Detection of organic molecules using asymmetric plasmonic nanostructures

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Abstract

We demonstrate the fabrication and characterization of an array of plasmonic metamaterial nanostructures based on asymmetric split H (ASH) resonators on a zinc selenide substrate that produce plasmonic resonances matched with the molecular vibrations of an organic material. Estrogenic hormones; 17β-Estradiol (E2) and Estrone (E1) were chosen as analytes for coupling with the plasmonic resonances. The experimental results show there is a good match with the molecular bond resonances of the C-H, C=O and C=C observed in estrogen and we have also shown that it is possible to differentiate the molecular bond resonance spectrum of E2 in a mixture with E1.

1. Introduction

Surface enhanced infrared absorption (SEIRA) spectroscopy is widely used in sensing applications for environmental monitoring and clinical diagnostics. By applying an organic analyte on the metal-air interface of the metamaterial structures, the characteristic molecular vibrations of the analyte material can be detected and enhanced if they coincide with the plasmonic resonant wavelengths. The resultant red-shift in the plasmonic resonance can be measured and used to calculate the sensitivity for use as an optical biosensor [1]–[3]. In this paper, we show that analytical techniques based on the plasmonic properties of gold nanostructures, to be eventually used for rapid environmental analysis. We present the plasmonic metamaterial nanostructure arrays of asymmetric split H (ASH) resonators that have been optimized to produce plasmonic resonances that match the resonant molecular vibrations of a biological material [4]. ASHs were designed for sensing organic molecules of two selected estrogens, 17β-Estradiol (E2) and Estrone (E1). Also, the target is to identify the common (O-H, C-H and C=C bonds) and different (C=O bonds) molecular bond resonances for the two estrogen molecules in the mid infrared (IR) wavelength range (2 to 8 μm).

Estrogen is one of the endocrine disruption compounds (EDC) that has been discovered regularly in various water sources. It has been found at concentrations as low as 1 to 10 ng/l due to its poor solubility. EDC contamination is potentially found in food, the water supply and consumer products and can lead to adverse health effects, particularly with regard to reproduction and the bodily development process. EU government has suggested monitoring the issues in the water source contamination because of the potential harm to the aquatic species, such as alterations of sexual development and inter-sex species (e.g feminization of male fish) [5]–[8]. E2 is a steroid hormone and a major sex hormone in females that functions in the development of reproductive systems and other physical features. E1 can be found after the menopause in the female body.

2. Plasmonic Metamaterial Nanostructures

We have fabricated ASH arrays using electron beam lithography on a zinc selenide (ZnSe) substrates. This transparent and high refractive index material allows detection in the longer wavelength range of 600 nm to 21 μm. The ASH nanostructures were formed with asymmetric vertical dipoles and cross bar dipoles. Scanning electron micrograph (SEM) images of ASHs are shown in Figure 1. The two different sizes of ASH labelled as ASH_1 and ASH_2, with ASH_1 arm length (L_1 and L_2) varying between 450 nm and 800 nm and ASH_2 arm lengths between 1.2 μm and 1.6 μm were chosen for the mid-IR region. When the incident wave is polarized along y-axis, parallel with the vertical asymmetric arms, the basic structure exhibits two plasmonic resonance peaks, due to the asymmetry of the arm-lengths.

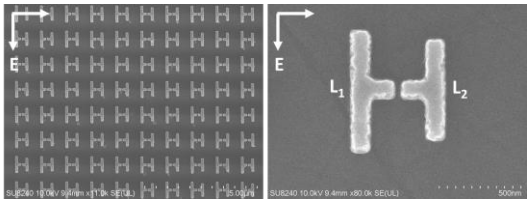


Figure 1: Scanning electron micrograph of (a) an array and (b) one-unit cell of asymmetric split H (ASH) resonators.

3. Optical Sensing of estrogenic hormones

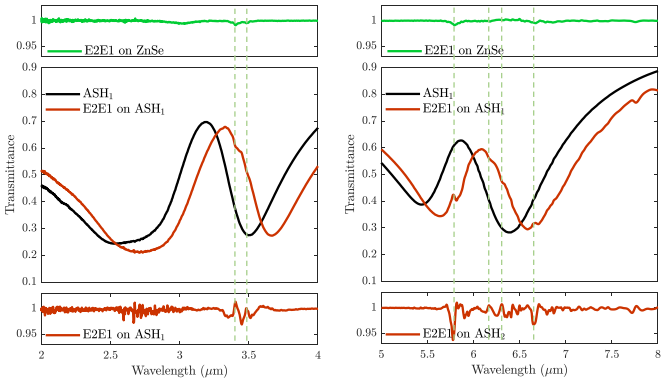
Table 1 shows that E2 and E1 exhibit a strong molecular vibration of the C-H bond at wavelengths between 3.40 μm and 3.49 μm. Carbon to carbon double bond stretching (C=C) also occurs in the wavelength range from 6.30 μm to 7.00 μm. The significant chemical difference between E1 and E2 lies in a single bond, which is a C-OH in E2 and the C=O bond in E1. Molecular vibrations for this C=O bond

occur at wavelengths of 5.79 μm and 5.85 μm. The plasmonic nanostructures were coated consecutively with a thin layer of E1 in absolute ethanol (1mg/ml), a thin layer of E2 (1mg/ml) and various mixtures of E2 and E1, all with a total estrogen concentration of 2mg/ml but different E2:E1 ratios. The samples were left to evaporate overnight before the measurements were performed - by which point the estrogen had crystallized on top the resonators. The ASH structures were tuned to resonate at the wavelength of the C-H bonds of interest and found good matches with ASH_1 resonant using the length sizes of L_1 = 800 nm, L_2 = 600 nm. While for ASH_2 the sizes of L_1 = 1.5 μm and L_2 = 1.2 μm demonstrated close matches to the two double bond resonances.

Table 1: Summary of molecular bonds features in 17β - Estradiol and Estrone in the mid-IR wavelength

Molecular Bonds	E1 (μm)	E2 (μm)
O-H	3.05	2.96
C-H	3.40	3.41
	3.49	3.48
C=O	5.79	x
	5.85	
C=C	6.30	6.30
	6.67	6.67
	6.80	6.80

A substantial resonance red-shift was produced between the positions for the uncoated ASHs and the corresponding positions when the ASHs were coated with estrogen. The resonance shifted 220 nm from the initial position of the uncoated ASHs. For instance, the resonant wavelength for ASH_2 were shifted from 5.46 μm to 5.68 μm and from 6.39 μm to 6.63 μm. When the mixture of E2 and E1 was deposited on the nanostructures, transmittance resonance (Figure 2 (a) and (b) in red lines) produced a small feature at a wavelength of around 5.79 μm as shown for ASH_2 in Figure 2(b), that matched the vibration of the C=O bond present in E1. The vibrational signal enhancement of estrogen deposited on nanostructure arrays could be quantified by comparison with the deposition of the estrogen mixtures on the bare ZnSe substrate (green line in Figure 2). Baseline corrections were used to extract the peak strengths of the various molecular vibrations. We found that the molecular bond resonances are typically five times larger, easily visible and differentiated the ASHs, as compared with those deposited on bare substrates. Additionally, we could quantitatively separate out the contribution of each type of estrogen.



(a) (b)

Figure 2: Plots transmittance resonances from the (a) ASH_1 and (b) ASH_2 with the mixture of E2 and E1 (50:50) show the vibrational resonances and the baseline corrected in the fingerprints of O-H, C-H, C=O and C=C bonds

4. Conclusions

In conclusion, we tuned the geometry of the asymmetric split H resonators which can be utilized to enhance the molecular C-H, C=O and C=C bond resonances of E2 and E1. The plasmonic resonance were red-shifted towards longer wavelengths through the deposition of organic materials on the nanostructures. This study will support the development of plasmonic biosensors that can be used to detect and differentiate the presence of small amounts of different organic molecules with lower detection limits.

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