Mid-infrared narrow band plasmonic perfect absorber for vibrational spectroscopy

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ABSTRACT

The introduction of narrow band perfect absorbers (PAs) operating in mid-infrared (IR) frequencies has the potential to improve the study of biomolecule monolayers using surface enhanced vibrational spectroscopy. However, wavelength dependent radiation and nonradiative losses are limiting factors to obtain narrow band absorption resonance, having full width at half maximum (FWHM) below 150 cm^{-1} in the mid-IR frequency range. In this work, we numerically and experimentally present an engineered narrow band PA with FWHM of 85 cm^{-1} operating in mid-IR frequencies. The PA is based on multi-layer metamaterial plasmonic nanoantennas. We used numerical and experimental work to fine tune the parameters of the PA in order to control its spectral response. The suggested PA system strongly provides high absorption values (100 %) in the mid-IR region and near-field enhancement factor of 10^3 at the corresponding resonance values. The fabricated PA shows strong narrow band resonance and all the resonance energy could be transferred to thin films (10 nm) for higher sensitivity. In addition, PA shows multi-band resonances within the mid-IR region, thus it can be effectively used for simultaneously detecting the different biomolecular fingerprints. In this sense, we experimentally observed absorption of carbonyl $\nu(\text{C}=\text{O})$ and asymmetric methyl $\nu(-\text{CH}_3)$ stretching bands of thin polymethyl methacrylate (PMMA) film on the narrow band resonances of PA. The suggested system has potential to be used in live cell-membrane investigations, as multi-band structure enables investigation of both lipids and proteins.

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1. Introduction

Among many optical biosensing techniques vibrational spectroscopy has been instrumental as it is capable of both identification and detection of molecules [1–3]. This technique is based on the fact that molecule-specific vibrations occur in mid-infrared (IR) range ($3\text{--}8\text{ }\mu\text{m}$ wavelengths) [4]. In this process, light is absorbed by the dipolar molecular bond at certain frequencies, and this absorption can be tracked to identify the molecules and molecular structures/orientations [5]. Surface enhanced infrared absorption (SEIRA) spectroscopy technique utilizes this approach for sensitive characterization of even few biomolecules [6]. Surface enhancement is provided by active plasmonic surfaces that act as an antenna which can direct the light to a biomolecule (lipid, protein, polymer,

etc.) at its specific absorption frequency. Thus, the energy radiated by the nanoantennas could be transferred to the biomolecule for enhancing the absorption signal intrinsic to molecular bonds [7–13]. The intensity of the directed light, also called the enhanced near electric field (E), is proportional to the absorption signal that arises from the biomolecule [14,15]. This implies that when the resonance band of the plasmonic nanoantenna is narrow, we could transfer more resonance energy towards the biomolecule, precisely at the absorption frequency of the molecular bonds [15]. That results in more significant absorption signal generation from the same number of molecules, thus higher sensitivity can be obtained by a narrow band resonance nanoantenna [16–18]. In addition, using narrow band plasmonic resonances, we can obtain resolutions that can probe each specific molecular absorption frequencies, even if they are separated only by 100 cm^{-1} . The IR vibrational fingerprints provide intrinsic information on the molecular structures of biomolecules and enable detection and more importantly identification of them. For instance, the amide I fingerprint of a protein contains conformational information that is crucial for understand-

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ing its function. Using the narrow-band antennas, one can also detect and sense the presence of such molecules, as well as acquire special information intrinsic to biomolecule [7].

Metamaterial PAs opened new doors to the field of optical energy harvesting devices. By providing narrow band plasmonic resonances, PAs have the potential to further improve the surface enhanced vibrational spectroscopy platforms. PAs can be typically designed using three functional layers that comprise a dielectric interlayer sandwiched between the bottom metal film and a patterned top metal plasmonic nanoantenna serving as a resonator [19]. Three-layered configuration includes an important parameter, dielectric layer thickness that allows to bring the absorption level to unity (100 %) and width of the resonance down to 85 cm^{-1} (Quality factor, $Q = \lambda / \Delta\lambda = 22$). The top layer of PAs which are subwavelength plasmonic antenna components, absorb most of the incident radiation at the operating frequency. In earlier reports of metamaterial PAs, near unity absorption was explained over a narrow frequency range by minimizing the reflectance with perfect impedance matching ($z = \sqrt{\mu/\epsilon} = 1$, complex electric permittivity (ϵ) and magnetic permeability (μ)) while eliminating the transmittance with the metal film [19]. Engineered PAs can create intense confined hotspots of the incident light which provide strong interaction with adjacent analytes and make them ideal candidates for biosensing and spectroscopy applications [20–22]. Resonance frequencies of these structures can be tuned to molecular resonance frequencies of biomolecules and polymers in mid-IR [10,23]. Functionalization of PAs with molecules results in coupling plasmonic resonances with molecular absorption [24]. This coupling supports Fano line shapes that occur in the presence of interference between one spectrally broad and one narrow energy state [25–28]. Molecular bands of polymers have narrow band infrared spectral features [29]. By designing narrow band metasurfaces, we can reach these molecular bands precisely one by one.

In this work, we present a new narrowband metamaterial PA operating in the mid-IR frequency regime that is relevant to analysis of biomolecules and demonstrate the usage of a narrow-band PA for sensing with vibrational spectroscopy for the first time. The structure is composed of multiple, stair-like changing-length rod antennas placed horizontally and vertically, as shown in Fig. 1(a). We analyze the nanoantenna design in finite difference time domain (FDTD) based commercial software Lumerical FDTD Solutions [30]. We analyze geometrical parameter sensitivity of the structure by changing the lengths of the nanorods finely to tune the resonance frequency to molecular absorption frequencies of polymethyl methacrylate (PMMA). At resonance frequencies, PA platform shows high near-field intensity enhancement ($|E^2|/|E_{\text{incident}}^2|$) with large area of hotspots which are indispensable to improve the light-matter interaction. In experimental study, an optically thick gold (Au) film and an ultra-thin ($< \lambda/50$) magnesium fluoride (MgF_2) spacer are coated orderly on silicon (Si) to prepare multilayered metamaterial perfect absorbers. By using standard e-beam lithography and lift-off processes, top metallic nanoantennas are formed on MgF_2 layer. We use a Fourier transform infrared (FTIR) spectrometer coupled to an IR microscope to obtain the absorption spectrums of the fabricated platforms. Once we tune the antenna resonance to the molecular absorption frequencies of PMMA, we experimentally place a 10 nm-thick PMMA film in the close vicinity of the PAs and match the plasmonic resonances of the PA with carbonyl ($\text{C}=\text{O}$) stretch band (1729 cm^{-1}) and asymmetric methyl ($-\text{CH}_3$) stretch band (2952 cm^{-1}) of the PMMA thin film. Using the narrow band metamaterial PA, we obtained very high molecular absorption signals from PMMA compared to prior reported PA's. Chen et al. [31] demonstrated experimental dual-band PA in the mid-IR regime. In that work, experimental FWHM values of dual-band resonances are signif-

icantly broader (167.5 cm^{-1}) compared to our results, thus the PMMA absorption signal observed on the antenna resonance is barely visible. Chen et al. used only 4 nm thick PMMA layer (in comparison to 10 nm), still the measured asymmetric methyl ($-\text{CH}_3$) stretch band signal has been significantly lower compared to the signal obtained by our narrow-band perfect absorber (1.5 % vs 0.5 % absorption unit). Recently, Durmaz et al. [32] experimentally designed a broadband PA for detecting PMMA thin layer. However, they did not report the asymmetric methyl stretch band signal, presumably because the signal could not be detected with their perfect absorber. This comparison reflects that the narrow band PA's can significantly improve the surface enhanced IR absorption spectroscopy.

2. Materials and methods

2.1. Numerical and experimental analysis of the designed PA

In this section, we explain the specific geometry of the resonant plasmonic perfect absorber. Top and cross-sectional view of the dual-resonant PA are shown in Fig. 1(a) and (b), respectively. The PA consists of an array of combined plasmonic rods separated from an optically thick non-transparent metallic ground plate. In the optimum configuration, we use a 100 nm-thick MgF_2 spacer between a patterned 80 nm-thick Au nanoparticle-based top layer and a 200 nm-thick Au ground plate. The whole sensing platform is designed on a silicon substrate with a thickness of 500 nm. Polarization of the illumination source is along the x-direction. The frequency-dependent dielectric constants of the metals are taken from Palik [33], and optical constants of MgF_2 dielectric spacer are taken from Dodge [34]. We determine lengths of rods as $L_1 = 2600\text{ nm}$, $L_2 = 2400\text{ nm}$, $L_3 = 2200\text{ nm}$, $L_4 = 2000\text{ nm}$, $L_5 = 840\text{ nm}$, $w_1 = 400\text{ nm}$, $w_2 = 200\text{ nm}$, and the array periodicities ($P_x = P_y$) are $3.2\text{ }\mu\text{m}$. We fabricate the PAs via electron-beam lithography (EBL) and a following lift-off process. Firstly, the 200 nm-thick Au film and 100 nm-thick MgF_2 dielectric spacer are deposited onto the Si substrate by using electron-beam evaporation. Secondly, the 200 nm-thick PMMA is coated as a positive photo resist on top of the MgF_2 layer by spin-coating. EBL is performed on PMMA. Then, EBL-defined patterns are removed by passing the chip through methyl isobutyl ketone-isopropyl alcohol (MIBK-IPA (1:3)) solution for 50 s. EBL-exposed parts are then covered with 5 nm-thick titanium (Ti) as an adhesion layer and 80 nm-thick Au by e-beam evaporation, respectively. Finally, the standard lift-off process is applied to obtain nanoantennas. Fabricated PA samples are characterized optically by a commercial Bruker Hyperion 2000 FTIR microscope that has a 15x Cassegrain objective ($\text{NA} = 0.4$) to collect reflection signals during the measurements. Due to the two-mirror configuration of the objective some part of the light may impinge on the sensor surface with up to 12° angle. The discussion in Fig. S1 (see Appendix A: Supplementary Information S1) shows that the effect of small incident angle change is tolerable for the experiments, and the experimental results still agree well with the simulations, especially for the first mode of PA. Absorption data is normalized via an optically thick Au film. Fig. 1(c) shows numerical and experimental absorption spectra of the PA. Numerical and experimental absorption spectra are in well agreement for the first mode at smaller wavenumbers in the terms of resonance frequency and absorption value. For the second mode at higher wavenumber, we obtain nearly the same resonance frequency and lower intensity. The full width at half maximum (FWHM) for experimental results are surprisingly narrower than the simulation results. This effect is still under investigation; however, we think it can be explained by the curved corners of the fabricated structures compared to the sharp edges used in the simulations [22,23]. We call this PA as a narrow band PA since previous studies on multi-mode multilayer PA's [31]

Fig. 1. The illustration of (a) top view and (b) cross-sectional view of the PA platform. Inset of (b) show the orientation of the electric field vector (E) and the wave vector (k) with respect to the unit-cell. (c) Numerical and experimental dual-resonant absorption spectra of the PA under x -polarized illumination source. (d) SEM image of the fabricated PA arrays. The PA unit cell is in the red square.

regularly provided considerably broader (167.5 cm^{-1}) FWHM values in the mid-IR regime. The PA platform supports two resonance modes; the first mode is observed at around $\nu_1 = 1830 \text{ cm}^{-1}$ with more than 90 % absorption. The deviation from unity absorption could be explained with usage of a Cassegrain objective where some part of the incident light fall on sensor surface with a small ($\sim 10^\circ$) angle. The second mode is obtained at $\nu_2 = 2810 \text{ cm}^{-1}$ with 70 % absorption, while numerical results show 90 %. This is because the electromagnetic coupling is not strong enough between the vertical and horizontal rods in the unit cell. This effect will be explained further in Section 3.3. We critically tune the resonances to ν_1 and ν_2 to target the absorption frequency of the molecular bonds of interest. Fig. 1(d) presents the scanning electron microscope (SEM) image of the fabricated PAs. The surface of the PA is smooth, and the unit cell is defined in the red box.

We design the simulation platform identical to the configuration that we take the spectroscopic measurements. Thus, the light illumination has been a plane wave, sent normally on the structures. There is no angle introduced on the IR light illumination, both in measurements and in simulations. From the simulations we know that the structures are polarization dependent, so we applied the same polarization direction that is used in the simulations to the IR illumination in the microscope. We have analyzed the effect of periodicity of PA, the effect of polarization angle and angle of incidence using simulations (see Appendix A: Supplementary Information S1). As the angle of incidence deviates from normal, the perfect absorption ($A = 1$) is lost and resonance intensity decreases. Similarly, when the polarization angle is changed from zero (respect to x -coordinate) to 30 degrees, the perfect absorption is lost. When we increase periodicity, there is no significant change for the first resonance mode, but the second resonance slightly red-shifts.

3. Results and discussions

3.1. Comparison of full width at half maximum (FWHM) values for particle and PA based nanoantennas

The narrowing on the resonance of the proposed PA is compared with the configuration where a geometrically identical antenna design is placed on top of the dielectric substrate as seen in Fig. 2(a). When the same top antenna design is placed on a 100 nm-thick MgF_2 substrate, we observe very broad reflection resonances. The numerical and experimental results clearly show that the PA has narrower resonances and higher absorption when a dielectric spacer with finite thickness is sandwiched between ground metal plate and top metal antenna layer in Fig. 2(b) and (c), respectively. The dielectric spacer has the maximum impact on the perfect absorption as shown in Fig. 2(d). The prior simulation results revealed that the perfect absorption ($A = 1$) can be achieved at various spacer thickness periodically at certain operation frequencies [31,35]. When the thickness is low ($< 200 \text{ nm}$) strong coupling between the top antenna and ground plate occurs. The thickness of the spacer has to be tuned critically to provide destructive interference of light that is directly reflected from the top antenna layer and reflections occurring in the spacer. In Fig. 2(d), we have also shown that the spacer thickness has to be tuned carefully in order to obtain near unity absorption. Any change of the spacer thickness slightly affects the FWHM, but the absorption changes dramatically.

3.2. The physical origin of the resonance frequencies

We analyze the near-field enhancement distributions to learn the physical origin of the resonance frequencies through FDTD

Fig. 2. Under x-polarization illumination source comparison of FWHM values between monolayer and multilayer structures. (a) Numerical reflectance spectra of the identical top layer metallic nanoantenna only on thick MgF₂ layer. (b) Numerical and (c) experimental absorption spectra of metal-MgF₂-metal perfect absorber. All dimensions are kept identical for all systems. (d) Experimental absorption spectrum of PA for different MgF₂ thickness. Keeping Au antenna thickness constant at 80 nm, the MgF₂ thickness has to be tuned carefully to obtain narrow band resonances and near unity absorption.

simulations. Fig. 3(a) shows calculated reflectance (R), transmittance (T), and absorption (A) spectra of the PA design in the mid-IR regime for the values of $L_1 = 2600$ nm, $L_2 = 2400$ nm, $L_3 = 2200$ nm, $L_4 = 2000$ nm, $L_5 = 840$ nm, $w_1 = 400$ nm, $w_2 = 200$ nm, and the array periodicity is $3.2 \mu\text{m}$. Absorption is defined as $A = 1 - R - T$ [31]. In order to achieve perfect absorption ($A = 1$), one should minimize the reflection and transmission. The transmission over the structures is zero as the light is fully blocked by the optically thick Au film. Since the metal ground plate is optically thick and not transparent, the absorption here can be defined as $A = 1 - R$. The perfect absorption can be explained using critical coupling [36,37], meaning that the rate of radiative loss or leakage rate of energy out of the resonator is equal to dissipative loss [38,39]. Maximum coupling can be obtained by matching the incident electric field pattern to the radiation pattern of a localized surface plasmon resonance, and light scattering in whole directions is eliminated [40,41]. The elimination of scattering means that the reflection is now reduced to zero, thus $A = 1$. The obtained reflectance and absorption spectra have dual-band resonances, due to the fact that the incident radiation mainly interacts with two different types of nanorods that are located at x- and y- axes at the same time.

Fig. 3(b) presents calculated near-field intensity enhancement values for the proposed PA at the mid-IR regime. After obtaining resonance frequencies of the structure at the maximum absorption, we have calculated near-field enhancement distributions and values via the same simulation program. We place vertical and hor-

izontal field monitors between MgF₂ film and nanoantenna where the energy is enhanced. When we use horizontal field monitors, we obtain near-field enhancement distributions and values in Fig. 3(b). The enhancement factor is 3800 at the first mode ($\nu_1 = 1700 \text{ cm}^{-1}$), and 5800 at the second mode ($\nu_2 = 2910 \text{ cm}^{-1}$). It is observed that the first resonant mode originates from the vertical nanorods, and the second from the horizontal ones. Along the mid-IR regime, enhancement values never reach zero due to the “lightning-rod effect” [42]. In order to calculate and visualize cross-sectional near-field distributions, we utilize vertical field monitors. The amplitude value of the incident field is 1. Fig. 3(c–f) show the calculated cross-sectional profiles of the near field intensity under x-polarized illumination source for the modes at ν_1 and ν_2 for electric and magnetic responses, respectively. Fig. 3(c) and (d) show total electric field intensity enhancement ($|E^2|/|E_{\text{incident}}^2|$) and distributions for the first and second mode, respectively. Highly enhanced local electric fields are mainly concentrated at the vertical and horizontal nanorods. Fig. 3(e) and (f) show total magnetic field intensity ($|H^2|/|H_{\text{incident}}^2|$) and distributions for the first and second modes, respectively. As it is seen in the Fig. 3(e) and (f), magnetic fields are mostly presented between MgF₂ and Au antenna border area due to the nature of multilayer structure. We obtain higher magnetic field values compared to the reported perfect absorbers [43]. At each resonance frequency, localized surface plasmons (LSPs) are supported by strong absorption at optical wavelengths. Hence, large near-field confinement can enable us to obtain high-throughput light-matter

Fig. 3. (a) Reflectance (R), transmittance (T) and absorption (A) spectra of the PA in the mid-IR regime. (b) Theoretical near-field intensities along the mid-IR regime. Calculated total electric field intensity enhancement ($|E^2|/|E_{\text{incident}}^2|$) and distributions for the modes at (c) $\nu_1 = 1700 \text{ cm}^{-1}$ (yz cross-section at $x = -800 \text{ nm}$) and (d) $\nu_2 = 2910 \text{ cm}^{-1}$ (xz cross-section at $y = 1200 \text{ nm}$). Calculated total magnetic-field intensity ($|H^2|/|H_{\text{incident}}^2|$) and distributions for the modes at (e) ν_1 (yz cross-section at $x = -800 \text{ nm}$) and (f) ν_2 (xz cross-section at $y = 1200 \text{ nm}$).

interaction applications such as simultaneous identification of different molecular fingerprints.

3.3. Dependence of the spectral response on parameter sweep

To demonstrate the fine-tuning mechanism, we have changed lengths of both vertical and horizontal nanorods in the unit cell of the PA. High parameter sensitivity of the suggested PA easily enables us to reach exact molecular resonance frequencies of polymers or biomolecules. In order to achieve easy tunability in a broader frequency range, we use a step-down structure instead of using a single rod with the same width. With the step-down structure we can enable broader resonance frequency tunability compared to the use of single rod. When we change L_1 from 2600 nm to 2400 nm, the change of resonance is broader for the

step-down structure. There is no significant change in the resonance frequency at the first mode for the no stepping-down structure (see Appendix A: Supplementary Information S2). More resonance shift by an incremental change in the length means that the step-down structure is more easily tunable over a broader frequency range, which is desired for surface enhanced IR spectroscopy. Fig. 4 shows the calculated and experimental parameter sweeps for L_1 and L_5 . For both numerical and experimental analyses, the length of the vertical rods (L_1 , L_2 , L_3 and L_4) in the unit cell is reduced by 200 nm. Fig. 4(a) presents calculated absorption spectra for different L_1 values. As L_1 increases, the first mode slightly red-shifts under x-polarized illumination source. The second absorption peak does not change its magnitude or does not change the resonance peak frequency under the same illumination. Fig. 4(b) shows the dependence of the calculated absorption

Fig. 4. Numerical absorption spectra of the PA platform with 100 nm-thick MgF_2 layer for (a) different L_1 lengths, while L_5 is kept constant (b) different L_5 lengths, while L_1 is kept constant. Experimental absorption spectra of the PA platform with 100 nm-thick MgF_2 layer for (c) varied L_1 lengths, while L_5 is kept constant (d) varied L_5 lengths, while L_1 is kept constant. The corresponding device parameters: $L_1 = 2600$ nm, $L_2 = 2400$ nm, $L_3 = 2200$ nm, $L_4 = 2000$ nm, $L_5 = 820$ nm, $w_1 = 400$ nm, $w_2 = 200$ nm, and the array periodicities ($P_x = P_y$) are $3.2 \mu\text{m}$.

spectra on L_5 . As L_5 is increased, the second mode significantly red shifts. The first resonance mode does not change when L_5 value is changed. In Fig. 4(c), experimental absorption spectra can be seen for different L_1 values. As L_1 increases, the red-shifting behavior of the first resonance mode in calculations agrees well with experimental results, under x-polarization. The behavior of the second resonance mode matches the calculations well in terms of the resonance peak frequency. Fig. 4(d) shows the dependence of the experimental absorption spectra on L_5 . As L_5 increases, the first mode agrees well with the calculated results. Even though all experimental results agree well with the calculations, there is a difference on the intensity of the second resonance mode. We believe that the lower intensity obtained at the second resonance mode of the fabricated PA is due to the dielectric spacer thickness and microscopic defects occurring on the surface of spacer. We experimentally showed that when the thickness of MgF_2 increases, the resonance intensities of the first and second modes also increase (Fig. 2(d)). For some PAs, after MgF_2 deposition we have observed bubbles in the film. Given that spacer thickness is critical for perfect absorption, we think that the surface roughness and small defects on the MgF_2 film affect the second resonance mode. The experimental and numerical results confirm the electromagnetic field distributions. We observe an additional small peak at 2300 cm^{-1} in both numerical and experimental results. In the simulations, we have confirmed that this small peak arises from the Ti adhesion layer (see Appendix A: Supplementary Information S3). As it

is seen in Fig. 4(c) and (d), the position of the Ti peak is not fixed. During the fabrication the intended Ti film thickness may vary couple of nm's with respect to the Ti thickness in simulations, and this causes a shift on the Ti peak. The most striking contrast between the calculated and experimental optical responses is that the fabricated PA has narrower FWHM compared to the calculations. While the FWHM value is 170 cm^{-1} for the calculated result, the experimental measurements show this value as 85 cm^{-1} . This effect is highly desirable for detecting the vibrational modes of polymers due to the fact that these vibrational modes mostly show narrow band feature. As previously stated, we think this effect happens due to the curved corners and edges of the fabricated structures compared to the sharp ones in simulations. The suggested narrow band plasmonic PAs provide more successful vibration band matching compared to the monolayer plasmonic antennas since they have a higher resonance quality factor, and thus can provide better sensitivity.

3.4. Experimental sensing capacity of the PA and the importance of matching the plasmonic resonance with molecular absorption bands

To demonstrate the capacity of the suggested narrow-band PA in surface enhanced infrared absorption spectroscopy, we performed simultaneous detection of two specific and spectrally far vibration modes of a PMMA film experimentally. Plasmonic resonances decay

Fig. 5. Surface enhanced infrared absorption spectroscopy of a 10 nm-thick PMMA film on fabricated narrow band perfect absorbers with 70 nm-thick MgF_2 layer when (a) L_1 is changed (c) L_5 is changed. Experimental difference spectroscopy (Experimental absorption of PA - experimental absorption of PMMA coated PA) for the (b) C=O band at the first resonance mode (d) $-\text{CH}_3$ asymmetric band at the second resonance mode are shown. The absorption difference varies between 13 % and 33 % of the PA resonance intensity for the C=O band and 1.5 % for the $-\text{CH}_3$ asymmetric band.

away from the surface of the metal and they are active up to 100 nm above the surface [44,45]. Thus, we coated a 10 nm-thick PMMA film by spin-coating (5000 rpm, 25 s.). Thickness of the PMMA film is characterized using J. A. Woollam Co. VASE ellipsometer (see Appendix A: Supplementary Information S4). Control measurements are performed on an Au coated MgF_2 film. No molecular absorption signals are obtained for the same PMMA film thickness on the control measurements. Fig. 5(a) and (c) present experimental absorption spectra of the PA platform with 70 nm-thick MgF_2 layer after being coated by PMMA film. The PA parameters L_1 and L_5 that overlaps with the PMMA absorption peaks are determined as 2400 nm and 790 nm, respectively. Absorption is more evident when L_1 increases since the overlap of carboxyl bond with PA resonance is maximum. As it is seen in the Fig. 5 (a), when we match plasmonic resonance frequency (1729 cm^{-1}) with the molecular absorption frequency of carbonyl bands, PMMA starts to absorb more energy from nanoantenna which offers the maximum enhanced field available. The carbonyl $\nu(\text{C}=\text{O})$ stretch band frequency is observed at 1729 cm^{-1} and asymmetric methyl $\nu(-\text{CH}_3)$ stretch band is observed at 2952 cm^{-1} . The absorption intensity of the carbonyl (C=O) band on the PA resonance is stronger than the absorption intensity of $-\text{CH}_3$ asymmetric band. When we look at the attenuated total reflection (ATR) spectroscopy result of the PMMA thin film (see Appendix A: Supplementary Information S5), we see that amount of absorbed energy is higher for carbonyl bond in comparison with the C-H bonds. Thus, observ-

ing a strong absorption signal from carbonyl is expected. Finally, we experimentally perform surface enhanced infrared absorption spectroscopy for all PA arrays in order to show the importance of matching narrow band resonances with molecular absorption bands. Absorption dip for the C=O stretch band (around 1729 cm^{-1}) can be clearly seen for all PAs in Fig. 5(a). When L_5 is equal to 790 nm, we obtain the strongest absorption signal of the $-\text{CH}_3$ asymmetric band stretch at 1752 cm^{-1} in Fig. 5(c). In Fig. 5(b) and (d), experimental difference spectroscopy of PMMA is shown. This data is obtained from the PMMA coated PA that has 70 nm-thick MgF_2 layer. The experimental spectra of PMMA coated PA is subtracted from the uncoated PA's experimental spectra (see Appendix A: Supplementary Information S6) for the C=O band (red line) and the $-\text{CH}_3$ asymmetric band (blue line), respectively. After PMMA binding no red-shift is observed on the PA resonance for the first mode (see Appendix A: Supplementary Information S6), thus we applied direct subtraction without correcting the shift with a polynomial fitting [44]. In order to reliably calculate the absorption difference ($\Delta\text{Absorption} = A_{\text{fit}} - A_{\text{PMMA}}$) in the presence of the spectral shifts for the second mode, we employ the fitting procedure [44] which shifts the bare response and performs a baseline fitting such that the PA absorption before PMMA coating (A_{fit}) fairly overlaps with one after PMMA coating (A_{PMMA}). In Fig. 5(b), when the resonance frequency of the PA is exactly matched with absorption frequency of the C=O band, absorption difference, and thus the sensitivity reaches its maximum value. Absorption difference decreases when

the PA resonance is even slightly off from the carbonyl absorption frequency. The absorption difference varies between 13 % and 33 % of the PA resonance intensity. Even when the PA resonance is very off from the carbonyl absorption frequency, we still see a strong signal obtained from an only 10 nm-thick PMMA film. The coupling between the plasmonic and PMMA vibrational modes results in spectral red-shift in the C=O absorption dip from their usual spectral position at 1729 cm^{-1} , as shown by the vertical red line in Fig. 5(b). When the PA supports a resonance frequency larger than 1729 cm^{-1} for L_1 values of between 1800 and 2200 nm, the absorption dip corresponding to the C=O band is observed at larger wavenumbers. When the PA supports a resonance frequency smaller than 1729 cm^{-1} for L_1 value of 2600 nm, the absorption dip corresponding to the C=O band is observed at smaller wavenumbers. When $L_1 = 2400\text{ nm}$, plasmonic resonance and the carbonyl absorption band are almost aligned. In Fig. 5(d), when $L_5 = 790\text{ nm}$, 1.5 % absorption difference is obtained for the $-\text{CH}_3$ asymmetric band stretch at 2952 cm^{-1} . For other lengths of L_5 , absorption differences at the $-\text{CH}_3$ asymmetric band stretch frequency is not significant.

4. Conclusion

In conclusion, we experimentally presented a narrow band multi-resonant perfect absorber operating in the mid-IR range for the first time and demonstrated its usage for surface enhanced infrared absorption spectroscopy. Firstly, we performed theoretical analysis to investigate the physical origin of the dual-resonant behavior with strong near-field intensity enhancement distributions. Then, we obtained a fine-tuning mechanism to control the spectral response of the PAs through the geometrical parameters. Finally, we fabricated the numerically designated PAs and observed that the fabricated systems show similar optical responses compared to the calculations. In addition, we realized that the fabricated PAs actually show narrower resonance bands compared to the simulations or monolayer plasmonic nanoantennas. We also used the fabricated PAs to experimentally detect molecular fingerprints obtained from a 10 nm-thick PMMA film. The SEIRA spectroscopy resulted in 33 % intensity change on the PA resonance, which shows the sensitivity improvement obtained from narrow band resonances in comparison to monolayer plasmonic antennas. Fine tuning of the narrow-band PAs with high quality factor resonances allowed us to exactly match the relevant vibrational molecular modes. Thus, the presented narrow band multi-mode PA system is a promising probe to study very thin protein-lipid combined systems, such as live cell-membranes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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