Near-field spatial mapping of strongly interacting multiple plasmonic infrared antennas†

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Near-field dipolar plasmon interactions of multiple infrared antenna structures in the strong coupling limit are studied using scattering-type scanning near-field optical microscope (s-SNOM) and theoretical finite-difference time-domain (FDTD) calculations. We monitor in real-space the evolution of plasmon dipolar mode of a stationary antenna structure as multiple resonantly matched dipolar plasmon particles are closely approaching it. Interparticle separation, length and polarization dependent studies show that the cross geometry structure favors strong interparticle charge–charge, dipole–dipole and charge–dipole Coulomb interactions in the nanometer scale gap region, which results in strong field enhancement in cross-bowties and further allows these structures to be used as polarization filters. The nanoscale local field amplitude and phase maps show that due to strong interparticle Coulomb coupling, cross-bowtie structures redistribute and highly enhance the out-of-plane (perpendicular to the plane of the sample) plasmon near-field component at the gap region relative to ordinary bowties.

1 Introduction

Plasmonic optical antennas lead to strong localization and enhancement of electromagnetic radiation below the diffraction limit.1–5 They are at the heart of some of the most innovative technological applications based on manipulation of photophysical processes at the nanometer scale. These include high-resolution microscopy and spectroscopy, solar energy conversion, photocatalysis, nanoscale optical circuits and quantum optics and communication.6–11

Since the local plasmon near-field distribution determines the effectiveness of antennas, their investigation has been the focus of several studies using techniques that involve either electrons12,13 or photons.14–20 These techniques have explored a number of parameters, including imaging of geometry-related spatial patterns of antenna resonances, intensity characterization of hotspots,21,22 energy-resolved plasmon eigenmodes,23,24 multi-photon photoluminescence,25,26 harmonic generation or frequency mixing,25,26,27 and emission patterns of nanoantennas.27,28

To achieve improved structures with superior function, designs that involve multiple nanoantenna components that are near-field coupled to each other are required.22,24,29–31 Various theoretical models have been proposed to elucidate near-field plasmon interactions.32–34 A fascinating analogy has been made between plasmon coupling and atomic orbital hybridization well-known in molecular physics.32,35 Beginning with the pioneering work of Prodan et al.32 the plasmon hybridization model has been used to explain plasmon resonances in metal nanoshells,15,32,36–37 thin metallic films,18,39 nanoparticles,40 spherical dimers,41 rod dimers,22,24,30 and nanoparticle aggregates,42 mainly in the optical frequency regime. Individual particle plasmon resonance modes corresponding to discrete orbital angular momentum values then form hybridized modes with other particles or cavities, depending on the geometry. However, direct experimental studies of the near-field interactions in the nanometer gap regime are difficult due to limitations imposed by both nanofabrication and nanocharacterization techniques. In particular, the nanoscale interactions of several plasmonic structures and the spatial evolution of the field distributions in real space remain mostly unexplored.4,20,43–47

Here we perform polarization-selective scattering-type scanning near-field optical microscope (s-SNOM) measurements to directly visualize the dipolar near-field distributions and couplings of plasmonic triangles, bowties and cross-bowtie antennas in the mid-infrared (9–11 μm) spectral regime. We systematically investigate the coupling mechanism by first imaging the near-field distribution of a single triangular antenna. While monitoring its
field distribution, we add another identical antenna closer and closer to it (essentially forming bowties of varying gap width). We then cross the existing bowtie with another bowtie (forming a cross-bowtie at varying proximity distances) and monitor the evolution of the strongly coupled dipolar field distribution modified through inter-antenna charge–dipole and dipole–dipole Coulomb interactions by performing polarization control measurements.

The triangular plasmonic metal nanostructures concentrate plasmons into the sharp end and smear them over the widened base, resulting in dipolar modes with higher field intensity at the sharp end, and a largely suppressed field at the base.\textsuperscript{48–51} We find that the aspect ratio, the base and sharp end width determine the symmetry and intensity of localized field profiles, both for single particles and particle aggregates.\textsuperscript{48,50,51}

Employing the cross-polarized S/P s-SNOM imaging scheme (exciting along the in-plane direction, S-excitation, and detecting the out-of-plane near-field component, P-detection), we further demonstrate that cross-bowtie structures could be used as active infrared polarization filters. Such devices would be of interest to realize antenna structures for surface-enhanced infrared absorption spectroscopy, to manipulate optical fields in subwavelength field distributions, plasmonic filtering and polarization selection applications.

## 2 Experimental

The experimental setup is a commercial s-SNOM system (NeaSNOM, neaspec.com), which has been described before.\textsuperscript{20,52,53} Briefly, a probing CO\textsubscript{2} laser is linearly S polarized throughout the experiment and is focused on the tip–sample interface at an angle of $\sim 50^\circ$ from the sample surface. The scattered field is acquired using a pseudoheterodyne interferometric detection scheme. Suppression of the background signal is achieved by vertical tip oscillation at the cantilever’s mechanical resonance frequency ($\Omega \sim 285$ kHz) and demodulation of the detector signal at higher harmonics $n\Omega$. In this work, second harmonic demodulation ($n = 2$) is used for all experiments. The combination of the scattered field from the tip and the reference beam passes through a linear polarizer which further selects the P polarization of the measured signal for analysis (see ESI†).

The Au plasmonic samples are fabricated \textit{via} electron-beam lithography as a grid of $\sim 26$ nm thick single triangle, bowtie or cross-bowtie structures atop a 3 nm Ti adhesion layer on a SiO\textsubscript{2} substrate. Each structure in the grid has systematically and symmetrically incremented the interparticle distance ($\sim 57–137$ nm) and length ($\sim 1284–1766$ nm), covering a wide range of possible geometric combinations.

Experimental results are theoretically supported by finite-difference time-domain (FDTD) simulations (Lumerical Inc., lumerical.com). For all simulations (unless otherwise specified), each Au triangle was modeled by a trapezoidal polygon, possessing a 26 nm thickness, 50 nm sharp tip width, 450 nm wide triangle base, and 1800 nm length. These dimensions were averaged from topography scan measurements. Each particle is simulated atop a SiO\textsubscript{2} substrate. The optical excitation source is a mid-infrared (9–11 $\mu$m) plane wave.

## 3 Results and discussions

Triangular antenna structures offer an extra degree of control since the hotspot field strength and spatial localization at the ends of the antenna can be controlled by varying the widths of the sharp and broad ends. Fig. 1 shows experimental topography, near-field amplitude and phase images of a single triangular antenna. The optical near-field amplitude and phase images were acquired using the S/P scheme, with excitation wavelength fixed at $\lambda = 10.5$ $\mu$m, and the polarization direction fixed along the longitudinal axis of the antenna structure. The amplitude image displays strong optical contrast at the sharp end and at the base, while the phase image shows a $180^\circ$ phase shift between each half of the triangle, confirming a dipolar resonance mode.\textsuperscript{45,54}

We performed FDTD calculations to explore the structural dependence of the plasmon field distribution across the antenna. Fig. 2(a) shows FDTD near-field intensity ($|E_z|^2$) images, calculated from the out-of-plane (perpendicular to the sample plane)
$E_z$ field, and corresponding line profiles extracted across the longitudinal axis (Fig. 2(b)). The width of the sharp end and the length of the rod are fixed at 50 nm and 1800 nm respectively.

As the width of the rod at one end increases, the intensity measured at the fixed end, marked in Fig. 2(a), decreases dramatically, while intensity at the expanding end decreases with a weak resonance peak at around 75 nm. When the base width of the triangle is equal to the fixed end width, the particle is essentially a rod, with a symmetric optical amplitude profile as shown in the inset in Fig. 2(c).\(^{17,29,30,48,50}\) Increasing the width of the base shifts the resonance peak to lower energy and localizes the strong near-fields at the ends of the triangle asymmetrically (see ESI†). Spectroscopic FDTD calculations show the higher amplitude signal at the tip than at the base of the triangles, which is a combination of strong field concentration at the tip and shift of resonance frequency as the base widens (see ESI†). These results indicate the importance of structure optimization for resonant hotspot localization in such plasmonic structures.

Fig. 3 displays experimental topography, optical near-field amplitude and phase images of a bowtie (Fig. 3(a)) and cross-bowtie (Fig. 3(b)) antenna structures. The amplitude and phase images were acquired at excitation wavelength fixed at $\lambda = 10.5$ $\mu$m, and the incident laser polarization direction is fixed along the longitudinal bowtie axis of the structures as shown by the white arrow in the amplitude image of Fig. 3(a). Optical images display no contrast in the gap region as a result of the white arrow in the amplitude image of Fig. 3(a). Optical images display no contrast in the gap region as a result of the white arrow in the amplitude image of Fig. 3(a). Optical images display no contrast in the gap region as a result of the white arrow in the amplitude image of Fig. 3(a). Optical images display no contrast in the gap region as a result of the white arrow in the amplitude image of Fig. 3(a). Optical images display no contrast in the gap region as a result of the white arrow in the amplitude image of Fig. 3(a).

In Fig. 4 we first systematically investigate using FDTD the effect of mutual interactions on the near-field intensity $(|E_z|^2)$ of a single antenna structure as bowtie and cross-bowtie structures are brought in close proximity to it. Line plots in Fig. 4(a)–(d) show FDTD calculations of the localized intensity as a function of interparticle separations calculated at the location “X” in each corresponding colored illustration (bottom of Fig. 4(a)–(d)). All single antenna structures have identical geometric dimensions (length 1800 nm, base width 450 nm, sharp tip width 50 nm) and the excitation polarization is oriented horizontally as shown in Fig. 4(d) by the double sided black arrow. The interparticle separation is measured along the black arrow shown in illustration, Fig. 4(a), (b) and (d). As a baseline for comparison, we show the constant intensity of a single triangular antenna structure at position “X” in Fig. 4(a), which can be thought of as an infinite sized gap bowtie (Fig. 4, dotted black line). The red dash-dotted curve (Fig. 4(b)) shows the intensity of a stationary triangle at the position “X” as a function of the separation with a second triangle. The comparison of curve (a) and curve (b) shows how the field intensity on a stationary structure is modified due to an approaching antenna. In the cross-bowtie structures, the minimum gap width is limited by the sharp tip widths. As a baseline for comparison, we show the constant maximum intensity value taken at a 60 nm gap bowtie shown by the green straight dashed line in Fig. 4(c), which may be considered to be a cross-bowtie antenna with infinite separation between vertical arm pairs. The solid blue curve in Fig. 4(d) shows the stationary bowtie near-field intensity modification taken at position “X” as a function of the vertical arm pair interparticle separation. These calculations show strong interparticle separation dependence on the field intensity and that cross antennas redistribute the fields, putting more field intensity near their gaps compared to bowties. Animation showing the evolution of the near-field intensity of a cross-bowtie as multiple antenna structures are assembled is shown in the ESI†.
Experimentally, we further explore this proximity effect on the plasmon near-field distribution by imaging several similar geometry cross-bowties with varying gap width. Fig. 5 compares experimental s-SNOM topography, second harmonic amplitude ($s_2$) and phase ($\phi_2$) images of the smallest and largest gap width cross-bowties imaged, 57 nm gap width (Fig. 5(a)) and 137 nm gap width cross-bowties (Fig. 5(b)). In both amplitude and phase images, the bowtie along the polarization direction is resonantly excited maintaining dipolar modes in each arm for the gap widths studied here.\(^{54}\) The cross-bowtie arm transverse to the polarization axis displays weak contrast with asymmetric splitting along the arm length. Without a priori knowledge to the polarization direction, the optical images could clearly indicate the incident beam polarization direction, showing that the cross antenna structures could serve as polarization indicators. The asymmetric splitting in the optical images is a result of slight misalignment of the sample with the excitation polarization; with a perfect alignment the splitting should be symmetric about the bowtie axis (see ESI† for FDTD calculation images). Further simulation results showing the evolution of the near-field intensity of a cross-bowtie as the sample is rotated with respect to a fixed polarization of the light source is shown in the ESI.\(^{†}\)

The amplitude images clearly show stronger optical contrast for a 57 nm gap width cross-bowtie compared to that of a 137 nm gap cross-bowtie. In Fig. 5(c), quantitative experimental optical amplitude signals (normalized to the SiO\(_2\) substrate) taken at the position marked by a green “X” in Fig. 5(a) and (b) are plotted as a function of measured gap widths, demonstrating the increase in amplitude contrast as the spacing between the cluster of particles decreases. This result is fully reproduced by FDTD calculations of the field intensity as a function of gap width shown in Fig. 5(d), using similar dimension cross-bowties to that for the experiment at excitation wavelength, $\lambda = 10.5$ $\mu$m. Calculations for bowties are also shown in the same figure for comparison, revealing for the same gap width stronger intensity in cross-bowties. We note that in Fig. 5(d) the cross-bowtie smallest gap width is limited by the width of the sharp tip.

We systematically further explore and quantify the outstanding capability of cross-bowties to enhance light in the gap region compared with single triangular antennas or bowties by performing controlled experiments and FDTD calculations. In Fig. 6(a)–(c) we show experimental normalized (to SiO\(_2\) substrate) near-field amplitude signal average (normalized to their minima) taken at the sharp end of a triangular antenna when it is isolated or forming a bowtie and a cross-bowtie antenna structures as a function of antenna length. In Fig. 6(e) we show amplitude maps of the antenna array for these measurements, while in Fig. 6(d)
we show FDTD simulation of the field intensity using the same parameters as that for the experiments. Since the length range studied in our experiment is smaller than the characteristic resonance length at $\lambda = 10.5 \, \mu m$, antenna field enhancement and so the normalized near-field amplitude contrast increases with length for all the structures shown in Fig. 6(a) and (b) which is also recently reported by Brown et al.\textsuperscript{55} We observe that the field intensity and so the dipolar amplitude contrast and its increase with length (comparing slopes in Fig. 6) are largest in cross-bowtie structures compared to bowties or single antenna structures as shown experimentally (Fig. 6(a)) and by FDTD calculations (Fig. 6(b)).

Both the gap dependence (Fig. 4 and 5) and the length dependence (Fig. 6) studies indicate that the field enhancement in cross-bowtie antenna structures is modified strongly by inter-antenna mutual interactions. To understand the nature of the interaction around the gap region better we performed FDTD simulation of the charge density distributions of the antenna structures with similar geometry and gap width to the experiments and compare their charge densities with each other and with their corresponding field intensities. Fig. 7 shows a zoom-in map of the charge densities of a single triangular antenna (Fig. 7(a)), a bowtie (Fig. 7(b)), and a cross-bowtie (Fig. 7(c)), and the corresponding field intensity images are shown in Fig. 7(d)–(f). Charge density distribution is calculated by taking the difference of $E_z$ 2 nm above and 2 nm below the top surface of structures, which is proportional to charge density by Gauss' Law. The spatial charge density images show strong dipolar charge localization along the polarization axis (shown in Fig. 6(a) with positive charges marked blue and negative charges red). The bowtie transverse to the polarization axis in Fig. 7(c) also shows charge distribution along the width of the bowtie with a dipole oriented along the excitation polarization direction. Comparison of the charge density values of the three structures at the locations marked by “X” in Fig. 7(a)–(c) reveals that the charge density on a cross-bowtie is 1.2 times that of a bowtie and 2.5 times that of an isolated triangular antenna. This corresponds to an intensity on the cross-bowtie which is 1.4 times than that of a bowtie and 3.9 times than that of an isolated triangular antenna. The extra charge on the cross-bowtie at the antenna tip location shown in Fig. 7(c) is due to dipole–dipole, charge–dipole and charge–charge complex interactions at dielectric proximity on a nanometer scale with the transverse bowtie. In addition to the effect of the dipole–dipole interaction of the other longitudinal arm of the bowtie, the charges at the tips of the bowtie oriented along the polarization axis feel attractive charge–charge, charge–dipole and dipole–dipole Coulomb interactions from both the upper and lower arms of the transverse bowtie. This is clearly shown in the charge density calculation in Fig. 7(c), where charge–charge interactions occur between the blue positively charged regions on the left side of the vertical arms and neighboring red negatively charged left bowtie arm, and similarly for the right side regions of opposite charges. Along the horizontal axis, each vertical arm forms a dipole, which also interacts with the charges on the individual neighboring bowtie arms. Moreover, the dipole formed across the horizontal bowtie gap interacts with the charges on the vertical bowtie arms. These additional Coulomb interactions pump more charge to the tips of the antennas generating strong light confinement at the gap region. As the gap width decreases, the mutual dipolar Coulomb coupling increases resulting in larger amplitude contrast as shown in Fig. 5. Inter-antenna Coulomb interaction becomes weak and so is the near-field enhancement as the triangular antennas are pulled apart from each other. As the length of the triangular antennas increase, Coulomb interactions between closely confined antenna structures also increase which in turn increases the field intensity associated with each antenna. Much larger enhancement could be found in the immediate area surrounding the tips of the antenna rods by forming such antenna structures using longer rods or tuning the excitation laser to their resonance peaks.

4 Conclusion

S-SNOM imaging and FDTD simulations show that triangular plasmonic antenna structures produce asymmetrical dipolar plasmon resonances, characterized by a highly confined field intensity hotspot at the sharp end compared to the wider base. Using cross-polarized s-SNOM amplitude contrast, we quantify plasmon nanoscale interactions of multiple infrared antenna structures. We find that the detected $P$ component of the amplitude in cross-bowties shows a stronger signal compared to bowties with similar gap width and geometry as evidence of multiple dipole–dipole and charge–dipole Coulomb interactions. The spatial evolution of the near-field intensity and polarization dependence in cross-bowties reveal that these structures act as infrared polarization selectors. Future wide wavelength range spectroscopic imaging experiments using broadband light source and varying particle geometry dependent studies, as well as the in-plane detection scheme where the hotspot in the gap region can be mapped in the coupling region of the antenna structures, will help to further elucidate the full details of the observed plasmonic coupling multiple interactions we present.

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