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A sensitive and selective terahertz sensor for the fingerprint detection of lactose

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ABSTRACT

Special recognition to molecules is essential for many biochemical processes, thus highly sensitive sensing methods for molecule recognition are strongly demanded. Recently, metamaterials present a unique platform for sensing applications owing to their exotic properties. In the current work, a metamaterial sensor for enhanced fingerprint detection of lactose based on resonant coupling of plasmonic modes of split-ring resonators (SRRs) and terahertz characteristic modes of lactose was theoretically and experimentally demonstrated. Large electric field enhancement (about 120 times) at the gap of SRRs allows for the highly sensitive detection. A narrow transmittance peak in the broader transmittance dip which corresponded to the characteristic modes of lactose was observed due to the resonant coupling, and the differential transmittance enhanced as the lactose concentration increased. The experimental result agreed well with the theoretical analysis. Moreover, the selectivity of this SRRs sensor for the target molecule was also verified by using fructose. A low amount of lactose, as small as 20 mg/mL was successfully detected in the experiment. Our study opens a new avenue to exploit new materials or devices for molecule sensing with high sensitivity and selectivity.

1. Introduction

In the past decades, metamaterial sensors have made great strides in structural development as well as applications. Their ability to confine light to nanoscale regions and their high selectivity have made metamaterial sensors attractive candidates for various applications in environmental monitoring, drug discovery, food safety control and temperature sensing and other areas [1–11]. Among various metamaterial structures, the split-ring resonators (SRRs) with excellent properties have attracted great interests and were widely studied in many research areas due to their strongly localized and confined field in the gap region, which allowed for the fingerprint detection of a trace amount of substances with increasing sensitivity. The sensing process of SRRs is based on the resonant coupling between its plasmonic modes and the characteristic modes of molecules.

The resonant coupling between the plasmonic modes of SRRs and the characteristic modes of molecules can be explained by the underlying concepts of hybridization induced transparency (HIT). In HIT, induced transparency can be achieved in a hybrid system composed of plasmonic structures and an ensemble of atoms [12]. If the mutual interaction between the plasmonic and molecules system can be controlled such that the broadband oscillations in the plasmonic structure interact with the narrowband oscillations of the atomic system to interfere destructively, induced narrowband transparency within the broadband absorption line can be observed [13]. Analogously, SRRs act as the plasmonic structure with a broadband absorption line, while the molecules behave as an ensemble of atoms with an extremely narrowband absorption line. The resonant coupling occurs when the characteristic frequency of molecules overlaps spectrally with the plasmonic resonance of SRRs. As a result, a narrow transmittance peak in the broader transmittance dip can be regarded as the molecular characteristic fingerprint. This is the principle of sensing using SRRs.

THz spectroscopy is a powerful technique for molecule analysis because molecular characteristic modes lie totally or partially in the THz region [10,11]. At present, the limited sensitivity and selectivity are the main limitation for a broad application of THz technology. For improving the sensitivity, various THz sensing techniques have been proposed. J. Yang et al. utilized corrugated parallel plate waveguide with gradient grooves to detect ethanol and found that a change in intensity greater than 3 dB could be observed when the thickness of the ethanol layer was greater than 0.1 μm [14]. H. R. Park et al. utilized enhanced dramatically electric field in the nanoantennas to detect

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extremely small quantities (near 40 ng) of RDX [15]. These methods enable the detection of trace sample, however, they require a high-efficiency THz coupler or a high-resolution THz spectrometer. Y. Francescato et al. reported a detection scheme based on the propagation of strongly confined antibonding plasmons supported by graphene sandwiches and the 2 nm-thick analyte caused up to 3 dB intensity changes [16]. However, the complexity and high cost of the graphene fabrication of graphene limited its applications. Recently, SRRs working at terahertz (THz) frequencies have attracted considerable attentions in the field of chemistry and life science. SRRs open up an opportunity for improving the sensitivity in THz sensing. These devices are able to effectively use the enhancement of the THz fingerprint signal of molecules situated on its surface to obtain the detailed information regarding the identity of those molecules. However, the previous works focused mainly on the detection of samples according to their different refractive indices [1,17–23]. Few works focused on detection of targets based on their fingerprints [24,25]. As far as we know, there is no any report on the study of SRRs sensor with high sensitivity and high selectivity up to now, which limits the use of SRRs in the field of THz sensing technology.

In this paper, we propose a square SRRs sensor based on resonant coupling for the fingerprint detection of lactose. The properties of the sensor were numerically and experimentally demonstrated. It was demonstrated that the electric field was highly concentrated and enhanced (about 120 times) in the gap of SRRs, making the proposed sensor suitable for high sensitivity detection. A narrow transmittance peak in the broader transmittance dip which corresponded to the characteristic modes of lactose was observed, and the differential transmittance enhanced as the lactose concentration increased. The experimental result agreed well with the theoretical analysis. Moreover, the selectivity of this SRRs sensor for the target molecule was also verified by using fructose. A low amount of lactose, as small as 20 mg/mL was successfully detected in the experiment.

2. Materials and methods

2.1. Simulation

The resonant coupling occurs when the characteristic modes of molecules overlap spectrally with the plasmonic modes of SRRs. Therefore, the first step was to design the structural parameters of SRRs to make its plasmonic resonance match the characteristic modes of target. The designed sensor in the present study consisted of a periodic array of square-shaped copper SRRs on the top of a quartz substrate ($n = 1.93$). The substrate was assumed to be semi-infinite and the SRRs structural parameters were as follows: period $a = 77\ \mu m$, thickness $t = 250$ nm, side length $l = 43\ \mu m$, line width $w = 4\ \mu m$, and split gap $g = 4\ \mu m$. To study the effect of aforementioned coupling mechanism on this SRRs sensor, a unit cell of SRRs was modeled using the finite-difference time-domain method (FDTD) method by applying periodic boundary conditions in the x and y directions and perfectly matched layers in the z direction along the propagation of incident plane wave. The copper was supposed to be highly conductive at the frequency band of interest thus can be treated as a perfect electric conductor. The polarization vector of the THz electric field was oriented along the gap of the SRRs in order to excite the magnetic SRRs resonance at normal incidence by electromagnetic cross coupling [26], as illustrated in Fig. 1a.

The electric field distribution of the bare SRRs, as well as the transmittance spectra of SRRs covered with a layer of lactose characterized with a Lorentz oscillator model was calculated. The parameters for the Lorentz oscillator model were referred to the data from the previous report [12]. In order to validate that the SRRs had a capacity for improving the fingerprint detection, the performance of the SRRs for sensing was compared to that of the quartz substrate. The selectivity of this sensor working for only the targeted molecule was also demonstrated.

2.2. Fabrication

The structure of the proposed SRRs was fabricated using the laser direct writing process, thermal evaporation method and lift-off processes. Firstly, the quartz substrate with a thickness of 2 mm was coated with AZ 5214E photoresists as a sacrificial layer. Then the photoresists were baked on a hot plate at 110 °C for 90 s and patterned using a laser direct writing system. Afterwards the substrate was immersed in a sodium hydroxide solution with a concentration of 0.01 g/mL for 85 s. After that, a 250 nm thick copper film with a 5 nm layer of chromium for adhesion was deposited on the coated substrate by the thermal evaporation method. Finally, a lift-off process was performed with acetone to wash out the sacrificial layer followed by rinsing the sample in an ethanol solution. Fig. 2 presents a typical optical microscopy image to show an overview of the fabricated structure and the inset gives an enlarged demonstration of its unit cell.

2.3. Measurements

α-lactose monohydrate was purchased from Sigma-Aldrich, Germany. The various concentrations of lactose solutions were prepared by diluting lactose solution (40 mg/mL) with deionized water by 5:2,5:3,5:4, and 5:5 volume ratio, producing four lactose solutions: 28, 25, 22, 20 mg/mL. We focused on these four lactose solutions ranging from 20 to 28 mg/mL, because it was found that the lactose was beginning to crystallize when its concentration was greater than 28 mg/mL, leading to an uneven lactose film. When the solution was lower than 20 mg/mL, the fingerprint features of lactose could not be detected due to the limited sensitivity of the sensor as well as the limited signal to noise ratio of our frequency domain terahertz system. Before spectral measurements, a droplet (20 μL) of lactose solution was dripped to cover the copper surface of SRRs. And then SRRs with the solution was heated at a temperature of 90 °C on a hotplate for 20 min to accelerate the crystallization process [27].

All the spectral measurements were conducted with a continuous-wave THz spectroscopy system (TeraScan 1550, TOPTICA Photonics AG). The system mainly consists of DLC smart electronics, two fiber-coupled InGaAs photomixers and four 90° off-axis parabolic mirrors, as shown in Fig. 3. Two laser beams from two different distributed-feedback diode (DFB) lasers were mixed in a fiber combiner to generate a laser beat operating at the difference frequency of lasers. The DFB lasers operated at the center wavelength of 1533 nm and 1538 nm, respectively, and could be tuned thermally by DLC smart. Therefore, the difference frequency could be steadily tuned on the MHz level by controlling the temperature accurately. In our setup, it could vary continuously from 50 GHz to 1220 GHz. The laser beat was then split evenly into two laser beams, which were fed into the transmitter to generate THz pulses and the receiver as a probing beam, respectively. The THz pulses generated in the transmitter were aligned by two off-axis parabolic mirrors and then focused onto the sample. The transmitted THz pulses were further aligned by another two off-axis parabolic mirrors and focused onto the receiver, together with the probing pulses, which travelled through a fiber directly to the receiver. A voltage in a receiver chip was generated and proportional to the incident electric field when the THz wave illuminated the receiver. The conductivity of the receiver was modulated by beat frequency. Consequently, photocurrent generated was proportional to the THz electric field amplitude. Finally, the photocurrent was amplified using a programmable gain amplifier module. The sample was placed in the common focus of two opposing parabolic mirrors. The transmittance spectra were collected by sweeping between 350 and 720 GHz at a step size of 150 MHz with an integration time of 10 ms operating in the fast scan mode to reduce the scan time. The polarization of the wave was aligned along the square-SRRs gaps. Extraction the THz photocurrent of