in forming the substrate may lead to a rough surface with typical roughness values in the range 1.6 – 4.0 nm, depending on the evaporation conditions. Such a high surface roughness may distort the designed plasmonic cavity resonance and impose stringent requirements on the nanofabrication process to realize sub-10-nm gaps in a uniform manner. On the other hand, the commercially available Si surface is usually atomically flat and thus the fabrication of dimers with $\sim 5$ nm gaps is feasible. It is also worth highlighting that the scattering cross-section of the bowtie-on-Si cavity is typically an order of magnitude smaller than that of the bowtie-on-Au cavity in the investigated spectral range. This is due to a (rather non-trivial) distribution of spectral weight among multiple resonant modes of the bowtie-on-Si cavity. Nevertheless, at longer wavelengths (1000 nm, beyond the range considered here), the scattering spectrum of this system is dominated by another mode with a peak cross-section $\sim 4.7$ times higher than that of the antenna mode. However, this mode displays a near-field gap hotspot located closer to the substrate, similar to the conventional bonding dimer plasmon mode of a Au bowtie device, and is therefore not of interest in the present study.
V. Engineering of the strong coupling

Figure 4: Engineering of plexcitonic strong coupling with the bowtie-on-Au cavity. (a) The scattering spectra of the plexcitonic system with varying bowtie height \( h \). In each case, the emitter wavelength \( \lambda_e \) is tuned accordingly to achieve the minimal (Rabi) splitting. Dashed lines indicate the scattering spectra of the corresponding, bare bowtie-on-Au cavities. (b) The effective coupling strength \( g_{\text{eff}} \) (black dots) extracted from (a) and the normalized coupling strength \( g_{\text{eff}}/\omega_c \) (blue circles) as functions of \( h \), where \( \omega_c \) is the frequency of the antenna mode. (c) Normalized spectral weight of the antenna mode as a function of \( h \), calculated in accordance with Eq. (1). (d) The scattering spectra for emitters with in-plane (blue line) and out-of-plane (black line) transition dipole moments. Inset: the respective dipole orientations. (e) The temporal dynamics of the normalized polarization \( |P|/\varepsilon_0|E_0| \) for a single emitter at the bowtie tip with a fixed magnitude of the transition dipole moment, \( \mu = 5 \) D, but different orientations. Dashed lines indicate the envelope of the polarization dynamics in each case. For \( \mu_\parallel \), the envelope bears an oscillatory modulation in addition to its exponential decay. (f) The temporal dynamics of the normalized polarization envelope for a single emitter at the bowtie tip with different transition dipole moments \( \mu \) but fixed, in-plane orientation. Unless stated otherwise, the reference bowtie geometry is identical throughout with \( w = 100 \) nm, \( h = 30 \) nm, \( d = 2 \) nm, \( \alpha = 60^\circ \), and \( r = 5 \) nm.

Finally, we investigate the effect of the bowtie geometry and emitter characteristics on the strong coupling behaviour, and explore the possibility of engineering the light-matter coupling via these parameters. As shown in Fig. 3, the bowtie-on-Au cavity presents a stronger scattering signal and more clearly resolved resonant modes; we therefore focus on
the bowtie-on-Au cavity in this section. Nevertheless, the engineering principles that will be discussed in the following are also applicable to the bowtie-on-Si cavity.

Among the geometrical parameters of the bowtie, the height $h$, and apex angle $\alpha$ can be well controlled in practical lithographic device fabrication, and offer flexibility to engineer the strong coupling via the sensitive dependence of the plasmonic field enhancement and the resonant wavelength on these properties. In Fig. 4(a), the scattering spectrum of the bowtie-on-Au cavity coupled with a layer of single quantum emitters is plotted for different bowtie heights $h$. As $h$ increases, the global scattering signal becomes stronger, and the antenna mode resonance (black dashed lines) is also red-shifted. Accordingly, for different $h$ values, the emitter transition wavelength $\lambda_e$ is also tuned to match with the antenna mode, thereby maintaining a Rabi splitting for the plexcitonic system (blue solid lines), denoted $\Omega$ and indicated in the figure. The effective coupling strength can then be extracted according to $\Omega = 2g_{\text{eff}}$. Note that the mode at $\sim 570$ nm is only weakly coupled with the quantum emitters, so that the spectra in this region are barely changed (note the overlapping blue and black lines). Furthermore, this mode is less sensitive to variations in $h$, since it partially originates from the coupling between the adjacent nanoprisms of the bowtie (see Fig. S4 in the Supporting Information).

Figure 4(b) shows the extracted coupling strength $g_{\text{eff}}$ as a function of the bowtie height (black line), which appears to decrease in a monotonic fashion as $h$ increases. Even if the coupling strength is normalized to the cavity resonance (blue line), $g_{\text{eff}}/\omega_c$ still exhibits a decreasing slope. This dependence is contrary to that of the local field enhancement $|E|$ on $h$, which becomes stronger as $h$ increases (see Fig. S3 in the Supporting Information). To better understand this behaviour, we focus on the optical response of the bare cavity, and examine in more detail the evolution of the plasmonic antenna mode with bowtie height. Specifically, we define a normalized measure for the spectral weight of each cavity mode in the form

$$S = \frac{\int_{\text{mode}} \sigma_{\text{scat}}(\lambda) d\lambda}{\int \sigma_{\text{scat}}(\lambda) d\lambda},$$

(1)
where $\sigma_{\text{scat}}(\lambda)$ is the scattering cross-section shown in Fig. 4(a) (black dashed lines), and the integration in the numerator is performed over the spectral range pertaining to the mode in question, while that in the denominator is performed over the entire spectrum. The quantity $S$ is plotted as a function of $h$ in Fig. 4(c), and exhibits a decreasing trend similar to the coupling strength itself. Our results imply that the higher-order mode around 570 nm accumulates spectral weight relative to the antenna mode as $h$ increases, and is thus excited more efficiently. This effect appears to dominate the larger field enhancements that would otherwise give rise to a larger splitting for higher $h$ values, producing the observed decrease of the coupling strength with bowtie height. On the other hand, this higher-order mode also couples to the layer of quantum emitters via its spatially overlapping hotspots (see Fig. S4 in the Supporting Information). As $h$ increases however, the red shift in the antenna mode requires the emitter transition wavelength to be increased also for spectral matching purposes, which in turn increases its detuning relative to the higher-order mode and compromises their interaction strength. Besides the bowtie height, the apex angle $\alpha$ can also be used to fine-tune the plasmonic resonance while maintaining the plexcitonic coupling. Detailed discussions can be found in the Supporting Information (see Figs. S3 & S7).

The properties of the quantum emitters provide an additional flexibility to engineer plexcitonic coupling, particularly through the magnitude and orientation of their transition dipole moments. We denote in-plane and out-of-plane orientations of the emitter dipole moment by $\mu_\parallel$ and $\mu_\perp$, respectively, and show the corresponding scattering spectra of the coupled system in Fig. 4(d). A prominent spectral splitting is incurred for the emitters with $\mu_\parallel$ (blue line), while the spectrum for $\mu_\perp$ (black line) almost resembles the optical response of the bare cavity [dashed line in Fig. 4(a)]. These results unambiguously demonstrate an efficient plexcitonic interaction due to the favourable alignment between the dominantly in-plane plasmonic cavity field [Fig. 2(a)iii] and the emitter dipole $\mu_\parallel$, and further suggest that the bowtie antenna mode is appealing for coupling 2D excitonic materials, whose transition dipoles are largely in-plane.
Having predicted the feasibility of a collective light-matter strong coupling using the bowtie-on-Au cavity, we now explore the fundamentally and technologically interesting regime of strong coupling in the single-emitter limit. We position a single, two-level quantum emitter in the gap hotspot of the bowtie-on-Au cavity and explore its temporal dynamics for different magnitudes and orientations of the transition dipole moment. A detailed description of the simulation methodology and numerical parameters can be found in the Supporting Information (see Sec. S5). Figure 4(e) presents the normalized polarization of the emitter as a function of time for two orthogonal dipole orientations. Clearly, the polarization envelope for $\mu_\parallel$ shows a faster decay than that for $\mu_\perp$, implying a stronger coupling with the cavity. More importantly, the oscillatory modulation (period of $\sim 115$ fs) in the envelope for $\mu_\parallel$ signifies a coherent energy cycling within the plexcitonic system and further proves the dominant in-plane nature of the field for the antenna mode. When the dipole moment is increased beyond 5 D, as shown in Fig. 4(f), the energy exchange occurs at a higher rate with more oscillations in the investigated temporal interval, together with an overall faster exponential decay. We note that the values of $\mu$ considered here span those of several real quantum emitters including large dye molecules and colloidal quantum dots, while even higher excitonic transition moments have been observed in monolayer TMDCs like WS$_2$. As such, our proposed bowtie-on-Au cavity appears to hold excellent potential as a platform for plasmonic cavity quantum electrodynamics and plexcitonic quantum devices, even in the single-emitter limit.

VI. Conclusions and Outlook

To conclude, we propose a three-dimensional engineering of plasmonic cavity hotspots at the nanometer scale via substrate selection. By placing a Au nanobowtie on Au and Si substrates, we observe an elevation of the hotspots to the exterior/upper surface of the nanobowtie, thus rendering them more readily accessible for quantum emitters to achieve plasmon-enhanced
light-matter interaction and a myriad of its pertinent practical applications. This hotspot elevation originates from the antenna mode that involves a coupling between the Au bowtie structure and substrate, and is fundamentally different from the widely explored bonding dimer plasmon mode supported by the bare nanobowtie or nanobowtie-on-glass cavity. Another feature of the antenna mode is the dominant in-plane electric field, which is especially favorable for interaction with excitonic 2D materials compared to, e.g., the popular NPoM cavity. Using this antenna mode, we demonstrated that strong coupling can be achieved simply by placing a layer of quantum emitters on top of the nanobowtie, unveiling the prospect of observing the plexcitonic regime in atomically thin materials such as monolayer TMDCs and doped graphene. Our system design is conducive to a high degree of engineering flexibility for coupling active quantum media, where both the bowtie geometry and choice of substrate enable spatiotemporal tunability of the plasmonic excitations. Furthermore, our design allows top-down fabrication, enabling scaling-up and mass production of plexcitonic chips, paving the way to room-temperature plexcitonic quantum technologies.

Aside from the realization of strong coupling with 2D materials, we also envisage that the investigated antenna mode will be harnessable in other contemporary applications. For example, leveraging the large spatial field gradients in the cavity, the antenna mode might be exploited for field-enhanced single-molecule spectroscopy. With the advent of precision methods for deterministic orientation of single molecules in nanogaps, mechanisms for controlled hotspot distribution allow different regions of an individual molecule to experience different local electromagnetic environments, which could, in turn, be exploited for temporally and/or spatially resolved spectroscopic characterization of different excitonic states. Recent research has also shown the possibility to create strong coupling with living organisms for the study of biological processes, e.g., photosynthesis or bacterial growth, since many electronic transitions in biologically relevant molecules occur in the ultraviolet and visible ranges. Multidimensional hotspot manipulation could offer greater flexibility for novel spectroscopic opportunities here as well.
The underlying principles of hotspot/substrate nanoengineering are general and can be readily applied to other metals and plasmonic nanoparticles. By using a different metal or changing the geometry of the antenna, the plasmonic resonance can be tuned to other spectral ranges for a variety of potential applications. For example, in the ultraviolet range, aluminum-based plasmonic cavities may be designed to enhance the efficiency of photocatalysis or photovoltaic energy conversion, enabling low-cost, CMOS-compatible plasmonic devices in an environmentally-friendly and sustainable economy. By coupling the antenna mode with 2D materials, powerful optoelectronic devices can be designed for mid-to-far infrared range functionality and may benefit a broad spectrum of applications, such as environmental monitoring, health care diagnostics and non-destructive inspection.

Substrate engineering could also facilitate novel opportunities for tailoring the functionality of diffractive arrays and metasurfaces. In particular, the high quality factor, spatially delocalized character and unique dispersion properties of surface lattice resonances supported by nanoantenna arrays render them as interesting candidates for polaritonic device technologies, but the additional design scope conferred by the substrate material has not yet been thoroughly explored. Recently, lattices of localized polariton condensates have shown the capability of forming topologically protected states and simulating many-body Hamiltonians. The complexity of such lattices also makes them superior in neuromorphic computing, which can be faster and more power-efficient than the von Neumann architecture. Our proposed material-based engineering of plasmonic nanocavity modes should create new design flexibility for emerging plexcitonic lattices, leveraging the potential of strongly interacting light-matter systems for fully parallel and ultrafast operations in novel artificial intelligence systems.

Acknowledgement

The Institute of High Performance Computing (IHPC) acknowledges financial support from
the A*STAR Strategic Program (No. C210917001). D.C. and O.H. gratefully acknowledge funding from Science Foundation Ireland via Grant No. 18/RP/6236. L.W. gratefully acknowledges the Start-Up Research Grant from Singapore University of Technology and Design via Grant No. SRG SMT 2021 169. The computational work reported in this article relied on support and infrastructure provided by the Trinity Centre for High Performance Computing, with funding from the European Research Council, Science Foundation Ireland and the Higher Education Authority, through its PRTLI program.

Supporting Information Available

The following files are available free of charge at https://pubs.acs.org/doi/xxxx. Numerical Models for Near-field Studies; Tunability of the Optical Response via the Bowtie Geometry; Higher-order Non-radiative Mode of the Bowtie-on-Au Cavity; Different Mechanisms for Hotspot Formation using Au and Si Substrates; Two-level Maxwell-Bloch Simulations; Scattering Spectrum in the Single-emitter Strong Coupling Regime; Dependence of the Plexcitonic Rabi Splitting on the Bowtie Apex Angle; Figures S1-S7 (PDF).

References

1. Xu, D.; Xiong, X.; Wu, L.; Ren, X.-F.; Png, C. E.; Guo, G.-C.; Gong, Q.; Xiao, Y.-F. Quantum plasmonics: New opportunity in fundamental and applied photonics. Advances in Optics and Photonics 2018, 10, 703–756.

2. Schweicher, G.; Garbay, G.; Jouclas, R.; Vibert, F.; Devaux, F.; Geerts, Y. H. Molecular semiconductors for logic operations: Dead-end or bright future? Advanced Materials 2020, 32, 1905909.

3. Ribeiro, R. F.; Martínez-Martínez, L. A.; Du, M.; Campos-Gonzalez-Angulo, J.; Yuen-
Zhou, J. Polariton chemistry: Controlling molecular dynamics with optical cavities. *Chemical Science* 2018, 9, 6325–6339.

4. Silva, R.; Del Pino, J.; García-Vidal, F. J.; Feist, J. Polaritonic molecular clock for all-optical ultrafast imaging of wavepacket dynamics without probe pulses. *Nature Communications* 2020, 11, 1–8.

5. Chikkaraddy, R.; De Nijs, B.; Benz, F.; Barrow, S. J.; Scherman, O. A.; Rosta, E.; Demetriadou, A.; Fox, P.; Hess, O.; Baumberg, J. J. Single-molecule strong coupling at room temperature in plasmonic nanocavities. *Nature* 2016, 535, 127–130.

6. Liu, R.; Zhou, Z.-K.; Yu, Y.-C.; Zhang, T.; Wang, H.; Liu, G.; Wei, Y.; Chen, H.; Wang, X.-H. Strong light-matter interactions in single open plasmonic nanocavities at the quantum optics limit. *Physical Review Letters* 2017, 118, 237401.

7. Groß, H.; Hamm, J. M.; Tufarelli, T.; Hess, O.; Hecht, B. Near-field strong coupling of single quantum dots. *Science Advances* 2018, 4, eaar4906.

8. Hensen, M.; Heilpern, T.; Gray, S. K.; Pfeiffer, W. Strong coupling and entanglement of quantum emitters embedded in a nanoantenna-enhanced plasmonic cavity. *ACS Photonics* 2018, 5, 240–248.

9. Xiong, X.; You, J.-B.; Bai, P.; Png, C. E.; Zhou, Z.-K.; Wu, L. Ultrastrong coupling in single plexcitonic nanocubes. *Nanophotonics* 2020, 9, 257–266.

10. Xiong, X.; Kongsuwan, N.; Lai, Y.; Png, C. E.; Wu, L.; Hess, O. Room-temperature plexcitonic strong coupling: Ultrafast dynamics for quantum applications. *Applied Physics Letters* 2021, 118, 130501.

11. Bogdanov, S. I.; Makarova, O. A.; Xu, X.; Martin, Z. O.; Lagutchev, A. S.; Olinde, M.; Shah, D.; Chowdhury, S. N.; Gabidullin, A. R.; Ryzhikov, I. A., *et al.* Ultrafast quantum
photonics enabled by coupling plasmonic nanocavities to strongly radiative antennas. 

*Optica* 2020, 7, 463–469.

12. Zhang, Y.; Meng, Q.-S.; Zhang, L.; Luo, Y.; Yu, Y.-J.; Yang, B.; Zhang, Y.; Esteban, R.; Aizpurua, J.; Luo, Y., *et al.* Sub-nanometre control of the coherent interaction between a single molecule and a plasmonic nanocavity. *Nature Communications* 2017, 8, 1–7.

13. Orgiu, E.; George, J.; Hutchison, J.; Devaux, E.; Dayen, J.; Doudin, B.; Stellacci, F.; Genet, C.; Schachenmayer, J.; Genes, C., *et al.* Conductivity in organic semiconductors hybridized with the vacuum field. *Nature Materials* 2015, 14, 1123–1129.

14. Bouchet, D.; Cao, D.; Carminati, R.; De Wilde, Y.; Krachmalnicoff, V. Long-range plasmon-assisted energy transfer between fluorescent emitters. *Physical Review Letters* 2016, 116, 037401.

15. Aeschlimann, M.; Brixner, T.; Cinchetti, M.; Frisch, B.; Hecht, B.; Hensen, M.; Huber, B.; Kramer, C.; Krauss, E.; Loeber, T. H., *et al.* Cavity-assisted ultrafast long-range periodic energy transfer between plasmonic nanoantennas. *Light: Science & Applications* 2017, 6, e17111.

16. Calafell, I. A.; Cox, J.; Radonjić, M.; Saavedra, J.; de Abajo, F. G.; Rozema, L.; Walther, P. Quantum computing with graphene plasmons. *npj Quantum Information* 2019, 5, 1–7.

17. Galego, J.; Garcia-Vidal, F. J.; Feist, J. Many-molecule reaction triggered by a single photon in polaritonic chemistry. *Physical Review Letters* 2017, 119, 136001.

18. Campos-Gonzalez-Angulo, J. A.; Ribeiro, R. F.; Yuen-Zhou, J. Resonant catalysis of thermally activated chemical reactions with vibrational polaritons. *Nature Communications* 2019, 10, 1–8.
19. Feist, J.; Galego, J.; Garcia-Vidal, F. J. Polaritonic chemistry with organic molecules. *ACS Photonics* **2018**, *5*, 205–216.

20. Franke, S.; Hughes, S.; Dezfoli, M. K.; Kristensen, P. T.; Busch, K.; Knorr, A.; Richter, M. Quantization of quasinormal modes for open cavities and plasmonic cavity quantum electrodynamics. *Physical Review Letters* **2019**, *122*, 213901.

21. Ciraci, C.; Hill, R. T.; Mock, J. J.; Urzhumov, Y.; Fernández-Domínguez, A. I.; Maier, S. A.; Pendry, J. B.; Chilkoti, A.; Smith, D. R. Probing the ultimate limits of plasmonic enhancement. *Science* **2012**, *337*, 1072–1074.

22. Tserkezis, C.; Esteban, R.; Sigle, D. O.; Mertens, J.; Herrmann, L. O.; Baumberg, J. J.; Aizpurua, J. Hybridization of plasmonic antenna and cavity modes: Extreme optics of nanoparticle-on-mirror nanogaps. *Phys. Rev. A* **2015**, *92*, 053811.

23. Kongsuwan, N.; Demetriadou, A.; Horton, M.; Chikkaraddy, R.; Baumberg, J. J.; Hess, O. Plasmonic nanocavity modes: From near-field to far-field radiation. *ACS Photonics* **2020**, *7*, 463–471.

24. Kongsuwan, N.; Demetriadou, A.; Chikkaraddy, R.; Benz, F.; Turek, V. A.; Keyser, U. F.; Baumberg, J. J.; Hess, O. Suppressed quenching and strong-coupling of purcell-enhanced single-molecule emission in plasmonic nanocavities. *ACS Photonics* **2018**, *5*, 186–191.

25. Ojambati, O. S.; Chikkaraddy, R.; Deacon, W. D.; Horton, M.; Kos, D.; Turek, V. A.; Keyser, U. F.; Baumberg, J. J. Quantum electrodynamics at room temperature coupling a single vibrating molecule with a plasmonic nanocavity. *Nature Communications* **2019**, *10*, 1049.

26. Baumberg, J. J.; Aizpurua, J.; Mikkelsen, M. H.; Smith, D. R. Extreme nanophotonics from ultrathin metallic gaps. *Nature Materials* **2019**, *18*, 668–678.
27. Mak, K. F.; Shan, J. Photonics and optoelectronics of 2D semiconductor transition metal dichalcogenides. *Nature Photonics* **2016**, *10*, 216–226.

28. Manzeli, S.; Ovchinnikov, D.; Pasquier, D.; Yazyev, O. V.; Kis, A. 2D transition metal dichalcogenides. *Nature Reviews Materials* **2017**, *2*, 17033.

29. Kleemann, M.-E.; Chikkaraddy, R.; Alexeev, E. M.; Kos, D.; Carnegie, C.; Deacon, W.; De Pury, A. C.; Große, C.; De Nijs, B.; Mertens, J., *et al.* Strong-coupling of WSe$_2$ in ultra-compact plasmonic nanocavities at room temperature. *Nature Communications* **2017**, *8*, 1–7.

30. Han, X.; Wang, K.; Xing, X.; Wang, M.; Lu, P. Rabi splitting in a plasmonic nanocavity coupled to a WS$_2$ monolayer at room temperature. *ACS Photonics* **2018**, *5*, 3970–3976.

31. Hou, S.; Tobing, L. Y.; Wang, X.; Xie, Z.; Yu, J.; Zhou, J.; Zhang, D.; Dang, C.; Coquet, P.; Tay, B. K., *et al.* Manipulating coherent light-matter interaction: Continuous transition between strong coupling and weak coupling in MoS$_2$ monolayer coupled with plasmonic nanocavities. *Advanced Optical Materials* **2019**, *7*, 1900857.

32. Fang, H.; Battaglia, C.; Carraro, C.; Nemsak, S.; Ozdol, B.; Kang, J. S.; Bechtel, H. A.; Desai, S. B.; Kronast, F.; Unal, A. A.; Conti, G.; Conlon, C.; Palsson, G. K.; Martin, M. C.; Minor, A. M.; Fadley, C. S.; Yablonovitch, E.; Maboudian, R.; Javey, A. Strong interlayer coupling in van der Waals heterostructures built from single-layer chalcogenides. *Proceedings of the National Academy of Sciences* **2014**, *111*, 6198–6202.

33. Meckbach, L.; Huttner, U.; Bannow, L. C.; Stroucken, T.; Koch, S. W. Interlayer excitons in transition-metal dichalcogenide heterostructures with type-II band alignment. *Journal of Physics: Condensed Matter* **2018**, *30*, 374002.

34. Torun, E.; Miranda, H. P. C.; Molina-Sánchez, A.; Wirtz, L. Interlayer and intralayer excitons in MoS$_2$/WS$_2$ and MoSe$_2$/WSe$_2$ heterobilayers. *Phys. Rev. B* **2018**, *97*, 245427.
35. Väkeväinen, A.; Moerland, R.; Rekola, H.; Eskelinen, A.-P.; Martikainen, J.-P.; Kim, D.-H.; Törmä, P. Plasmonic surface lattice resonances at the strong coupling regime. *Nano Letters* **2014**, *14*, 1721–1727.

36. Santhosh, K.; Bitton, O.; Chuntonov, L.; Haran, G. Vacuum Rabi splitting in a plasmonic cavity at the single quantum emitter limit. *Nature Communications* **2016**, *7*, 1–5.

37. Liu, W.; Lee, B.; Naylor, C. H.; Ee, H.-S.; Park, J.; Johnson, A. C.; Agarwal, R. Strong exciton-plasmon coupling in MoS$_2$ coupled with plasmonic lattice. *Nano Letters* **2016**, *16*, 1262–1269.

38. Kang, E. S.; Chen, S.; Sardar, S.; Tordera, D.; Armakavicius, N.; Darakchieva, V.; Shegai, T.; Jonsson, M. P. Strong plasmon-exciton coupling with directional absorption features in optically thin hybrid nanohole metasurfaces. *ACS Photonics* **2018**, *5*, 4046–4055.

39. Shan, H.; Yu, Y.; Wang, X.; Luo, Y.; Zu, S.; Du, B.; Han, T.; Li, B.; Li, Y.; Wu, J., *et al*. Direct observation of ultrafast plasmonic hot electron transfer in the strong coupling regime. *Light: Science & Applications* **2019**, *8*, 1–9.

40. Gupta, S. N.; Bitton, O.; Neuman, T.; Esteban, R.; Chuntonov, L.; Aizpurua, J.; Haran, G. Complex plasmon-exciton dynamics revealed through quantum dot light emission in a nanocavity. *Nature Communications* **2021**, *12*, 1–9.

41. Schmidt, F. P.; Ditlbacher, H.; Hofer, F.; Krenn, J. R.; Hohenester, U. Morphing a plasmonic nanodisk into a nanotriangle. *Nano Letters* **2014**, *14*, 4810–4815.

42. Boyd, R. W. *Nonlinear Optics*; Academic Press, Burlington, 2008.

43. Hess, O.; Pendry, J. B.; Maier, S. A.; Oulton, R. F.; Hamm, J. M.; Tsakmakidis, K. L. Active nanoplasmonic metamaterials. *Nature Materials* **2012**, *11*, 573–584.

44. Wuestner, S.; Hess, O. Active Optical Metamaterials. *Progress in Optics* **2014**, *59*, 1–88.
45. Kongsuwan, N.; Xiong, X.; Bai, P.; You, J.-B.; Png, C. E.; Wu, L.; Hess, O. Quantum Plasmonic Immunoassay Sensing. *Nano Letters* **2019**, *19*, 5853–5861.

46. Leng, H.; Szychowski, B.; Daniel, M.-C.; Pelton, M. Strong coupling and induced transparency at room temperature with single quantum dots and gap plasmons. *Nature Communications* **2018**, *9*, 4012.

47. Baranov, D. G.; Wersäll, M.; Cuadra, J.; Antosiewicz, T. J.; Shegai, T. Novel nanostructures and materials for strong light–matter interactions. *ACS Photonics* **2018**, *5*, 24–42.

48. Tavis, M.; Cummings, F. The exact solution of N two level systems interacting with a single mode, quantized radiation field. *Physics Letters A* **1967**, *25*, 714–715.

49. Mahapatro, A. K.; Scott, A.; Manning, A.; Janes, D. B. Gold surface with sub-nm roughness realized by evaporation on a molecular adhesion monolayer. *Applied Physics Letters* **2006**, *88*, 151917.

50. Dong, Z.; Asbahi, M.; Lin, J.; Zhu, D.; Wang, Y. M.; Hippalgaonkar, K.; Chu, H.-S.; Goh, W. P.; Wang, F.; Huang, Z.; Yang, J. K. W. Second-harmonic generation from sub-5nm gaps by directed self-assembly of nanoparticles onto template-stripped gold substrates. *Nano Letters* **2015**, *15*, 5976–5981.

51. Dong, Z.; Wang, T.; Chi, X.; Ho, J.; Tserkezis, C.; Yap, S. L. K.; Rusydi, A.; Tjiptoharsono, F.; Thian, D.; Mortensen, N. A.; Yang, J. K. W. Ultraviolet interband plasmonics with Si nanostructures. *Nano Letters* **2019**, *19*, 8040–8048.

52. Coles, D. M.; Yang, Y.; Wang, Y.; Grant, R. T.; Taylor, R. A.; Saikin, S. K.; Aspuru-Guzik, A.; Lidzey, D. G.; Tang, J. K.-H.; Smith, J. M. Strong coupling between chlorosomes of photosynthetic bacteria and a confined optical cavity mode. *Nature Communications* **2014**, *5*, 1–9.
53. Knight, M. W.; King, N. S.; Liu, L.; Everitt, H. O.; Nordlander, P.; Halas, N. J. Aluminum for plasmonics. *ACS Nano* **2014**, *8*, 834–840.

54. Ghori, M. Z.; Veziroglu, S.; Hinz, A.; Shurtleff, B. B.; Polonskyi, O.; Strunskus, T.; Adam, J.; Faupel, F.; Aktas, O. C. Role of UV plasmonics in the photocatalytic performance of TiO$_2$ decorated with aluminum nanoparticles. *ACS Applied Nano Materials* **2018**, *1*, 3760–3764.

55. Li, W.; Valentine, J. G. Harvesting the loss: Surface plasmon-based hot electron photodetection. *Nanophotonics* **2017**, *6*, 177–191.

56. Dubey, A.; Mishra, R.; Hsieh, Y.-H.; Cheng, C.-W.; Wu, B.-H.; Chen, L.-J.; Gwo, S.; Yen, T.-J. Aluminum plasmonics enriched ultraviolet GaN photodetector with ultrahigh responsivity, detectivity, and broad bandwidth. *Advanced Science* **2020**, *7*, 2002274.

57. Yu, X.; Yu, P.; Wu, D.; Singh, B.; Zeng, Q.; Lin, H.; Zhou, W.; Lin, J.; Suenaga, K.; Liu, Z., *et al.* Atomically thin noble metal dichalcogenide: A broadband mid-infrared semiconductor. *Nature Communications* **2018**, *9*, 1–9.

58. Yu, X.; Li, Y.; Hu, X.; Zhang, D.; Tao, Y.; Liu, Z.; He, Y.; Haque, M. A.; Liu, Z.; Wu, T., *et al.* Narrow bandgap oxide nanoparticles coupled with graphene for high performance mid-infrared photodetection. *Nature Communications* **2018**, *9*, 1–8.

59. Lukman, S.; Ding, L.; Xu, L.; Tao, Y.; Riis-Jensen, A. C.; Zhang, G.; Wu, Q. Y. S.; Yang, M.; Luo, S.; Hsu, C., *et al.* High oscillator strength interlayer excitons in two-dimensional heterostructures for mid-infrared photodetection. *Nature Nanotechnology* **2020**, *15*, 675–682.

60. Liu, W.; Wang, Y.; Zheng, B.; Hwang, M.; Ji, Z.; Liu, G.; Li, Z.; Sorger, V. J.; Pan, A.; Agarwal, R. Observation and active control of a collective polariton mode and polaritonic band gap in few-layer WS$_2$ strongly coupled with plasmonic lattices. *Nano Letters* **2020**, *20*, 790–798.
61. Li, B.; Zu, S.; Zhang, Z.; Zheng, L.; Jiang, Q.; Du, B.; Luo, Y.; Gong, Y.; Zhang, Y.; Lin, F., et al. Large Rabi splitting obtained in Ag-WS$_2$ strong-coupling heterostructure with optical microcavity at room temperature. *Opto-Electronic Advances* 2019, 2, 190008.

62. St-Jean, P.; Goblot, V.; Galopin, E.; Lemaître, A.; Ozawa, T.; Le Gratiet, L.; Sagnes, I.; Bloch, J.; Amo, A. Lasing in topological edge states of a one-dimensional lattice. *Nature Photonics* 2017, 11, 651–656.

63. Klembt, S.; Harder, T.; Egorov, O.; Winkler, K.; Ge, R.; Bandres, M.; Emmerling, M.; Worschech, L.; Liew, T.; Segev, M., et al. Exciton-polariton topological insulator. *Nature* 2018, 562, 552–556.

64. Berloff, N. G.; Silva, M.; Kalinin, K.; Askitopoulos, A.; Töpfer, J. D.; Cilibrizzi, P.; Langbein, W.; Lagoudakis, P. G. Realizing the classical XY Hamiltonian in polariton simulators. *Nature Materials* 2017, 16, 1120–1126.

65. Ballarini, D.; Gianfrate, A.; Panico, R.; Opala, A.; Ghosh, S.; Dominici, L.; Ardizzone, V.; De Giorgi, M.; Lerario, G.; Gigli, G., et al. Polaritonic neuromorphic computing outperforms linear classifiers. *Nano Letters* 2020, 20, 3506–3512.