High-sensitivity detection of chlorothalonil via terahertz metasensor

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Abstract
Given the complex pretreatment and low sensitivity of pesticide residue detection with the conventional testing method, a Terahertz metasensor consisting of the four-division ring resonator (FSRRs) was proposed and fabricated for the identification and detection of chlorothalonil. Through simulations, the theoretical sensitivity of this metasensor was found to reach 156.3 GHz/RIU (RIU, refractive index unit) under an analyte layer 1 μm thick. Through experiments, firstly, the characteristic fingerprint spectrum of chlorothalonil in the THz band was obtained by detecting solid chlorothalonil with THz time-domain spectrum system. Then, Terahertz metasensor was used to detect the chlorothalonil solutions of different concentrations. The experimental results showed that the resonant peak of the metasensor was redshifted with the increase of chlorothalonil concentration. Compared with the detection strategy only using the characteristic fingerprint spectrum, the sensitivity of the metasensor improved 106 times, which was up to a minimum of 1 mg l⁻¹. This study indicates that the metasensor is a promising optical device for detecting the pesticide residues with a very high sensitivity.

1. Introduction
Pesticides have been widely used for pest control, sterilization, and weeding due to their broad-spectrum activity and low production costs. However, excessive pesticide residues cause great harm to the environment and human health. Therefore, the detection of pesticide residues has become an important issue in the field of food safety. Traditional pesticide residue detection methods include high-performance liquid chromatography [1], gas chromatography [2], and capillary electrophoresis [3]. These methods generally have high detection sensitivity and have been successfully applied in food safety testing. However, the above methods generally require complex pre-processing steps and professional testing operators before testing. For other methods based on spectral analysis, such as infrared, mid-infrared, and Raman spectroscopy [4, 5], although the detection processes are convenient and time-saving, their sensitivities are relatively low. Therefore, it is necessary to develop the new techniques for rapid detection of pesticide residues.

In the past few years, terahertz (THz) spectroscopy has become a promising technology, enabling unlabeled, non-contact and non-destructive detection of chemical and biological substances [6, 7]. In particular, the recently developed portable THz spectroscopy tool is capable of detecting and identifying target materials on-site with high signal-to-noise ratios [8]. Since the effectiveness of this method in the detection of the substances has been proven, the application of this method to detecting the pesticide residues or microorganisms in food has aroused great interest of people. Pesticide molecules are mostly organic molecules. Although the characteristic fingerprint spectrum can be identified in the THz frequency range [9], so far, rare research has quantitatively given the pesticide residue content through THz wave detection. In other words, the terahertz (THz) spectrum can identify the type of residual pesticide. However, it cannot accurately give the content of residual pesticide, that is, the sensitivity of terahertz detection is not high enough.
As we know that electromagnetic waves can be modulated by many specific or designed structures, such as some nanostructures [10, 11], 2D material [12], near-zero-index dielectric waveguide [13] and some metastructures [14, 15]. Metamaterials have many characteristics that are different from natural materials. The local field enhancement effect makes them have wide applications in the field of medical diagnosis [16]. Based on the variable birefringence of some metastructures, this kind of materials can be used for communication [17]. The local enhancement effect of metamaterials can also contribute to efficient absorption within certain frequency bands, and then researchers have designed the metamaterial absorbers [18]. But in general, the research on metamaterial sensors in the field of food safety did really just start [19–21]. Especially as people pay more attention to health, the content of some harmful substances allowed in food will be less and less, and the requirements for detection methods or detection devices tend to become much higher. For terahertz detection, whether the underlined theories or techniques need to be studied deeply, especially for detection with high sensitivity, batch detection or parallel detection with high efficiency. This article takes chlorothalonil detection as an example. With the appropriate metasensor structure and the geometric dimensions of the sensor, a higher chlorothalonil detection sensitivity is obtained, and the required dosage of the tested substance is relatively small.

Chlorothalonil is a broad-spectrum fungicide that replaces benzene, and is widely used to kill various pests on the plants, such as fruit trees, vegetables and leaves. However, some studies have found that high doses of chlorothalonil are extremely harmful to the human eye and are incredibly toxic to fish. The maximum residue limit of chlorothalonil in vegetables and fruits in China cannot exceed 0.0003 mg kg\(^{-1}\) according to the regulations. Therefore, the combination of the THz-TDS system and metamaterial is not only appropriate for identifying the characteristic fingerprint spectrum of chlorothalonil, but also accurately measuring the content of chlorothalonil. In this work, we designed a metasensor with a distinct resonance peak at 1.47 THz. The experimental measurement results are in good agreement with the simulation results. In theory, the 1 μm-thick analyte layer has a sensitivity of 153.6 GHz/RIU (RIU, refractive index unit).

2. Research method

Through simulation, we designed a variety of open resonance ring structures. Combining with the results of experiments, one structure characteristic of the four-split ring resonators (FSRRs) was chosen to demonstrate the effectiveness of the metasensor and elucidate the underlined mechanism. We chose 10 μm thick polyimide (PI) as the substrate, the specific parameters of the structure are set as shown in the figures 1(a) and (b). The experimental process diagram is shown in figure 1(c). The incident THz wave penetrates from the PI to the metal layer, and the chlorothalonil adheres to the metal layer, as shown in figure 1(d). The specific structural parameters of the designed metasensor are also given. In this study, we used the FDTD algorithm for simulation. We carried out a numerical research on the spectral response of the designed metamaterial structure. The permittivity \(\varepsilon\) and tan\(\delta\) of PI layer were 3.1 and 0.05, respectively [16]. Open boundary conditions were set in the z-direction, and unit cell boundary conditions were set in the x and y directions, respectively. According to the design results, a metasensor sample was fabricated during our research. The manufacturing process is as follows. First, a PI layer was coated on a high-resistance silicon substrate, and baked to make the PI ionized. Then, a metamaterial pattern was obtained by standard photolithography (ABM mask aligner), and then 20 nm chromium and 200 nm Au layers were deposited by FHR magnetron sputtering, respectively. Acetone and isopropyl alcohol were used for 5 min to peel off the specimen. The specimen was divided into 8 mm × 8 mm with a Disco cutter, soaked in HF for 2 min, rinsed three times with deionized water, and blown dry with nitrogen. The PI film was removed with tweezers. Subsequently, the resonance characteristics of the metamaterial samples were tested with a THz-TDS system, Advantest TAS7400 terahertz time-domain spectrometer system. In this system, two femtosecond laser pumped photoconductive antennas with slightly different frequencies are applied for generating and detecting terahertz waves through asynchronous sampling. The frequency range that TAS7400 can effectively detect is 0.2–5 THz, and the frequency resolution can reach up to 1.9 GHz.

In order to prove that the designed metasensor can be used to accurately detect the pesticide residues, here we first used the THz-TDS system to detect the solid chlorothalonil without using metamaterials. Then, in the case of using the metamaterial as a detection sensor, 20 μl of chlorothalonil solution was dropped on the metasensor surface, and the resonance characteristics of the metamaterial were tested by a THz-TDS system. By comparing the sensitivity of two types of detection methods, the influence of metamaterial devices on THz detection results were analyzed. The chlorothalonil solid with a purity of 98% was purchased from J & K Scientific Ltd. PE powder was provided by Shanghai Maclean Biochemical Co, Ltd. This article took chlorothalonil solid samples and liquid samples as research targets.
In the preparation of solid samples, to prevent excessive absorption, polyethylene powder was added as a dispersant. Chlorothalonil and polyethylene powder were crushed and ground (100 mesh sieve) into small particles, respectively. Then, these small particles were dried in a vacuum drying box at a temperature of 50 °C for one hour to remove moisture. We prepared a mixture of chlorothalonil solid and PE powder with

![Figure 1](image1.png)

**Figure 1.** The structural configuration shown in (a) and (b) is composed of basic lattice units of metamaterials. The corresponding structural parameters are $l = 80 \, \mu m$, $h = 10 \, \mu m$, $g = 8 \, \mu m$, $i = 20 \, \mu m$, $j = 15 \, \mu m$, $k = 60 \, \mu m$, $m = 20 \, \mu m$, $n = 4 \, \mu m$. (c) FSRRs-based THz metasensor formed by depositing 20 μl chlorothalonil solution onto an area of $8 \times 8 \, mm^2$. (d) In the designed FSRRs geometry, the THz wave is incident through the PI layer, and the chlorothalonil residue is attached to the metal structure.

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different mass proportions (0 g kg$^{-1}$, 10 g kg$^{-1}$, 50 g kg$^{-1}$, 100 g kg$^{-1}$, 300 g kg$^{-1}$, 500 g kg$^{-1}$). To mix the powder evenly, we carefully ground the mixture with an agate pestle and an agate mortar. The mixture was then pressed into a solid sample of 1 mm thickness, a diameter of 13 mm, and a mass of 200 mg. Before the spectra were collected, the solid sample was relaxed for 30 min and then the dimensional change was not obvious. During the test, we selected 4 positions of the sample and tested the spectra for 3 times at each position. The average value of the above 12 spectra was used as the spectrum result of the corresponding sample.

In the preparation of liquid samples, by dissolving the appropriate amount of chlorothalonil powder into acetone, chlorothalonil solutions with different concentrations (0 mg l$^{-1}$, 0.05 mg l$^{-1}$, 0.1 mg l$^{-1}$, 0.2 mg l$^{-1}$, 1 mg l$^{-1}$, 2 mg l$^{-1}$, and 10 mg l$^{-1}$) were prepared, and each concentration was tested 3 times. The average of three measurements is considered to be the resulted spectrum for each concentration. After each concentration measurement, we immersed the metasensor in the acetone for 10 min to wash off the residual chlorothalonil, immersed it in anhydrous ethanol for 10 min to wash away the acetone, and then rinsed it with deionized water for 10 min. Finally it was dried in a nitrogen-filled environment for the next test.

3. Analysis and discussion

In order to understand the potential resonance mechanism of the designed metamaterial structure, the transmission of the metamaterial was simulated and measured, as shown in figure 2(a). Strong resonance peaks were observed around 1.47 THz both through experiments and simulations. However, the amplitude of the obtained resonance peak was slightly different. The reason may be due to the slight deviations of the simulation conditions from the actual situations and the fabricating errors during the preparation of the metamaterial device. Figure 2(b) is an image of the fabricated metamaterial under an optical microscope. To further analyze the resonance response of the metamaterial, we analyzed the electric field strength at 1.47 THz, the magnetic field in the Z direction and the surface current, as shown in figures 2(c)–(e).

The results in figure 2(c) show that at 1.47 THz, the electric field distribution induced by this metamaterial structure is in the inverse resonance mode. So the asymmetric Fano resonance in the transmission spectrum is
attributed to the electric dipole (bright mode) and magnetic dipole (dark mode) [16]. The dipole plasmon mode can effectively interact with the external electromagnetic fields through radiation, so it is often called the bright mode. Conversely, for narrow linewidth modes with very small net dipole moments, their radiation is extremely weak, making their interaction with external electromagnetic fields extremely weak, so they are often referred to as dark modes. In other words, the dark mode cannot be directly excited by the external electromagnetic fields. Fortunately, the bright mode that can be directly excited can excite the dark mode through near-field coupling. After the dark mode is excited by the bright mode, and then reacts to the bright mode through near-field coupling. The interaction between them causes the Fano resonance. Therefore, the coexistence of bright and dark modes forms the basis of Fano resonance in metal nanostructures. Similar phenomenon was observed and analyzed in reference [22]. In figure 2(e), four circulating currents flow at the four corners (wrapped by the black dotted lines). Due to this circulating current flow, the magnetic field is generated within the space surrounded by the metal ring, as shown in figure 2(d), thereby increasing its field strength and generating magnetic dipole resonance.

3.1. Pesticide detection in solid samples
Time-domain signals of air and the solid samples were collected and converted to the frequency-domain spectra using a fast Fourier transform. The refractive index \( n(\omega) \) and absorption coefficient \( \alpha(\omega) \) can be obtained as follows [23, 24]:

\[
n(\omega) = \frac{\phi(\omega) c}{\omega d} + 1
\]

\[
\alpha(\omega) = -\frac{2}{d} \ln \frac{4n(\omega)}{A(\omega)[n(\omega) + 1]^2}
\]

\( \phi(\omega) \) represents the phase difference between the reference signal and the sample signal, \( A(\omega) \) represents the amplitude ratio of the sample to the air, \( \omega \) is the angular frequency, \( d \) is the thickness of the sample and \( c \) is the speed of light in the vacuum.

The time-domain signals and absorption spectra of the solid samples were shown in figure 3. And figure 3(a) gives the time domain signals of the solid samples with different mass ratios of chlorothalonil. The absorption spectra of the solid samples are shown in figure 3(b). Compared with the 0 g kg\(^{-1}\) sample, the solid sample with a high chlorothalonil content has the individual absorption peaks around 0.74 THz. This is due to the effect of chlorothalonil, which has its characteristic absorption peak within the THz band. These characteristic peaks can be used for the identification of chlorothalonil molecules [25]. As can be seen from figure 3(b), when the mass ratio of chlorothalonil is below 100 g kg\(^{-1}\), the absorption peak around 0.74 THz is not so obvious or nearly disappears. Therefore, during our experiments, we think that the lowest concentration of chlorothalonil in the solid samples that can be detected by THz time-domain spectroscopy is about 100 g kg\(^{-1}\), which is too insensitive, because the permitted maximum residue limit of chlorothalonil in vegetables or fruits is 0.0003 mg kg\(^{-1}\) in China. Compared with Li's absorption spectrum result of chlorothalonil [25], the peak value of the absorption peak drops a lot. We analyze that it is due to the effect of moisture in the humid air during the process from tableting to detection. Additionally, there also exists one characteristic peak between 1.3 THz-2 THz. As the mass ratio of chlorothalonil increases, the absorption peak gradually decreases. This result is also consistent with the experimental results of Li [25]. So from the above results, it is found that chlorothalonil can be effectively identified by THz-TDS technology through mixing it with polyethylene powder for tableting. However, it lacks sensitivity and the test results are not intuitive and quantitative. Therefore, we thought of using the metamaterials in combination with THz-TDS technology, which not only took advantage of THz-TDS to effectively identify the object, but also made up for its low detection sensitivity.

3.2. Pesticide detection in liquid samples
First, theoretical analysis about the designed metasensor was performed through simulations. We discussed the influence of the analyte thickness on the sensitivity of the sensor. By changing the refractive index of the analyte, the theoretical sensitivity (S) defined by the derivative of the transmission frequency shift to the refractive index change can be obtained. It can be seen from figure 4(a) that as the refractive index changes from 1 to 1.9, the transmission peak redshifts from 1.469 THz to 1.323 THz. In addition, as are shown in figures 4(b) and (c), it can be seen that when the thickness grows from 1 to 11 \( \mu \)m, the frequency shift \( \Delta f \) is improved from 30.6 to 90 GHz. The effect of the analyte layer thickness is shown in figure 4(c). It is obviously
found that with increasing the analyte thickness, the frequency shift increased accordingly. However, when the analyte thickness increases too much, the increasing of $\Delta f$ tends to be saturated at about 90 GHz. The relationship between the relative frequency shift ($\Delta f$) and the refractive index ($n$) is extracted and shown in figure 4(d). We can find that, with increasing the analyte thickness, the metasensor sensitivity also increases. Based on the metasensor we designed, the theoretical sensitivity can reach 156.3 GHz/RIU when the analyte thickness is 1 $\mu$m. This result is much higher than the maximum theoretical sensitivity of 49.3 GHz/RIU reported by Ranjan [26].

Many researches have been done to describe the output electromagnetic performances of some typical artificially created media [27–31]. During our researches, LC oscillator model is applied to describe the split ring resonator (SRR). When the refractive index of the analyte changes, the resonance frequency of the sensor is redshifted. Its resonance frequency is given by $\Omega = 1/\sqrt{LC}$, where L and C are the equivalent inductance and capacitance of the SRR model. $C = \varepsilon A/d$, where A is the area, d is the distance, and $\varepsilon$ is the dielectric constant of the capacitor. Therefore, chlorothalonil connected to the THz sensor causes an increase in the effective dielectric constant, which causes the resonance frequency to shift red [32].

In our experiments, because of the strong volatility of acetone, the acetone is completely evaporated within 5–10 min when 20 $\mu$l of the solution is added dropwise. Since the purity of chlorothalonil solids and acetone is 98% and 99%, on the metamaterial surface only leaves the solute chlorothalonil after acetone evaporates, which indicates that the factor that affects the dielectric constant change during these experiments is mainly determined by the remained solute chlorothalonil. In figure 5(a), the position of the resonance peak shifts with the concentration change, and the resonance frequency at 0 mg l$^{-1}$ is very close to 1.47 THz. It is because the FSRRs structure we designed has a strong local enhancement effect around 1.47 THz.

In order to observe more details, zooming the part within 1.38–1.52 THz, shown in the inset of figure 5(a), when the concentration of chlorothalonil increases from 0 mg l$^{-1}$ to 10 mg l$^{-1}$, the resonance peak moves from...
1.46 THz to 1.436 THz. As the chlorothalonil concentration increases, the position of the resonance peak shifts to red, which is similar to Qin’s test results for carbendazim in 2018 [19]. The resonance peak frequency shift at 0.05 mg l\(^{-1}\) is 0 GHz. That is to say the resonance peak is almost consistent with that at 0 mg l\(^{-1}\), which indicates that the detecting sensitivity cannot reach 0.05 mg l\(^{-1}\). When the concentration is 0.1 mg l\(^{-1}\), the resonance peak frequency shift is observed to be about 1.9 GHz. According to this value, we cannot infer that 0.1 mg l\(^{-1}\) is the concentration the metasensor sensitivity can reach, because the frequency resolution of TAS7400 is also 1.9 GHz. As shown in figure 5(b), the frequency shift value becomes very obvious as the solution concentration increases. The frequency shift value of the resonance peak can reach about 13.3 GHz, when the concentration increases from 1 mg l\(^{-1}\) to 2 mg l\(^{-1}\). So for the liquid sample, the metasensor could detect a small amount of chlorothalonil.

In order to appropriately determine the minimum sensitivity of chlorothalonil solution that can be detected by the metasensor, and furtherly study the statistical difference about the sensitivity detection, we conducted an analysis of variance for seven different concentrations of chlorothalonil solution. In the case of \( \alpha = 0.05 \) (\( \alpha \) indicates significant level), there was no significant difference between the concentrations of chlorothalonil solution 0 mg l\(^{-1}\) and 0.05 mg l\(^{-1}\), 0.1 mg l\(^{-1}\), and 0.2 mg l\(^{-1}\). That was to say \( F < F_{0.05} \). There are significant differences among 0 mg l\(^{-1}\) and 1 mg l\(^{-1}\), 2 mg l\(^{-1}\), and 10 mg l\(^{-1}\). That is to say \( F > F_{0.05} \). Therefore, we determined that the sensitivity of the designed metamaterial combined with THz-TDS equipment to detect chlorothalonil solution was 1 mg l\(^{-1}\).

For each test, the chlorothalonil solution added was 20 \( \mu l \). After the acetone was completely evaporated, we can get the mass of chlorothalonil remaining on the metasensor from the chlorothalonil solution. So for the liquid sample, the metasensor could detect a small amount of chlorothalonil.

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As is shown in table 1, we have provided the typical performance parameters of the sensors obtained recently. Under the same detection method, we can detect pesticide residue with a concentration limit of 1 mg l\(^{-1}\), while the detecting limit of another sensor proposed in \[19\] can only reach 5 mg l\(^{-1}\). Additionally, from the view of the effectiveness degree of using the metamaterial sensors, the sensitivity obtained with our sensor improved 10\(^6\) times, which is 100 times higher than that in Reference \[19\]. According to our knowledge, in the field of pesticide detection with THz wave, Zhao \textit{et al} \[20\] has obtained the highest detection sensitivity 175.5 GHz/RIU, slightly bigger than our result. But in Reference \[20\], analyte thickness during detection is 2 \(\mu\)m, twice as much as the thickness used in our research. As we know that with increasing the analyte thickness, the detection sensitivity will increase accordingly, as we analyzed in figure 4. during our research, when the analyte thickness is 1 \(\mu\)m, the detection sensitivity is about 156.3 GHz/RIU. When the thickness is 2 \(\mu\)m, the detection sensitivity is about 225.3 GHz/RIU, which is higher than the result in Reference \[20\]. Although the detection sample volume is slightly higher than the detection sample volume in \[21\], the sensitivity of our sensor is much greater than the sensitivity given in \[21\]. The above comparisons indicate that the metasurface structure we designed can locally enhances the electromagnetic wave more effectively, and then increase the detection sensitivity.

4. Conclusion

In this article, we designed a THz metasensor that can be used to detect the pesticide chlorothalonil. This sensor has a clear resonance peak near 1.47 THz. The experimental measurement results are in good agreement with the simulation results. In theory, a 1 \(\mu\)m-thick analyte layer has a sensitivity of 153.6 GHz/RIU (RIU, refractive index unit). Through the THz Fano metasensor, we can not only identify the characteristic fingerprint spectrum of chlorothalonil, but also accurately measure the minimum content of 1 mg l\(^{-1}\) by adding only 20 \(\mu\)l chlorothalonil solution. Compared with measuring with THz-TDS without the metasensor, the sensitivity of THz detection of chlorothalonil solution is increased by about 10\(^6\) times. This means that the THz metasensor is very effective for identifying the pesticide residue with a high sensitivity and has a potential application in the field of food safety. However, if a variety of pesticide residues are mixed in the object, our metasensor will not be
Table 1. Sensor performance comparison.

| Device structure name | Analyte thickness/The volume of the sample | Detection limit | Sensitivity | Compared with the detection sensitivity results without metamaterials | Year |
|-----------------------|-------------------------------------------|-----------------|-------------|---------------------------------------------------------------|------|
| The four-split ring resonators\(^a\) | 1 \(\mu\)m(20 \(\mu\)l) | 1 mg l\(^{-1}\) | 156.3 GHz/RIU | 10\(^6\) | 2020 |
| The ohm ring arrays [19] | | 5 mg l\(^{-1}\) | | 10\(^4\) | 2018 |
| Split ring resonators with three splits [20] | 2 \(\mu\)m | | 175.5 GHz/RIU | | 2020 |
| Five square rings with two micro-gaps in the ring [21] | 7 \(\mu\)l | | 28.3 GHz/RIU | | 2020 |

\(^a\) stands for this article.
able to accurately distinguish them. Therefore, how to identify pesticide residue types and accurately the content of them, this is our reasearch direction in the future.

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