Research article

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Ultra-wideband enhancement on mid-infrared fingerprint sensing for 2D materials and analytes of monolayers by a metagrating

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Abstract: Mid-infrared absorption spectroscopy is a powerful tool to identify analytes by detecting their material fingerprint in a label-free way, but it faces barriers on trace-amount analysis due to the difficulties in enhancing the broadband spectral signals. Here, we propose a sensing scheme based on the angular scanning of polarized light on a dielectric metagrating, and demonstrate it by numerical simulation. This approach not only indicates a series of significant signal enhancement factors over 30 times in an ultra-wide mid-infrared band, but also enables the explicit identification for various analytes, including 2D materials and trace-amount thin film samples. Our method would facilitate mid-infrared sensing for 2D materials and trace-amount analysis, and enable many new applications on non-destructive molecular identification.

Keywords: 2D materials; mid-infrared fingerprint; trace-amount analysis.

1 Introduction

Mid-infrared (mid-IR) spectroscopy is capable of detecting and identifying many kinds of molecules by diverse fingerprint spectra of absorption, which are induced by various vibrational modes of material microstructures [1, 2]. This approach directly extracts the specific chemical information of some critical components within a

complicated specimen. Due to the non-destructive and label-free features, mid-IR spectroscopy has wide applications in many fields, such as safety inspection, healthcare, food security, environmental monitoring, and characterization of emerging 2D materials [3–10]. In the detection of bulk samples, one is able to obtain distinct mid-IR absorption features based on the Beer–Lambert law, in which the spectral signals of molecular vibration are strong enough due to the sufficient light attenuation through the large optical thickness in the samples [11]. However, in the detection of trace-amount substances or 2D materials, the sample thickness is typically much smaller than the mid-IR wavelengths, which leads to very weak light–matter interaction and extremely low detection performance. In the past few years, many efforts have been made on surface-enhanced infrared absorption spectroscopy (SEIRAS) in order to overcome the limitation of detecting trace-amount substances or 2D materials [12–14]. As one important solution of SEIRAS, the use of plasmonic nanostructures demonstrates significant absorption enhancement on the mid-IR molecular fingerprint spectra; nevertheless, plasmonic enhancement suffers from large damping in noble metals and isolated narrowband enhancement that hinder broadband fingerprint detection [15–19]. In order to detect broadband absorption features, some SEIRA studies are focused on the dynamic tunability by using graphene or phase change materials [20–22]. These efforts not only achieve relatively low detection enhancement but also require specific control by voltage or temperature, which obstructs their further applications in various practical environments. The molecular barcoding by using dielectric metasurfaces has brought about an effective way for broadband fingerprint detection, but it needs a series of complicated metasurfaces involving dedicated nanofabrication and still lacks the dynamic tunability on a fixed sensing structure [23, 24]. Very recently, Leitis et al. have reported a promising dynamic tuning scheme for broadband SEIRA of molecules by using an angle-multiplexed metasurface with the zigzag array of elliptical dielectric resonators [25]. This work implies that

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the polarization and angle manipulation on a metasurface has a great potential for broadband molecular fingerprint sensing. Therefore, in order to have better sensing performance for more demanded analytes, more efforts could be made on optimizing the light–matter interaction by the polarization and angle tuning on a metasurface or an analog.

Instead of using a metasurface, we propose a simpler design of dielectric metagrating to achieve broadband enhancement on mid-IR fingerprint detection for 2D materials and trace-amount substances. We illuminate this design by a series of numerical simulation. By means of the polarization and angle manipulation on a metagrating, the localized field is well-confined and strengthened on the analytes, and the mid-IR fingerprint spectra are enhanced significantly. Furthermore, the detection for various analytes is evaluated and demonstrates a powerful capability to identify the 2D material hexagonal boron nitride (*hBN*) or other ultrathin analytes by their mid-IR fingerprint spectra.

2 Design and methods

In this study, we design a metagrating based on the angle-multiplexed spectral signals, as shown in Figure 1a. With the aim to achieve broadband sensing, the metagrating is intended to have narrowband optical reflection around a specific resonance wavelength for each incidence angle θ . In the detection process, the trace-amount analyte has a much smaller thickness compared with the designed sizes of the metagrating. In view of this, the incident wave is intended to have the electric field sufficiently located within the ultrathin layer at any incident angle. Based on our previous work, an incidence of TE wave is better to make the light–matter interaction as strong as possible [26–28]. Therefore, we mainly focus on the use of TE wave for the detection. The metagrating consists of the periodical array of zinc sulfide (ZnS) microstrips on a calcium fluoride (CaF₂) layer, followed by a flat substrate. Except for the analyte layer, all the materials are assumed to be optically lossless and nonmagnetic. In the mid-IR range, the refractive index values of ZnS and CaF₂ are 2.2 and 1.35, respectively [29, 30]. An extremely thin layer of analyte (from 0.34 to 8 nm) is coated on the metagrating conformally. In order to obtain all the spectral results and field distributions, we perform a series of 2D optical simulation based on the frequency-domain finite element method by using the commercial software Comsol Multiphysics [31]. In the simulation, all the materials are assumed to be isotropic, the unit cell of a subwavelength grating is adopted with periodic Floquet boundary conditions. The

triangular meshing is used to discretize the unit cell. In order to simplify the simulation model, the perfect electric conductor boundary condition is used for the metal mirror substrate. The minimum triangular mesh size is as small as 1/5543 of the unit cell period, and the largest mesh element dimension is kept below one-tenth of the smallest wavelength used. In addition, the monolayer *hBN* is extremely thin (0.34 nm) compared with the smallest wavelength, and the interaction between the mid-IR light and *hBN* is originated from the carrier migration in the atomic plane of *hBN*, so the *hBN* layer can be also treated as an effective conductive boundary in the simulation. Compared with the bulk configuration for *hBN*, the use of a conductive boundary reduces the number of mesh and simulation time significantly. Besides, the incidence angle of TE wave changes from 0° to 65° with the 1° step, and the angle interval depends on the kind of detected analyte. Furthermore, a possible state-of-the-art fabrication method for the proposed sensing structure is shown in Figure S1 in the supplementary material.

In Figure 1b, we show the mid-IR reflectance as a function of the free space wavelength λ and the incident angle θ , which indicates multiple narrow reflectance bands. As observed from these reflectance bands, the one in a relatively large wavelength range from 6.9 to 9.4 μm indicates that the wavelength of maximum reflectance has a linear monotone increase as the incident angle θ enlarges from 5° to 45°. This feature can be observed more explicitly by the reflectance spectra shown in Figure 1c. Such optical response can be interpreted by the theory of guided-mode resonance (GMR) [32–34], which refers to a light beam that enters the grating waveguide at an angular orientation and forms a resonance in it at a specific wavelength. The light can be trapped and concentrated in the grating waveguide in such a resonance mode. In order to couple the incidence wave to the guided mode, it is necessary to fulfill the phase-matching condition, and the effective propagation constant within the metagrating without a substrate can be determined by the following equation [34],

$$\beta_m = k_0 \left(N_0 \sin \theta - \frac{m\lambda_R}{P} \right) \quad (1)$$

where m denotes the order of a diffraction wave, k_0 is the wavenumber of the free space, N_0 is the refractive index of the incident medium (here is the refractive index of air), λ_R is the resonance wavelength, and P is the periodicity of the grating structure. Particularly, when m equals 1, Equation (1) represents the basic mode of this resonance. The other high order modes correspond to the reflectance bands from 3 to 6.4 μm , as shown in Figure 1b, and they

Figure 1: (a) Schematic drawing of the angle-multiplexed metagrating. The symbols w , P , t_1 , t_2 , and θ represent the width of ZnS, grating periodicity, thickness of ZnS, thickness of CaF_2 , and incident angle, respectively. (b) Reflectance as a function of λ and θ and (c) the corresponding angle-dependent reflectance spectra ($m = 1$) for the unloaded metagrating with a metallic substrate; (d) GMR wavelength as a function of θ for the unloaded metagrating without a metal substrate, where $w = 2.16 \mu\text{m}$, $P = 4.9 \mu\text{m}$, $t_1 = 1 \mu\text{m}$, $t_2 = 1.78 \mu\text{m}$.

have some overlaps and cover smaller wavelength ranges as the linear change of angle, which is less advantageous than the basic mode. As shown in Figure 1d, we plot the GMR wavelength ($m = 1$) as a function of the incident angle. The analytical calculation based on Equation (1) shows good consistency with the FEM simulation result. Both of the two results demonstrate that the GMR wavelength is linearly increased with the incident angle becoming larger. The central wavelength and bandwidth of the GMR are based on structural parameters such as the grating depth and periodicity, as well as the thickness of the flat dielectric layer. So, we can design and optimize the metagrating structure for diverse sensing applications. In the detection process, the scanning angles can be tuned along with the fingerprint spectral range of the analyte to be detected.

In this study, we evaluate the sensing performance for the typical 2D materials of boron nitride, namely *cBN*

(cubic boron nitride) and *hBN*. *cBN* can be used as protective coating films for microelectronic devices at high temperatures, whereas *hBN* can be one component in novel microelectronic devices due to its good electrical insulation, thermal conductivity and stability. The non-destructive mid-IR fingerprint detection is a fast and convenient way to identify these two materials in their applications. In the modeling, the *hBN* is assumed as a kind of van der Waals monolayer with the in-plane phonon mode in the mid-IR range. An oscillator model is used to describe its in-plane relative permittivity function [35],

$$\epsilon_{hBN}(\omega) = \epsilon_{\infty} + \sum_i \frac{S_i^2}{\omega_i^2 - \omega^2 + i\omega\gamma_i} \quad (2)$$

where $\epsilon_{\infty} = 4.95$ and ω are the high-frequency dielectric permittivity and the angular frequency, respectively. The parameters for the strong in-plane phonon mode are

$\omega_1 = 1370 \text{ cm}^{-1}$ and $s_1^2 = 3.9 \times 10^6 \text{ cm}^{-2}$. The corresponding damping constant is $\gamma_1 = 19 \text{ cm}^{-1}$. The complex refractive index of *h*BN can be calculated by the following equation,

$$N(\omega) = \sqrt{\varepsilon_{h\text{BN}}(\omega) \cdot \mu_0} = n(\omega) + ik(\omega) \quad (3)$$

where $\mu_0 = 1$ is the vacuum permeability, and $n(\omega)$ and $k(\omega)$ represent the refractive index and extinction coefficient, respectively.

3 Results and discussion

3.1 Broadband sensing mechanism

We first evaluate the effects of light–matter interaction for the coated analyte. As one of the most popular 2D materials, the *h*BN monolayer is introduced to be detected for the investigation [36, 37]. It is worth mentioning that the metagrating with a metallic substrate demonstrates much stronger light–matter interaction compared with the free-standing one without a substrate. As shown in Figure 2a, both the metagratings with and without a substrate support the GMR at the wavelength of $7.18 \mu\text{m}$ by two different excitation angles, but the use of a metallic substrate enhances the local magnetic and electric fields surrounding the grating much more significantly. The maximum electric near-field enhancement of $|E/E_0|$ is up to 45.5, which is higher than the simulated result in Ref. [23] and implies the

metagrating might have a higher efficiency of near-field enhancement than the metasurface. Particularly, the electric field of resonance on the extremely thin layer of *h*BN ($\sim 0.34 \text{ nm}$) is greatly enhanced, and this effectively strengthens the interaction between the incident light and the 2D material, which can be further explained by the calculation of optical absorption. In *h*BN, the optical absorption is determined by the following equation [38, 39],

$$A(\lambda) = \frac{4\pi c}{\lambda} \cdot n(\lambda) \cdot k(\lambda) \cdot \int_V |E_l|^2 dV \quad (4)$$

where c is the speed of light in free space, λ is the free space wavelength, V is the volume of *h*BN, and E_l is the local electric field. Based on Equation (4), the enhancement of the in-plane electric field on *h*BN can lead to high optical absorption at the resonance wavelength.

We next demonstrate the broadband detection mechanism of the proposed scheme by coating the *h*BN analyte on the metagrating conformally. According to the previous work [40], this kind of coating is feasible in fabrication. The imaginary part of the complex refractive index of *h*BN in Figure 2b implies the obvious optical loss in the wavelength range from 7 to $7.6 \mu\text{m}$ [41], which denotes the in-plane optical phonon mode of *h*BN monolayer. When a series of incident angles (0° , 13° , 17° , 18° , and 20°) are applied on the metagrating, the different GMR wavelengths lead to diverse mid-IR absorbance spectra, and these spectral peaks reflect the value differences of the extinction coefficient for *h*BN. For instance, the absorbance peak at

Figure 2: (a) Field distributions for the *h*BN-coated metagrating with and without a metallic substrate, which is underneath CaF_2 ; (b) optical constant and angle-dependent absorbance spectra for *h*BN on the metagrating; (c) field distributions at the wavelength of $7.29 \mu\text{m}$, where the structure parameters are consistent with Figure 1.

Figure 3: (a) A series of reflectance spectra by angular scan from 16° to 25° and their corresponding envelope curve for the *h*BN-coated metagrating; (b) absorbance envelope curve and the reference absorbance spectrum of *h*BN, where the structure sizes are consistent with Figure 1. (c) Absorbance enhancement factors for *h*BN detection.

$\lambda = 7.29 \mu\text{m}$ for $\theta = 18^\circ$ corresponds to the maximum of the material extinction coefficient, whereas there is no obvious spectral peak for $\theta = 0^\circ$ because the resonance wavelength is far away from the peak value wavelength of the extinction coefficient. To further provide the physical insight, we plot the magnetic and electric field distributions for different incident angles at the fixed wavelength of $7.29 \mu\text{m}$ in Figure 2c. As the incident angle gradually changes from 13° to 20° , a remarkable magnetic field enhancement appears for $\theta = 18^\circ$ due to the GMR at this wavelength. The magnetic field is mainly confined in the ZnS grating, and induces strong electric field along the surface of the metagrating. The stronger local in-plane field leads to higher mid-IR absorbance in the *h*BN monolayer, according to Equation (4). Because the enhanced local field is mainly concentrated surrounding the interface between the air and grating, one can place the samples of 2D materials or other trace-amount analytes on the metagrating and apply the angular scanning for improved sensing performance.

3.2 Detection of 2D material

After understanding the broadband detection mechanism, we continue to have a comprehensive evaluation of the mid-IR fingerprint sensing for the 2D material *h*BN. In the detection, a series of reflectance spectra is obtained by scanning the incidence angle from 16° to 25° (one reflectance spectrum for each angle), as shown in Figure 3a. By linking all the valley values of the reflectance spectra (in gray), we acquire an envelope curve (in red), which has a dip around $7.29 \mu\text{m}$ and clearly denotes the in-plane optical phonon mode of *h*BN. To have a comparison with the absorbance spectrum of *h*BN on an unpatterned substrate, we plot the envelope curve of the absorbance spectra, as shown in Figure 3b. It shows that the spectral signal intensity is enhanced from 0.11 to 3.74% at the wavelength of

$7.29 \mu\text{m}$, which demonstrates 34 times of enhancement. Compared to the simulated infrared reflection absorbance spectrum of Figure S2 in the supplementary material, the enhancement is much more remarkable. The signal enhancement is not only limited in a certain narrowband range, but also extended to the entire wavelength range from 6.0 to $9.0 \mu\text{m}$. Due to the enhancement, the fingerprint of *h*BN can be observed much more clearly as shown in Figure 3b. In order to have a comprehensive understanding of the broadband detection effects, we define the factor of absorbance enhancement by the standard decibel (dB) unit as shown below,

$$\alpha = 10 \lg \left(\frac{\int_{\lambda_1}^{\lambda_2} A_{\text{meta}}(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} A_{\text{flat}}(\lambda) d\lambda} \right) \quad (5)$$

where λ_1 and λ_2 represent the starting and ending wavelengths of a narrowband for calculation, respectively; $A_{\text{meta}}(\lambda)$ is the absorbance of the analyte on a metagrating as a function of wavelength; $A_{\text{flat}}(\lambda)$ is the absorbance of the analyte on an unpatterned flat substrate. The broadband enhancement factors for *h*BN is calculated and shown in Figure 3c. For the band from 6.0 to $9.0 \mu\text{m}$, the angular manipulation on a metagrating provides about 15 dB of enhancement for the fingerprint detection of *h*BN, which shows significant broadband sensing improvement. Therefore, the proposed method can generally bring about a considerable increase in the signal-to-noise, which is very critical in practical measurement.

3.3 Identification of the isomer

To further illuminate the broadband sensing enhancement, we also detect an ultrathin film of cBN (cubic boron nitride), which is an isomer of *h*BN. The fingerprint

spectrum of cBN is remarkably different from that of hBN, and the detection of fingerprint spectra would provide a critical method to identify the two kinds of materials. As shown in Figure 4a, there is a maximum value for the extinction coefficient of cBN at the wavelength of $9.37\text{ }\mu\text{m}$ [42]. As a comparison, the envelope curve derived from the reflectance spectra by incident angle scanning has a dip at the same wavelength, which corresponds to the material microstructure vibrational mode of cBN. As observed in Figure 4c, the envelope spectral signal is also much stronger than the reference absorbance spectrum, and its peak value is 77.13% at the wavelength of $9.37\text{ }\mu\text{m}$, which is about 5.4 times of that for the unpatterned reference. As calculated in Figure 4d, the enhancing factors of absorbance are from 7.1 to 8.6 dB, showing broadband enhancement. The enhancement factors depend on the electric near-field distribution, the analyte thickness compared with the resonance wavelength, and the corresponding (n, k) values shown in Equation (4). The cBN layer has a much larger thickness versus the scanning wavelengths, so it shows smaller enhancement factors. Despite of this, the broadband sensing enhancement for cBN is still sufficient for its detection. These results indicate that one can use the non-destructive scheme to distinguish the

extremely thin materials of isomers by the enhanced fingerprint signal, which would definitely enable many new applications of 2D materials.

3.4 Detection of trace-amount analytes

Our method can not only identify 2D materials, but also detect other trace-amount analytes. Here, we finally evaluate the broadband molecular fingerprint sensing for an ultrathin layer of perfluoropolyether (PFPE), which is a kind of polymer widely used as a lubricant in magnetic recording and aerospace systems [43]. The complex refractive index of PFPE is shown in Figure 5a, the extinction coefficient of which implies two obvious peak features at the wavelengths of about 8.3 and $9.1\text{ }\mu\text{m}$, respectively. In the metagrating, the PFPE layer is also extremely thin (8 nm), and the electric field can be effectively localized and enhanced on it by using the GMR effects. As shown in Figure 5b, we can retrieve the envelope curve from the reflectance spectra scanned by the angle between 20° and 65° . The reflectance envelope shows the fingerprint features by the spectral dips at about 8.3 and $9.1\text{ }\mu\text{m}$, respectively. In Figure 5c, we also compare the

Figure 4: (a) Complex refractive index of cBN. (b) Reflectance spectra (θ from 10° to 40°) and their envelope curve for a 2 nm thick cBN layer; (c) absorbance envelope curve and the reference spectrum of cBN, where $w = 2.16\text{ }\mu\text{m}$, $P = 6.5\text{ }\mu\text{m}$, $t_1 = 1\text{ }\mu\text{m}$, $t_2 = 2\text{ }\mu\text{m}$. (d) Absorbance enhancement factors for cBN detection.

Figure 5: (a) Complex refractive index of PFPE. (b) Reflectance spectra (θ from 20° to 65°) and their envelope curve for the PFPE layer with a 8 nm thickness; (c) absorbance envelope curve and the reference spectrum of PFPE, where $w = 2.16 \mu\text{m}$, $P = 4.78 \mu\text{m}$, $t_1 = 1 \mu\text{m}$, $t_2 = 1.78 \mu\text{m}$. (d) Absorbance enhancement factors for PFPE detection.

absorbance envelope and the reference absorbance spectrum. It shows that the sensing by an unpatterned scheme has very low absorbance (less than 5%) with indistinct peak features in the wavelength range from 7.5 to 9.5 μm , which would denote the main vibrational bands of the PFPE molecule. In contrast, the retrieved absorbance envelope greatly enhances the fingerprint features, especially amplifying the peak values to 42.9 and 24.3% at the wavelengths of 8.3 and 9.1 μm , respectively. The absorbance enhancement factors are extracted in Figure 5d in order to show the boost of broadband sensing performance. The PFPE layer is much thicker than the *h*BN and *c*BN analytes, and its wider angular scanning has more influences on the near-field distribution surrounding the analytes, so its enhancement factor shows relatively stronger change with the wavelength than the other two analytes. Figure 5d indicates that all the enhancement factors are above 8 dB in the wavelength range from 7.5 to 9.5 μm , which further confirms that the proposed scheme is capable to strengthen the weak fingerprint spectrum in a wide band for the trace-amount analysis.

4 Conclusions

In summary, we propose a kind of mid-IR fingerprint detection scheme by the angle-multiplexed sensing on a dielectric metagrating. By using the guided-mode resonance, the metagrating can be designed to identify 2D materials and other ultrathin analytes through fingerprint retrieval from a series of absorbance spectra. The mid-IR angular scanning on the dielectric resonance structure enhances the broadband fingerprint spectral signal significantly, which will facilitate many new applications on non-destructive trace-amount analysis.

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