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Metasurface

Metageometries for Polycyclic Aromatic Hydrocarbons Detection at THz Range in Food Systems

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Abstract— Polycyclic aromatic hydrocarbons, when present in food systems, have been shown to have a detrimental effect on human health, producing carcinogenic elements. So, the implementation of processes for their detection and identification is of vital importance. Nowadays, there are different methodologies for this purpose, but they consist of expensive and time-consuming processes. Due to their enhanced sensitivity and more accurate detection capability, metageometries operating in the terahertz band arise as a new methodology to identify and detect different chemical or biological substances. In this work, we propose a labyrinth metageometry able to detect different polycyclic aromatic hydrocarbons collected in European regulations as the most critical compounds with high experimental sensitivity. Our design is also capable to distinguish between different compounds at the same concentration. This work leads the way to the design of new metastructures able to improve the current detection limits, and thus obtain a new methodology, easier and less time-consuming that the actual methods.

Index Terms— chemical sensing, metasurface, terahertz, PAHs

I. INTRODUCTION

Due to its importance in human health as well as in basic research, safety and quality assurance in the food industry is gaining an increased interest within the scientific community. Among the risky products, the EU has regulated the limit of polycyclic aromatic hydrocarbons (PAHs) in food, and up to 16 PAHs compounds have been described in foodstuffs [1]. Benzo(a)pyrene belongs to this group of PAHs and is used as a marker for the presence of and the effect of carcinogenic compounds in food. Regulation (EU) No 835 of 2011 amended the maximum level for PAH in foodstuffs by introducing new maximum levels for the sum of four substances: benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene and chrysene, which contain other PAHs.

PAHs comprise a class of organic compounds of petrogenic origins or generated from the incomplete combustion of organic matter which takes place during food processing by heat treatment in smoked meat products and charcoal grilled meat [2], [3]. The greatest concern has been raised about the possibility of cancer induction in humans exposed to PAHs from contaminated food; or ingested foods processed at high temperatures by smoking or barbecue processes [1], [4]. Therefore, many regulations and reports regarding strategies and results of food monitoring have been published, including performance criteria for the sampling, chemical analysis and maximum permitted levels of these contaminants in food [5]. The Food and Agriculture Organization of the United Nations (FAO/WHO) [6] and the Scientific Committee on Food (SCF) [7] consider PAHs to be genotoxic and carcinogenic and recommend monitoring the presence of PAHs in food.

The main techniques used for the detection and quantification of PAHs from food matrices include gas chromatography (GC) coupled to mass spectrometry (MS) [8], high performance liquid chromatography (HPLC) with fluorescence detection (FL) [9], and HPLC coupled to MS [10]. All these techniques allow detecting concentrations as low as 1 ppb, with extremely good sensitivity. Fat extraction and clean-up steps are often required for the determination of PAHs from complex matrices such as food [5]. Although all these techniques are useful to detect and quantify PAHs, they are expensive, time consuming and technically complex.

In this context, metasurfaces operating at the Terahertz (THz) band are emerging as great alternatives for reliable label-free sensing. The THz range (0.1-10 THz) presents unique absorption features dominated by the excitation of weak interactions such as van der Waals forces, or intermolecular and intramolecular unique vibrations, such as hydrogen bonds, giving access to relevant information about the chemical composition of substances impossible to get in other frequency bands. From a food safety point of view, THz spectroscopy has been used to determine the presence of pesticide and antibiotic residues in agri-food industry, or to identify genetically modified food, among others [11], [12]. However, there are still few studies on the

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detection of harmful compounds that are present in food systems, and very related with human health. Despite these promising features, detection in the THz range is still very difficult when working with very small samples or thin films, since there is not enough interaction between the sample and THz radiation.

Regarding metasurfaces, they are designed to present an arbitrary electromagnetic response and are composed, in most cases, of an array of subwavelength resonators. They usually produce a high electric field confinement at localized spots (conventional metasurfaces, or meta-atoms), leading to an enhancement of the interaction of any substance or analyte under analysis placed on, or at the vicinity of, the metasurface. In the last years, more elaborated geometries have been proposed, in order to have high electric field concentration distributed all along its surface (metageometries), instead of only at discrete points [13]. This high electric field concentration gives rise to strong changes in the spectral response that can be exploited in sensing applications enhancing the detection of very small samples. In the last years, metasurfaces and metageometries operating in the THz band have shown promising results in the identification of macromolecules such as aminoacids and proteins [14], [15], DNA sequencing [16], thin-film sensing [13], [17]–[19], microorganism detection [20], [21], or even biomedical applications, such as cancer cells and tumor detection [22], [23]. Apart from these biomedical applications, THz and metamaterials have also arisen as a new method of food quality monitoring and characterization [11], [24], [25].

In this work we merge two different fields of study (metasurface engineering and food technology), and try to find alternatives to the expensive and time-consuming processes available for PAH detection. Our aim is to demonstrate the behavior of ultrasensitive sensing platforms based on metasurfaces for agri-food applications. For this, we employ a labyrinth metageometry [26] and demonstrate its ability to detect different concentrations of PAH solutions and identify different PAH compounds, with worse results in terms of sensitivity, but employing a much easier and cheaper measurement method than the current traditional strategies. This way, we extend the reach of THz sensors based on metageometries towards the detection and identification of liquid samples with different concentrations.

II. MATERIAL AND METHODS

A. Labyrinth Metageometry

The designed absorber metageometry presents the labyrinth shape shown in Figure 1, whose convoluted pattern allows the electric field to be uniformly distributed over the surface, and not only localized at discrete points of the unit cell surface, as discussed in [13], [20]. This could potentially enable better sensitivity results with very small, thin or poorly concentrated samples, since we have a larger area of high sensitivity to changes in its environment. This metageometry consist of a triangular-lattice array metallic pattern laying on a flexible polypropylene (PP) slab 29 μm thick with a back metallization acting as a ground plane (GP), and was taken from [13], where the design was extensively numerically and experimentally evaluated in the band of 120-150 GHz using the commercial simulator CST Microwave Studio® [13], [20]. The most relevant dimensions are periodicity, d = 231 μm; distance between metallic strips, s = 8.9 μm; strip width w = 11.1 μm; and metallization thickness t = 0.4 μm.

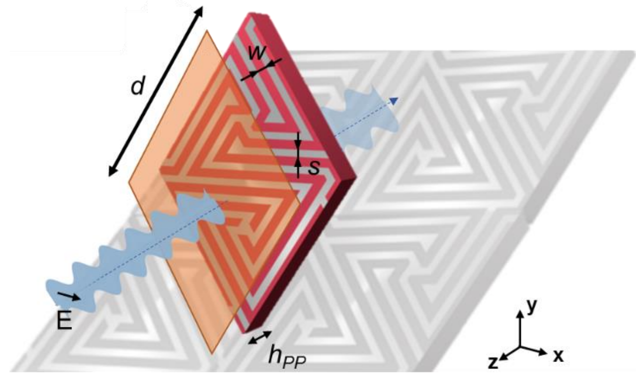

Fig. 1. Front view of the designed labyrinth unit cell with relevant dimensions. Operating and polarization scheme employed in measurement.

B. Sample preparation and experimental setup

The sensing capability of the metageometry was evaluated by coating its surface with different PAH concentrations and substances: chrysene, benzo(a)pyrene, benzo(b)fluorantene, and benzo(a)anthracene. All the samples were prepared by taking small amounts of pure compounds (provided by Scharlab® and measured on a precision balance) dissolved in a mixture of Cyclohexane-Ethyl Acetate in a proportion of 9:1. This solvent was chosen due to its ambient temperature evaporation. Different dissolutions of 100, 250, and 500 parts per million (ppm) were prepared for all the standards except for benzo(b)flourantene, for which concentrations of 250, 500, and 1000 ppm were made (due to its lower sensitivity).

The experimental characterization was carried out with an ABmm Vector Network Analyser (VNA) MVNA-8-350-4 equipped with a quasioptical bench working in the reflection configuration. The frequency span was 120-150 GHz, with a frequency resolution of 100 MHz (301 acquisition points). Before each measurement, a calibration of the setup was done by putting a flat mirror in the sample holder and measuring the reflection coefficient. At each measurement, 300 μL of the solution were poured onto the labyrinth surface. The sample was then deposited on a flat surface, where it was air dried for 10 minutes to allow evaporation of the solvent. Once the solvent was evaporated, the PAH residues were measured in the VNA, and their absorption coefficients obtained.

The quality of the designed metasensor was determined by two parameters, sensitivity (S) and Figure of Merit (FOM), calculated as follows: $S = \Delta f/C$ where $\Delta f = | f_0\text{-}f_c |$ with f_c the resonance wavelength at each concentration, f_0 the resonance frequency without PAH, and C the concentration, in ppm; FOM = S/FWHM, where FWHM is the the full width at half minimum in frequency dimensions when working in reflection. This parameter, also takes into account the spectral linewidth of different curves, and can be also related with the quality factor, Q. Thus, a high FOM ensures a good frequency shift along with a narrow spectral linewidth, what avoids overlapping between different curves, more appropriate for sensing purposes, as in that case, the discrepancy between different curves becomes easier to detect.

III. RESULTS AND DISCUSSION

A. Quantitative response

The sensing performance of the labyrinth metageometry was tested by coating its surface with different PAH compounds and concentrations, at a volume of 300 μL. Figure 2 shows the reflection coefficient for several concentrations (ppm) of chrysene (panel a), benzo(a)pyrene (panel b), benzo(b)flourantene (panel c), and benzo(a)anthracene (panel d). As observed there, a frequency shift of the fundamental metageometry resonance occurs when the PAH concentration increases, giving rise to noticeable changes in the spectral response. This principle of operation is based on the changes occurred in the dielectric properties in the vicinity of the metasurface. When we deposit some sample on the surface, the effective permittivity of the medium surrounding the metasurface experiences variations, which are translated in changes in the resonance frequency. As plotted in Fig. 2, the different PAH compounds behave differently, and present different frequency displacements depending on the deposited concentration. With these curves, we can calculate the sensitivity and FOM as described in the previous section.

For each of the studied PAHs, we experimentally obtained the mean sensitivities and FOMs shown in Table 1. As observed there, all PAH compounds present similar sensitivity values, except for the case of benzo(b)fluorantene, where the *S* value is drastically reduced. This was in agreement with the fact that, in order to correctly detect significant concentrations of this compound, it was neccesary to increase the minimum detectable concentration from 100 ppm to 250 ppm. Regarding the FOM results, we can observe that benzo(a)pyrene and benzo(b)flourantene compounds show significantly higher values than the other PAHs, even though sensitivity values were similar. Note that these compounds have been chosen due to its relevance according to European regulations that limit their presence in food.

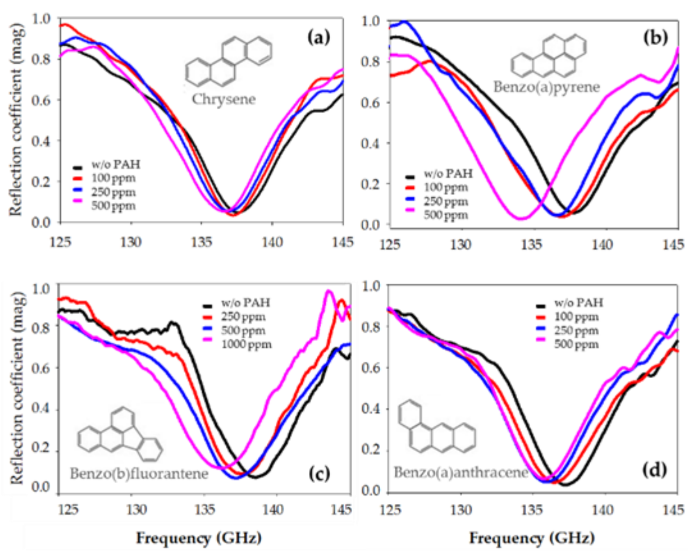

Fig. 2. Experimentally measured spectra of the reflection coefficient for the labyrinth metageometry under different PAH compounds and concentrations: chrysene (a), benzo(a)pyrene (b), benzo(b)flourantene (c) and benzo(a)anthracene (d).

Table 1. Quality parameters of the labyrinth metageometry when measuring different PAH compounds.

PAH	Mean Sensitivity (GHz/ppm)	Mean FOM $(ppm)^{-1}$
Chrysene	5.47×10^{-3}	0.3
Benzo(a)pyrene	5.47×10^{-3}	0.62
Benzo(b)flourantene	5.4×10^{-3}	0.62
Benzo(a)anthracene	2.5×10^{-3}	0.3

B. Qualitative response

In this section we analyze qualitatively the performance of the labyrinth metageometry and its identification capability, that is, its ability to distinguish between different compounds. To do so, we coated its surface with different PAH compounds at the same concentration of 500 ppm, and volume (300 μL). Figure 3(a) shows the reflection coefficient magnitude for the different PAH compounds, where it can be clearly noticed that each of the analyzed PAHs experiences different frequency variation for the same concentration and volume. Concretely, the minimum shift was 1 GHz, achieved by chrysene; whereas the maximum one of 2.3 GHz was achieved by benzo(a)pyrene. This is in agreement with the results of previous section, in which it was found that this compound was the one that offered the highest sensitivity.

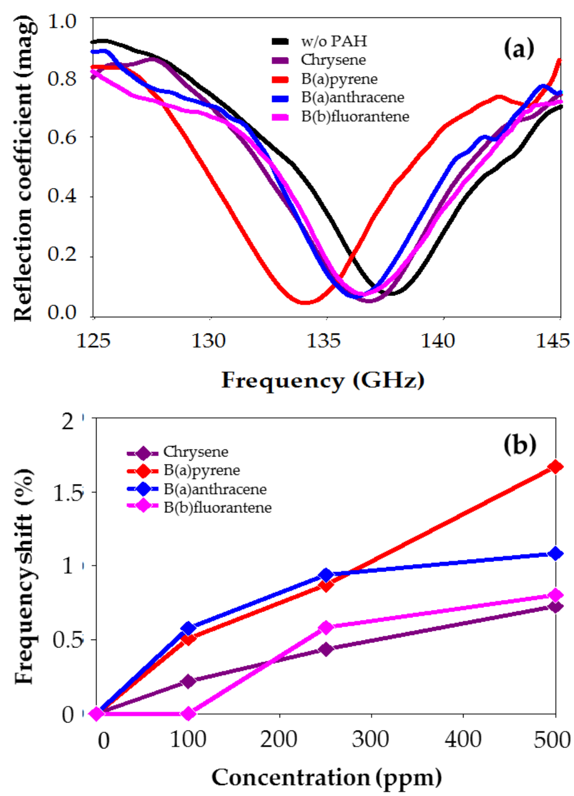

Fig. 3. (a) Experimentally measured reflection coefficient for a 500 ppm concentration sample of the different PAH studied. (b) Frequency shift as the concentration increases for different PAH studied in this work.

From these results we can obtain the frequency shift for all the studied PAH compounds as the concentration is increased, displayed in Figure 3(b). It is noteworthy the high sensitivity of the labyrinth metageometry, able to discriminate between compounds even for relatively low concentrations. As observed there, PAHs behave differently depending on the concentration of the analyzed samples.

For the lowest concentration in which all PAH compounds can be detectable (250 ppm), it is noticed that chrysene is, again, the one that experiences the lowest frequency displacement, whereas benzo(a)anthracene is the one that has the largest shift. On the other hand, for higher concentrations (beginning with 300 ppm) these roles are reversed, and benzo(a)pyrene is the one that undergoes a larger displacement, in agreement again with the previously observed results. This could be due to differences in the dielectric properties of the different compounds studied. Usually, compounds with a higher dielectric constant (or refractive index) tend to experience larger frequency displacements. However, further research is needed to clarify this aspect for the substances analyzed here.

IV. CONCLUSIONS

To conclude, we have reported here a labyrinth metageometry operating in the lower band of the THz range working as a chemical PAH sensing device. This subject is of great interest due to the risk of these compounds on health when ingested by humans. The designed device has been experimentally measured, showing notable frequency displacements when increasing the concentration of different compounds. Concretely, the most favorable detection was achieved for benzo(a)pyrene, showing a sensitivity and FOM of 5.47×10^{-3} GHz/ppm and 0.62 ppm^{-1} respectively. With a quantitative analysis we have proved that this labyrinth metageometry is capable to distinguish between different PAH compounds at the same concentration. Besides, two main conclusions can be extracted: for low concentrations (up to 250 ppm) benzo(a)anthracene achieves the highest sensitivity values, or, equivalently highest frequency shift; whereas for high concentrations, benzo(a)pyrene becomes the most sensitive compound. Despite the high sensitivity achieved by the labyrinth metageometry, we are still a long way from detecting those values contained in the European regulations (amounts below 1 ppm). However, this work means a starting point for successive efficient and sensitive designs, with which we can get closer to the proposed limits. Thus, the THz technology along with the use of metageometries opens the path to a new methodology to control that PAH levels in food systems are maintained at levels that do not involve a health risk.

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