Experimental and numerical characterization of a mid-infrared plasmonic perfect absorber for dual-band enhanced vibrational spectroscopy

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ABSTRACT

Plasmonic perfect absorbers (PPAs) have promising properties to be utilized in molecular sensing and spectroscopy applications such as surface enhanced infrared absorption (SEIRA) and surface enhanced Raman spectroscopy (SERS). In order to employ these properties and demonstrate the great potential of PPAs, investigation and demonstration of PPA designs and their sensing applications are highly needed. In this context, we present the design, optical characterization, experimental realization and dual-band sensing application of a subwavelength PPA array for infrared detection and surface enhanced spectroscopy applications. We analyze the PPA to investigate the absorption spectra and the fine-tuning mechanism through the parameter sweep simulations and experiments. In order to understand the absorption mechanism, we investigate the charge and current density distribution maps with electric and magnetic field enhancement effects. Additionally, we demonstrate the potential usage and reliability of the proposed PPA by presenting the experimental results of the dual-band detection of a conformal polymethyl methacrylate layer with nanometer-scale thickness atop the PPA. According to the experimental and simulation results of this study, the proposed PPA can be utilized in multiband molecular detection and high sensitive spectroscopy applications.

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1. Introduction

Interaction of light with metal nanoparticles results in localized surface plasmons (LSPs) which are defined as the non-propagating electron density oscillations [1,2]. Plasmonic metamaterials (PMMs) are artificial, subwavelength-sized metallic-structures which can be engineered to have electromagnetic properties for almost any application [3—5]. Furthermore, PMMs have exotic electromagnetic properties such as negative index of refraction [6—8], subwavelength focusing [9,10] and optical magnetism [11] which are unattainable with natural electromagnetic materials. Through the utilization of these fascinating properties, PMMs have enabled many exciting applications such as super resolution imaging [12], spasers [13,14], super lenses [15], near-field lithography [16] and all-optical devices [17,18].

In the last two decades, owing to the development in the nanofabrication methods, many PMM device concepts have been developed such as hyperbolic [19], semiconductor-based [20], and plasmonic perfect-absorber (PPA) [21—26] metamaterials. Particularly for the infrared and visible regions, narrowband and broadband PPAs have gained great interest due to their near-unity absorption capability and potential applications including the selective thermal emitters [27,28], spectroscopy [29—31], and energy conversion [32,33]. In order to obtain perfect absorption, the common design principle of PPAs depends on minimizing the reflectance through impedance matching and removal of the transmittance by maximizing the losses. Additionally, the excitation of electric and magnetic resonances on the nanoantennas of PPAs results in the trapping of light energy and dissipation of this energy through resistive losses [34]. Furthermore, unity-absorption caused by the LSP resonances on the nanoantennas of PPAs, increases the light-matter interaction and also enables the ultra-sensitive spectroscopy and biosensing applications through highly confined local electromagnetic fields [35,36]. In particular, PPAs can

be used in surface enhanced infrared absorption (SEIRA) spectroscopy which is a robust biochemical analysis tool as it has been employed for the characterization of biomolecules such as polymers, proteins, and lipids in the fingerprint region of the mid-infrared spectrum [37]. SEIRA spectroscopy has enabled the elucidation of molecular structure even in dynamic molecular processes by the enhancement of the characteristic vibrational modes of molecules with a variable dipole-moment perpendicular to the substrate surface [38]. In this context, it is essential for PPAs to have properties such as multispectral absorption, high near-field enhancement with large number of hot-spots, and tunability to be employed in SEIRA spectroscopy applications. Therefore PPAs with crucial functionalities ought to be developed and investigated.

In this study, we present the design, optical characterization, experimental realization and sensing application of a sub-wavelength PPA array for infrared sensing and surface-enhanced spectroscopy applications. Design of the proposed PPA depends on the nanorod-based linear dipole nanoantennas which provide compelling properties for sensing applications such as tunable dual-band perfect absorption, high near-field enhancement, and high sensitivity characteristic in the mid-infrared regime. With the aim of characterizing the proposed PPA, we systematically investigate the absorption spectra and reveal the fine-tuning mechanism through the parameter sweep simulations and experiments. In order to understand the absorption mechanism, we investigate the charge and current density distributions with electric and magnetic field enhancement effects for the corresponding resonant modes. Additionally, for the purpose of demonstrating the potential usage and reliability of the proposed PPA in SEIRA spectroscopy, we experimentally show the dual-band detection of a conformal polymethyl methacrylate (PMMA) layer with nanometer-scale thickness atop the PPA through the amplification of the characteristic vibrational absorption bands. Due to its crucial properties, the proposed PPA can be utilized in multiband molecular detection and high sensitive spectroscopy applications. Furthermore, the experimental and simulation results of this study can be beneficial for the development of plasmonic sensor devices for spectroscopy applications.

2. Design of the proposed PPA

In order to obtain a straightforward tuning mechanism, we utilize linear dipole-nanoantennas for the construction of the PPA unit-cell. Due to its biocompatibility and high plasmonic response, we use gold (Au) for the metal layers. Additionally, for the dielectric layer, we utilize magnesium fluoride (MgF_2) owing to its low refractive index and high transmissivity in the infrared spectrum. The schematic view of the proposed PPA unit-cell with the geometrical parameters and the direction of illumination are given in Fig. 1(a). In this figure, L_1 and L_2 are the lengths of the longer and shorter horizontal rod-shaped nanoantennas, respectively. L_3 is the length of the vertical rod which connects the longer and shorter rod-shaped nanoantennas. D is the distance between the upper and lower parts of the nanoantennas while P_x and P_y are the periodicities of the array cells. W is the width of the rod-shaped nanoantennas. The functional layers of unit-cell from bottom to top are silicon (Si) substrate, Au ground layer, MgF_2 spacer layer, and the Au nanostructures. The ground layer eliminates the transmission through the structure and the spacer is used in order to provide light trapping by the near-field coupling among the top nanoantennas and ground layer. Measured and calculated absorbance spectra for the periodic arrangement of the proposed unit-cell are given in Fig. 1(b). Here, the absorbance spectrum A is calculated from the information of reflection R and transmission T spectra ($A = 1 - T - R$) and due to the multilayered design, the transmission

is to be nearly zero for the corresponding spectrum. Experimental spectra are acquired by using a Fourier transform infrared (FTIR) spectrophotometer and the simulation results are obtained by using a commercial electromagnetic simulation software (Lumerical FDTD Solutions) which utilizes finite difference time domain (FDTD) method. The realistic dispersion data of Au is taken from Palik's Handbook of Optical Constants of Solids [39] and the refractive index of MgF_2 is taken constant as 1.37 [29]. Fig. 1(b) shows the absorption spectra for the polarization angle ϕ values of $0°$ and $90°$ under normal incident ($\theta = 0°$) plane wave. We observe in Fig. 1(b) that the designed PPA has triple-band absorbance under the x-polarized ($\phi = 0°$) source and the resonance modes are represented by M_1^x, M_2^x, and M_3^x from lower to higher frequency, respectively. Under the y-polarized ($\phi = 90°$) source, the structure exhibits dual-band behavior with the resonant modes M_1^y and M_2^y as shown in the lower-part of Fig. 1(b). We obtain perfect absorbance for the lower frequency resonance modes with a good agreement between the experimental and theoretical results, particularly under x-polarization. However, we observe a discrepancy between the theoretical and experimental results for the higher frequency resonance mode M_3^x which is caused by the fabrication tolerances. Meanwhile, the dual-band absorbance under y-polarized source has a good agreement between the theoretical and experimental results. Additionally, we observe that the resonance bands of the experimental results are slightly broader than the resonance bands of the theoretical results especially for the modes M_2^x and M_2^y. In order to explain the broadening, we investigate the effect of the angle of incidence θ on the absorption spectrum through the simulations and present the results in Fig. 1(c) and (d) for the transverse electric ($\boldsymbol{k}$ is in y-z plane) and transverse magnetic ($\boldsymbol{k}$ is in x-z plane) polarizations, respectively. In Fig. 1(c), it is observed that the Lorentzian line shape of the spectrum is distorted and in Fig. 1(d), we observe that the widths of the resonance bands slightly increase with a line-shape distortion while increasing the value of the angle of incidence. According to the results in Fig. 1(c) and (d), we believe that the broader resonance bands obtained from experimental measurements are caused by the non-vanishing divergence angle of the incident light. For the following analyzes, normal incident plane wave excitation is used during the simulations and experiments.

3. Results and discussion

For the purpose of obtaining information about the origin of absorption resonances, we investigate the electric field maps with charge distributions. Fig. 2 shows these maps for all the resonant modes under x- and y-polarized light, on the top surfaces of the nanoantennas and the metal ground layer. Fig. 2(a) shows the electric field maps on the top surfaces of the nanoantennas and the ground layer for the mode M_1^x (1564 cm^{-1}). We observe that the origin of this mode is the dipolar charge density oscillation on the surface of the longer nanoantennas. Additionally, it is observed that the charge polarization of the longer nanoantennas is mirrored by the ground layer which indicates a strong near-field coupling between the top nanoantennas and the ground layer for the mode M_1^x. Fig. 2(b) shows the electric field enhancement with charge polarizations on the top surfaces of the nanoantennas and the metal ground layer for the resonant mode M_2^x (3355 cm^{-1}). As a result of the investigation of Fig. 2(b), mode M_2^x is originated from the dipolar charge oscillation on the surface of the shorter nanoantennas. Due to their dipolar characteristics, modes M_1^x and M_2^x provide perfect absorption with strong near-field coupling between the top nanoantennas and the ground layer. In Fig. 2(c) we observe that the origin of mode M_3^x (4453 cm^{-1}) is the quadrupolar charge density oscillation on the longer nanoantennas and the dipolar