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Robust plasmonic hot-spots in a metamaterial lattice for enhanced sensitivity of infrared molecular detection

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High-density and long-lived plasmonic hot-spots are an ideal system for high-sensitive surfaceenhanced infrared absorption (SEIRA), but these conditions are usually incompatible due to unwanted near-field coupling between the adjacent unit structures. Here, by fully controlling plasmonic interference in a metamaterial lattice, we experimentally demonstrate densely packed long-lived quadrupole plasmons for high-sensitive SEIRA. The metamaterial consists of a strongly coupled array of super- and sub-radiant plasmonic elements to exhibit an electromagnetic transparency mode at 1730 cm^{-1} , which spectrally overlaps with the C=O vibrational mode. In the SEIRA measurement, the C=O mode of poly(methyl methacrylate) molecules is clearly observed as a distinct dip within a transmission peak of the metamaterial. The corresponding numerical simulations reveal that constructive interference uniformly forms coherent quadrupole plasmons over the metamaterial lattice, leading to a stronger molecular signal from the system. Our metamaterial approach provides a robust way to construct ideal hot-spots over the sample, paving the way toward a reliable sensing platform of advanced infrared inspection technologies. *Published by AIP Publishing*. https://doi.org/10.1063/1.5004703

Controlling the near-field coupling of metallic nanostructures has played a central role in the field of plasmonics with potential applications in integrated optics, solar energy harvesting, and bio-chemical sensing.¹⁻⁴ Recent advances in nanofabrication have further developed plasmonic complexes, allowing for interesting hybridized responses inaccessible by individual elements. $^{5-8}$ In particular, it is well known that a plasmon mode can be either super- or subradiant depending on radiative losses, and their coupling gives rise to asymmetric Fano resonance with the steep dispersion.^{9–11} The quality factor of Fano resonance can be also very high by engineering their coupling strengths, thereby efficiently trapping the incident light into a long-lived sub-radiant mode.^{12,13} Such geometry-dependent plasmon characteristics offer a new capability to manipulate optical confinement at the nanoscale, i.e., plasmonic hot-spots, as well as their spectral responses.^{14,15} A plasmonic metamaterial is an advanced example,^{16–18} where macroscopic optical properties, permittivity and permeability, of plasmonic ensembles can be tailored at will, overcoming fundamental limitations in conventional optics.^{19–25}

Surface-enhanced infrared absorption (SEIRA) is the promising application by fully utilizing plasmonic resonant

nature for strong optical interaction with molecules.²⁶ Plasmonic hot-spots have been traditionally investigated on metal island films, but they suffer from poor reproducibility due to the uncontrolled surface nanostructures.²⁷ Well-defined plasmons in optical nanoantennas were recently proposed for the resonant SEIRA where the spatial and spectral mode overlapping were dramatically improved between the plasmons and molecular vibrations.^{28–33} Engineered infrared (IR) metamaterials were also demonstrated for the backgroundsuppressed SEIRA to gain a large vibrational signal contrast for better sensitivity.^{34,35} Based on such hot-spot engineering in tailored plasmonic nanostructures, atto/zeptomole sensitivity of SEIRA is now practically possible for specific conditions. On the other hand, for reliable IR inspection of small amounts of molecules, the surface density of hot-spots over the sample is also crucial to trap as many as possible molecules contributing to the vibrational signal from the system.³⁶ However, once plasmonic elements with enhanced hot-spots are closely packed, unwanted near-field coupling between the adjacent unit structures usually modifies their mode profiles, thereby rendering the hot-spots broad and weak; therefore, increasing the hot-spot density while maintaining their quality factors remains a major challenge.^{37–40}

Here, we address this issue by fully controlling plasmonic interference in a metamaterial lattice for high-sensitive SEIRA. Specifically, we study the near-field coupling in a metamaterial consisting of a strongly coupled array of super- and sub-radiant

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plasmonic elements to exhibit classical analogue of electromagnetically induced transparency (EIT) arising from Fano resonance.^{41–44} Different from our previous work,³⁵ we introduce lateral displacement of the unit cells in the EIT metamaterial to engineer their near-field coupling and the resultant spectral response. Based on constructive interference of longlived quadrupole plasmons in the lattice, highly dispersive dense hot-spots are uniformly formed over the sample. The high-sensitive SEIRA is then demonstrated by utilizing the resonant coupling between the EIT mode of the metamaterial and IR vibrational mode of polymer molecules.

Figure 1(a) shows the schematic super-cell of the fabricated EIT metamaterial consisting of four unit cells where each unit cell is made of a horizontal Au bar coupled with a pair of vertical Au bars. The overall structure of the metamaterial was carefully designed by considering not only the intra-/inter-unit cell coupling but also their balance. The fabrication process started with spin-coating of a 100-nm thick poly(methyl methacrylate) (PMMA) resist (MicroChem, 950-A2) onto a 325- μ m thick double-side polished non-dope Si substrate. A two-dimensional periodic pattern of the metamaterial was exposed by an electron beam (EB) lithography system (Elionix, ELS-S50) over an area of $100 \times 100 \,\mu\text{m}^2$. The sample was then completed by Cr/Au (2/20 nm) deposition using a resistive heating evaporator and liftoff process. The geometrical parameters were w = 200, $l_{x(y)} = 950$ (850), $g_{x(y)} = 550$ (150), and $P_{x(y)} = 1500$ (1350) nm. As shown in the scanning electron microscopy (SEM) images [Figs. 1(b)-1(d)], three types of metamaterials were fabricated with different lateral displacements of d=0 (green), $P_x/4$ (blue), and $P_x/2$ (red) to control the near-field coupling among the adjacent unit cells. Depending on plasmonic interference in



FIG. 1. Design and fabrication of metamaterials. (a) Schematic super-cell of an EIT metamaterial on a Si substrate consisting of 20-nm thick Au bars coupled with Au bar pairs. The geometrical parameters are w = 200, $l_{x(y)} = 950$ (850), $g_{x(y)} = 550$ (150), and $P_{x(y)} = 1500$ (1350) nm. (b)–(d) SEM images of the fabricated metamaterials with different lateral displacements of d=0(green), $P_x/4$ (blue), and $P_x/2$ (red) to control the near-field coupling among the adjacent unit cells, thereby tuning the excitation of the EIT mode at 1730 cm⁻¹.

the lattice, the quadrupole mode in the bar pairs is constructively excited at 1730 cm^{-1} , which spectrally overlaps with the C=O vibrational mode.

The transmission properties of the metamaterials were experimentally characterized by using a Fourier-Transform Infrared Spectrometer (FT-IR) equipped with a polarized infrared microscope (JASCO, FT/IR-6300FV and VIRT-3000). To improve the signal-to-noise ratio of the spectra, a square aperture with an area of $100 \times 100 \ \mu m^2$ was installed at the pupil plane of the microscope and a sample chamber was purged with dry nitrogen gas. Figure 2(a) shows the measured transmission spectra of the metamaterials with different lateral displacements for the x-polarized incident light. Here, the measured spectra were normalized by those of a bare Si substrate to discuss only the optical responses of the metamaterials. Without a lateral displacement of d=0 (green), a typical transmission dip is observed in the shaded region due to the dipole plasmon resonance of the horizontal bars. For $d = P_x/4$ (blue) and $P_y/2$ (red), on the other hand, an EIT-like transmission peak clearly appears within the dip due to constructive interference of the quadrupole plasmons in the lattice. These observations are well supported by the corresponding numerical results in Fig. 2(b), which were obtained by using the three-dimensional electromagnetic simulation software, CST Microwave Studio, with $\varepsilon_{Si} = 11.56$ and the empirical value for ε_{Au} .⁴⁵ For the y-polarization, on the other hand, only the dipole plasmon resonance of the vertical bars was observed at a higher frequency (see supplementary material, Fig. S1).

Figure 3 shows the corresponding mode profiles of the metamaterials at 1750 cm^{-1} in Fig. 2(b). Note that Figs. 3(b) and 3(c) are plotted using the same color bar such that the amplitude of J_x and J_y can be directly compared with each other. At the unit cell level, the x-polarized incident light is predominantly coupled to the dipole mode in the horizontal bars, and then the quadrupole mode in the bar pairs is excited through the near-field coupling. The plasmonic interference between these super- and sub-radiant (dipole and quadrupole) modes forms Fano resonance characterized by an EIT-like optical response. In the metamaterial lattice, however,



FIG. 2. IR characterization of metamaterials. (a) Experimentally measured transmission spectra of the metamaterials and (b) corresponding numerical results, which well reproduced the experimental ones qualitatively and quantitatively. With a lateral displacement, an EIT-like transmission peak clearly appears in the shaded region due to constructive interference of the quadrupole plasmons in the metamaterial lattice.



FIG. 3. Mode profiles of metamaterials. (a) Schematic of the charge distributions and numerically simulated (b) J_x , (c) J_y , and (d) |E| distributions at 1750 cm⁻¹ in Fig. 2(b). For d=0 (the left column), only the dipole mode in the Au bars is allowed due to the near-field coupling between the vertical neighboring unit cells, while the quadrupole mode in the Au bar pairs is constructively excited for $d=P_x/2$ (the right column). The $d=P_x/4$ (the center column) is the intermediate state where both the dipole and quadrupole modes are excited simultaneously.

the additional near-field coupling among the adjacent unit cells dramatically modifies the mode profiles and resultant spectral responses. In the case of d=0 (the left column), since the charge distributions of the quadrupole mode in the bar pairs always conflict between the vertical neighboring unit cells, the quadrupole mode is strictly prohibited; therefore, only the dipole mode in the horizontal bars is allowed in the lattice, exhibiting a single transmission dip, as shown in Fig. 2. For $d = P_x/2$ (the right column), on the other hand, a half-period lateral displacement allows constructive interference of the quadrupole plasmons through the horizontal bars within the super-cell. Such a mode profile coherently extends over the lattice to exhibit a pronounced EIT-like transmission peak, as shown in Fig. 2. The $d = P_x/4$ (the center column) case is the intermediate state where both the dipole and quadrupole modes are excited simultaneously.

Since the metamaterial lattice with $d = P_x/2$ offers not only a highly dispersive EIT spectral response but also highdensity hot-spots over the sample, it can be a robust and reliable sensing platform for high-sensitive SEIRA. Here, we explore EIT metamaterial-enhanced IR absorption by utilizing the resonant coupling between the plasmonic modes of the metamaterials and IR vibrational modes of molecules. In the SEIRA measurement, PMMA was used as a test specimen to exhibit a typical C=O stretching vibrational mode at 1730 cm⁻¹. PMMA resist (MicroChem, 950-A2) was uniformly spin-coated onto the metamaterial surface with a thickness of 50 nm, which was determined by using an optical surface profiler (Zygo, NewView 7300). Using the PMMA molecular weight (950×10^3) and solid density (1.2 g/)cm³), ~630-attomole PMMA molecules, i.e., $\sim 3.6 \times 10^{12}$ C=O bonds, existed within the sample area $(100 \times 100 \,\mu\text{m}^2)$ for the current experimental condition. Figure 4(a) shows the measured transmission spectra of the PMMA-coated metamaterials with different lateral displacements. Minor absorption dips near 1450 cm^{-1} and 1380 cm^{-1} are due to CH₂ and CH₃ bending vibrational modes. In the case of d = 0 (green), the resonant coupling between the dipole and C=O modes produces a clear anti-resonant peak within a transmission dip of the metamaterial. For $d = P_x/2$ (red), on the other hand, a distinct antiresonant dip appears within an EIT-like transmission peak of the metamaterial. The molecular signal strength for the $d = P_x/$ 2 (red) case is about 2 times larger than that for the d=0(green) case; this can be naturally understood by considering the double hot-spot density in the $d = P_x/2$ (red) lattice, compared to that in the d=0 (green) lattice. Note that such enhanced sensitivity was also obtained for the unpolarized incident light (see supplementary material, Fig. S2).

To better understand the underlying mode interactions in the metamaterial-molecular coupled system, another set of numerical simulations was carried out as shown in Fig. 4(b). In the calculation, the C=O bond in the PMMA layer was modeled as a Lorentz oscillator with the functional form: $\varepsilon_{PMMA} = \varepsilon_b + \frac{f_m \omega_0^2}{\omega_0^2 - \omega^2 - i\gamma\omega}$, where ε_b is the background relative permittivity, f_m is the reduced oscillator strength, ω_0 is the C=O vibrational frequency, and γ is the damping constant (FWHM).^{33,46} The parameters, ε_b , f_m , ω_0 , and γ , were appropriately chosen such that the oscillator model emulated the



FIG. 4. EIT metamaterial-enhanced IR absorption. (a) Experimentally measured transmission spectra of a 50-nm thick PMMA film on the metamaterials and (b) corresponding numerical simulations. The resonant coupling of the quadrupole (dipole) and C=O modes at $\omega_{C=O}$, indicated by the dashed lines, results in an anti-resonant dip (peak) within the spectral line-shape of the metamaterials. (c) Numerically simulated |E| distributions at $\omega_{C=O}$ in (b). The highly dispersive dense quadrupole mode for $d = P_x/2$ (the right) is strongly disturbed by the C=O mode, giving a stronger molecular signal compared to the dipole mode case for d = 0 (the left).

vibrational absorption of the C=O mode. An excellent agreement between the experiment and simulation was obtained not only for the signal strength but also for deformation of the spectral line-shape of each metamaterial lattice.

Figure 4(c) shows the corresponding |E| distributions at $\omega_{C=0}$ in Fig. 4(b). In the metamaterial-molecular coupled system, the C=O mode behaves as a local oscillator with a finite absorption to disturb each metamaterial lattice in different ways. In the case of d=0 (the left), the C=O mode quenches the dipole plasmons in the horizontal bars, producing a typical anti-resonant peak within a transmission dip of the metamaterial. Compared to the left (green) of Fig. 3(d), the mode profile in the horizontal bars remains the same, but the electric field intensity around the bars drops by $\sim 70\%$ due to the quenching by the C=O mode. For $d = P_x/2$ (the right), on the other hand, the C=O mode strongly disturbs sensitive interference of the quadrupole plasmons in the lattice, rather than the quenching. As a result, the pure quadrupole mode [the right (red) of Fig. 3(d)] is dramatically modified as a mixture of the dipole and quadrupole modes, translating into distinct far-field spectral responses. Such a highly dispersive dense quadrupole mode contributes to a stronger molecular signal compared to the dipole mode case for d=0 (the left). Note that additional evaluation in the SEIRA measurement (see supplementary material, Fig. S3) showed that the ultimate sensing capability of the metamaterial lattice was the zeptomole level, which is comparable to the previous works.^{33,35}

In conclusion, a spectroscopic technique based on highdensity and long-lived hot-spots was proposed and demonstrated by fully controlling plasmonic interference in an EIT metamaterial lattice. The resonant coupling of the EIT mode of the metamaterial and IR vibrational mode of polymer molecules was demonstrated for high-sensitive SEIRA. The corresponding numerical simulations revealed that constructive interference uniformly forms coherent quadrupole plasmons over the metamaterial lattice, leading to a stronger molecular signal from the system. Our approach based on robust hotspots in a metamaterial lattice may hold great promise for realizing a reliable sensing platform of advanced IR inspection technologies.

See supplementary material for the polarization dependence of the transmission spectra and the ultimate sensing capability of the metamaterial lattice.

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