Terahertz volatile gas sensing by using polymer microporous membranes

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Abstract: A compact, inexpensive, low loss, highly sensitive gas sensor is important for various biomedical and industrial applications. However, current gas sensors still have an inadequate study in terahertz (THz) frequency range. In this study, simple multilayer-stacked microporous polymer membranes are experimentally validated in the THz regime for organic vapor sensing under ambient atmosphere and room temperature. The hydrophilic porous polymer structure provides a large surface area to adsorb polar vapors, and exhibits excellent discrimination in different types of organic vapors based on distinct dipole moments. Various concentrations of volatile vapors can also be successfully distinguished by detecting the limits of low ppm concentrations. Furthermore, the microporous structural gas sensor has a reasonable response time in repeat usage. This study would provide new perspectives on toxic gas sensing and exhaled breath detection applications in the THz spectral frequency.

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References and links

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1. Introduction

Gas sensing is important in certain applications, such as gaseous chemical and environmental pollutant monitoring, medical breath analysis, and leaky molecules detection for various toxic, volatile, or explosive gases. Various types of gas sensors based on different detection principles have been developed, such as gas chromatography–mass spectroscopy [1], electrochemical [2], and optical sensors. The electrochemical sensors, like metal oxide semiconductors [3, 4], are often operated at a raised temperature for high sensitivity, causing high power consumption and sparking risks in explosive gas detection. The optical sensing scheme can solve this problem of unsafe operation, because it is advantageous to room temperature operation, without electric contact, and with electromagnetic immunity. Terahertz (THz) radiation, which lies between the infrared and microwave regions, can strongly interact with polar molecules via rotational or vibrational level transitions. The absorption strength for gas molecules in the THz frequency range is typically on the same order of magnitude as the mid-infrared ray (IR) region and is approximately 10^7 to 10^8 stronger than that in the microwave region [5]. The low photon energy of the THz wave is relatively safer than that of mid-IR radiation and has a stronger polar molecular interaction than that of the microwave region [6–8]. THz gas sensing techniques have been validated by using two fundamental methods. One method is to radiate THz waves directly on the gaseous analytes and acquire their spectral information, such as the fingerprint feature or decay signals of a pulse [9] as response signals for sensing purposes. As reported in literature, the systems
include photo-mixing [10], heterodyne detection [1, 11], and chirped-pulse THz spectroscopy [12]. The spectroscopic approach has been used to analyze the gas mixtures of more than 30 chemicals [1] and distinguish gases that possess similar compositions by fingerprint spectra information. This recognition system provides high selectivity based on the rotational/vibrational transition of gas molecules. Nevertheless, the THz spectroscopic system should be equipped with a long folded multipass gas cell [1, 9, 12], a cryo/sorbent pre-concentration system, and a heating apparatus [1, 11] to improve the sensing limit from the ppm concentration to the ppb level. The overall configuration is complicated, bulky, expensive, and consumes high power. Recently, quantum cascade laser is presented as a THz laser source for gas sensing applications [13, 14] to simplify THz wave generation. However, the use of THz laser source has some operational constraints, particularly in the low-temperature condition [14], which limits practical applications. The other method is to use the THz resonance field in a photonic crystal [15, 16] or a waveguide device [17, 18] for gas sensing. This method is sensitive to slight variations of the refractive index. For example, a THz antiresonant waveguide has been successfully validated for volatile vapor sensing and its sensitivity is approximately 1.6 nmol/mm³ [18]. One-dimensional photonic crystal cavity based on silicon slabs [15] and 2D photonic crystal resonators [16] based on pillar arrays have also been validated for non-specific gas sensing in the THz frequency range. The proposed resonator structure has a high quality factor and is able to detect slight changes in the refractive index. The demonstrated detection limit for hydrogen gas is approximately 6% concentration change [15]. The approved minimum detectable amount of oxygen or argon is approximately 1 µmol [16]. Although the resonator-type THz gas sensor is relatively compact, portable, and consumes low power, its short interaction length inside the chip essentially leads to the limited sensitivity and poor selectivity.

In recent decades, various porous materials [19–23], such as porous silicon (PS) [19, 20], porous zinc oxide [21], carbon nanotubes [22], and mesoporous powder [23], have been extensively used for optical gas sensing. Porous materials have sponge-like structures with a large internal surface capacity; thus, such materials can adsorb large amounts of gas molecules inside the pores to modify the original optical properties. When the gas molecules increase inside the nanopores, capillary condensation will generally occur and cause evident changes in the refractive index. Optical sensor responses, such as the apparent spectral shifts of interference fringe and resonant peaks or dips [19], are significantly enhanced. The interaction length between electromagnetic waves and analytes can also be easily decreased to achieve a compact size for the sensing unit. For example, PS is often fabricated into various configurations, such as multilayer-stacked photonic crystal devices [20], periodically arranged colloidal beads [24], or a single membrane [19], to identify various volatile organic gases with the sensitivity of several hundreds of ppm levels [19, 20, 24]. However, the PS structure is fragile and cannot be easily acquired because of complicated fabrications [25]. Although porous materials are extensively used in the optical regime as biological substances [26] and gas sensors, applications in the THz regime have not yet been reported.

In this study, we experimentally validate a microporous structure for organic vapor sensing in the THz frequency range. The simple microporous structure can be easily fabricated by hand by stacking multiple layers of flexible plastic porous membranes with different porosities. Different types and concentrations of volatile vapors have been successfully distinguished at room temperature and ambient atmosphere by analyzing the THz wave attenuation and refractive index change in the microporous structure. In experiment, we successfully detected 17 ppm of acetone vapor. The detection limit extrapolated from the linear fitting curve, that is, the minimum detectable concentration variation, can be less than 7 ppm, which corresponds to a molecular density of 125 pmol/mm³. To our knowledge, this study is the first to combine such a polymer microporous structure with THz spectroscopy for gas sensing. The advantages of the sensor are flexibility, inexpensive/easy preparation, low THz-wave loss, and high sensitivity compared with the...
resonance-type THz sensors [15–18]. Furthermore, the sensor has a reasonable response time in repeat usage with the removal of analytes by purging airflow. In situ response and recovery properties of the sensor are also discussed in this study.

2. Porous polymer structure for gas sensing and experimental setup

A multilayered porous structure for gas sensing is alternatively stacked by two types of polyethylene terephthalate (PET) membranes, which are clamped by a rectangular acrylic ring with a clear aperture of 1 cm × 1 cm [Fig. 1(a)]. The PET membranes are purchased from SEFAR AG (Switzerland). The two types of PET membranes (SEFAR PET1000) have different square pore sizes, that is, 249 (Mesh Number 27-120W PW) and 90 µm (Mesh Number 61-64W PW) of the side length. The corresponding porosities are 45% and 30%. The two pieces of the different porous membranes are considered as a unit, and the microporous structure is composed by 11.5 units, including 12 pieces of 45%-porosity membrane and 11 pieces of 30%-porosity membrane. Figure 1(b) shows the microscopic photographs of the two membranes. The surface of the PET porous membrane is modified to be hydrophilic for adsorbing polar gaseous molecules. For the gas sensing experiment, the microporous structure is enclosed in a sample chamber that is approximately 36 mL of the total volume and made of Teflon material. As shown in Fig. 1(c), a microfluidic channel at the bottom of the sample chamber is connected to a flexible plastic tube for injecting different volatile liquids from the liquid inlet. An air pump with a flow speed of 23 L/min is connected to the outlet port of the chamber to investigate the response and recovery times of the microporous gas sensor. It should be noted that once the air-pump works, the Teflon chamber is not kept sealed. The liquid inlet was opened for removing all the vapors from the chamber and replacing with the atmospheric air.

The injected volatile liquid is naturally evaporated into gas molecules at ambient atmosphere until saturated vapor pressure is achieved in the chamber. Thereafter, the volatile vapor fills the microporous structure for gas sensing. One part of the vapor is adsorbed on the hydrophilic membrane surface, and the other part infiltrates into the empty space of the porous structure. Thus, multiple gas samples can be detected when THz waves pass through the microporous structure. Herein, four vapor species of acetone, methanol, ethanol, and ammonia are used as the test samples in the experiment; these vapor species respectively
belong to the three types of volatile organic compounds (VOCs), namely, ketone, alcohol, and ammonia. Their distinct saturated vapor pressures are 32.5, 17.7, 8, and 68 kPa, respectively [19], under normal temperature and pressure conditions.

As shown in Fig. 1(c), the focused THz beam is normally incident on the device and the transmitted THz waveform for different vapor analytes in the microporous device is measured by using the transmission-type THz time domain spectroscopy (THz-TDS) system [18] to characterize sensing performance. A THz pulse, generated from a LT-GaAs-based photoconductive antenna, was collimated by a parabolic mirror and directly focused on the microporous structure by a plastic lens with an effective focal length of 25mm. The THz signal transmitted through the microporous structure was then collected by a pair of plastic lenses and coupled into a photoconductive detector for THz waveform measurement. Different types and concentrations of volatile gases are distinguished on the basis of the effective absorption coefficients and refractive indexes of micropores in the device. The transmitted THz spectra of the microporous structure with and without vapor analytes are defined in Eqs. (1) and (2):

\begin{equation}
P_{v_p}(\omega) = P_0(\omega)e^{-2\alpha_{v_p}(\omega)L},
\end{equation}

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\end{equation}

The subscripts \(p\) and \(v + p\) in the equations represent the sample chamber without and with vapor analytes, respectively. \(P_0(\omega)\), \(\alpha(\omega)\), and \(L\) represent the input THz wave power, effective absorption coefficient of micropores, and thickness of the multilayer-stacked device, respectively. According to effective medium theory, the effective absorption coefficient of the microporous structure with vapor analytes can be approximately written as follows:

\begin{equation}
\alpha_{v+p} = \alpha_v f + \alpha_{PET}(1-f).
\end{equation}

For the blank structure, the effective absorption coefficient is written as follows:

\begin{equation}
\alpha_p = \alpha_{air} f + \alpha_{PET}(1-f).
\end{equation}

\(f\), \(\alpha_v\), \(\alpha_{air}\), and \(\alpha_{PET}\) are the filling ratio of micropores in a microporous structure and the absorption coefficients of vapor analyte, air, and PET material, respectively [Eqs. (3) and (4)]. \(\alpha_{v+p}\) and \(\alpha_v\) in Eqs. (1) and (2) are substituted by Eqs. (3) and (4). The filling ratio is defined as the occupied percentage of the air pore volume inside the 23-layered microporous structure. Thereafter, the absorption coefficient variation \((\alpha_v - \alpha_{air})\) is derived as \(\ln(P_p / P_{v+p})/(2fL)\), which approximates to \(\alpha\) because the THz wave absorption of air is as small as \(10^{-5}\) cm\(^{-1}\) [27].

Furthermore, the phase difference for the unit volume of pores with and without vapors in the structure can be defined as \(\Delta \phi' = \Delta \phi / V_{pore}\), where \(\Delta \phi = \phi_{v+p} - \phi_p\) and \(V_{pore}\) are the phase difference for microporous structures with and without vapors and the total pore volume, respectively. The phase difference \(\Delta \phi\) and the total volume of the micropore \(V_{pore}\) can be individually estimated from the relations of \((\omega / c) \cdot \Delta n \cdot L\) and \(A_{beam} \cdot f \cdot L\), where \(\Delta n\), \(\omega\), \(c\), and \(A_{beam}\) are the refractive index variation, angular frequency, light speed in vacuum and input THz beam size on the structure, respectively. On the basis of the aforementioned correlations, the phase difference for the unit volume of pore \(\Delta \phi'\) can be rewritten as follows:

\begin{equation}
\Delta \phi' = \Delta \phi / V_{pore} = \omega |c| \Delta n',
\end{equation}

where \(\Delta n' = \Delta n / (A_{beam} \cdot f)\). The effective refractive index variation of micropore \(\Delta n'\) can be extracted from the phase information of the measured THz waveforms and correlated to the pore volume \(V_{pore}\). For the 23-layered PET microporous structure, the total volume of structure, \(V_{total}\), and the pore-volume, \(V_{pore}\), are respectively 6.11 and 2.99 mm\(^3\) within a 1.5
mm spot size. As a consequence, the calculated average pore-filling ratio of the device, $f = V_{pore}/V_{total}$, is approximately 49%. Based on the aforementioned calculation procedure, the detected signals of absorption coefficient and refractive index variation are measured and compared with and without vapors infiltration in the microporous structure. Therefore, the intrinsic absorption and scattering loss from any material along the propagation axis can be excluded.

3. Sensing results

The sensing capability of the microporous structure was first investigated under different amounts of acetone vapor exposure by recording the absorption coefficients of micropores. Figure 2(a) shows the THz transmission spectra of the microporous structure before and after exposure to different concentrations of acetone vapor. The THz spectra are evidently distinct when acetone aqueous solutions with concentrations of 2.5% to 100% naturally evaporate until the individually saturated vapor pressure is achieved inside the chamber. According to the Raoult’s law [28], the aqueous acetone concentration is approximately proportional to the vapor pressure inside the chamber, that is, the large concentration of acetone aqueous solution generates a large vapor pressure of acetone.

![Figure 2(a) Transmission power spectra and (b) the correlated effective absorption coefficient spectra of micropores in the microporous structure for various aqueous acetone concentrations.](image)

Figure 2(a) shows that the increased amount of acetone vapor results in power reduction in the THz frequency range of 0.1 THz to 0.45 THz. Figure 2(b) shows the THz absorption coefficient spectra of micropores under different concentrations of acetone vapor exposure, which is extracted from the information including spectral transmittance, structure thickness of 3.5 mm, and average pore-filling ratio of 49%. The detailed calculations are shown in Eqs. (1) to (4). Evidently, the absorption coefficient increases with increasing THz frequency and vapor molecular density. Thus, on the basis of the ideal gas formula and vapor pressures of different acetone concentrations in aqueous solutions, the correlated molecular densities of acetone vapors inside the chamber (denoted as $\rho$ in this study) can be obtained. The vapor pressures for different concentrations of acetone solutions are estimated based on the experimental database in [29] and not by using Raoult’s law.

In vapor sensing experiment, our THz-TDS system provides sufficient signal-to-noise ratio (SNR) at 0.10~0.45THz as shown in Fig. 2(a). Within the frequency range, the extracted absorption coefficients for different acetone vapor concentrations achieve the largest distinction at around 0.4THz as shown in Fig. 2(b). Therefore, considering the reliable SNR and the best THz photon response of acetone vapor in the spectroscopic system, we apply the 0.4 THz wave to probe analytes with various molecular densities inside the chamber. Figures 3(a) and 3(b) show the sensing results of 0.4 THz to detect different concentrations of acetone vapors with and without using the microporous structure inside the chamber, respectively.
Fig. 3(a), the absorption coefficient ($\alpha$) and refractive index variation ($\Delta n$) at the micropores are apparently increased within an acetone vapor density of 6 nmol/mm$^3$ and become saturated at high density. This consistent trace trend between $\alpha$ and $\Delta n$ in Fig. 3(a) implies that the increased vaporized acetone molecules not only significantly absorb the THz wave (represented by $\alpha$) but also introduce considerable phase retardation in the THz electric field oscillation (represented by $\Delta n$). In this experiment, the high vapor density certainly enhances the infiltration of vapor molecules into the micropores and increases the molecular adsorption capacity of the hydrophilic surface [30], that is, the increase in vapor density confined in the micropores and adsorbed on the pore surface causes the increase in $\Delta n$ and $\alpha$ in the microporous structure. The absorption coefficient versus the vapor density can be well fit by the Langmuir adsorption isotherm with an $R^2$ value greater than 97%; this value is depicted as the cyan curve in Fig. 3(a).

![Fig. 3](image.png)

Fig. 3. Measured effective absorption coefficients (blue square dot) and refractive index variation (red circular dot) at 0.4 THz for various acetone vapor densities in the chamber (a) with and (b) without the microporous structure. The mathematical fit of the proportional relationship is denoted by the blue line. The Langmuir adsorption isotherm for the microporous structure is denoted by the cyan curve.

The Langmuir fitting indicates that the monolayer adsorption of acetone vapor molecules on the hydrophilic microporous surface is mainly caused by physisorption. For the molecular density of less than 6 nmol/mm$^3$, the proportional response of the 0.4 THz wave absorption versus the acetone vapor density can be linearly fit as $\alpha = 0.036 + 0.52\rho$ and considered the sensitive region of the sensor (denoted by the blue line in Fig. 3(a)). In experiment, the lowest detected concentration of acetone vapor is 291 pmol/mm$^3$, which is indicated as the first blue data point of Fig. 3(a) and corresponding to 17 ppm. From the slope of the linear fitting curve and measured inaccuracy of the THz absorption coefficient (about 0.01 ~0.02 cm$^{-1}$), the minimum detectable concentration change of acetone vapor determined by using the PET microporous gas sensor can be estimated less than 125 pmol/mm$^3$, which is equivalent to 7.25 ppm. Therefore, microporous structures are particularly advantageous for minute vapor sensing with detection limits of low ppm levels.

Figure 3(b) shows the sensing result for different densities of acetone vapor inside the blank chamber (i.e., without the porous structure). For the same vapor densities, the 0.4 THz wave absorption and index variation inside the blank chamber are smaller than those measured with the microporous structure. That is, $\alpha$ in Fig. 3(a) is about twenty times larger than that in Fig. 3(b), and $\Delta n$ in Fig. 3(a) is two orders of magnitude larger than that in Fig. 3(b) for the same acetone vapor density. Obviously, the microporous structure can enhance both $\alpha$ and $\Delta n$ in vapor sensing compared with the blank chamber condition. Otherwise, $\alpha$ and $\Delta n$ slowly increase with vapor density and without the saturation effect for the blank chamber measurement in contrast to the microporous structure condition. At an acetone liquid concentration of 100%, which corresponds to a vapor molecular density of ~13 nmol/mm$^3$, the absorption coefficient at 0.4 THz is approximately 0.18 cm$^{-1}$ in Fig. 3(b), which is on the
same order and reasonably agreed with the published value of 0.45 cm\(^{-1}\) in [31]. According to the slope of the linear fitting curve shown in Fig. 3(b) and the uncertainty of the absorption coefficient in the THz-TDS system, the minimum detectable molecular density variation of acetone vapor is approximately 0.558 nmol/mm\(^3\), which corresponds to 32.37 ppm. This result reveals that the sensitivity of volatile gas detection by the microporous structure is higher than that by a traditional THz-TDS system. Given that the microporous structure can congregate volatile vapors inside the micropores and adsorb on the hydrophilic surface, the interaction strength between THz radiation and polar gas molecules can be enhanced via the adsorbent medium to significantly increase the absorption and index variations.

Fig. 4. (a) Measured effective absorption coefficients and (b) refractive index variations at 0.4 THz for different methanol, ethanol, and ammonia vapor densities using the microporous structure.

In addition to identifying different amounts of acetone vapors via the microporous structure, different VOCs, including methanol, ethanol, and ammonia with different vapor densities, can also be detected in this manner. As shown in Fig. 4, for the three vapor species, the \(\alpha\) and \(\Delta n\) of the micropores at 0.4 THz increase with increasing vapor densities. The increased trends are similar to the acetone vapor sensing result shown in Fig. 3 except for the saturated trend at high vapor densities. The sensing device exhibits remarkable differences in THz absorption coefficients and effective refractive index variations for different types of VOCs, which are derived from the enhanced adsorption and infiltration of vapors in the micropores. In this sensing configuration of the microporous polymer structure, capillary condensation of vapors does not occur in the micron-sized pores for all vapor species [23, 24].
Figure 5(a) shows the absorption coefficients of micropores at 0.4 THz under different concentrations of acetone, methanol, ethanol, and ammonia vapor exposures, with the magnitude order of the 0.4 THz wave absorption coefficient of ketone > alcohol > ammonia. The linear fitting curves of the THz absorption coefficients (denoted by the dashed lines in Fig. 5(a)) represent the response curves of the microporous sensor to various vapor species and are significantly different for the three VOC classes. Each type of vapor analyte has a distinct $\alpha$ curve that can be used to distinguish from other vapor analytes. In this study, we suspect that the molecular distinction can be ascribed to the different THz interaction strengths of distinct polar vapor species and to the adsorption capabilities of various vapor analytes on the hydrophilic surface of the porous structure. The larger dipole moment of a VOC can be strongly perturbed by THz radiation and induce predominantly molecular motion to increase the THz absorption coefficient. Further investigation of the sensing mechanism is necessary. The magenta columns in Fig. 5(b) show the magnitudes of the dipole moments of the four polar vapors in the following order: ketone > alcohol > ammonia [32], which is consistent with the magnitude sequence of the THz absorption coefficients shown in Fig. 5(a). The THz interaction strength of acetone vapor is stronger than those of the other types of vapor species. Methanol and ethanol vapors are alcoholic VOCs and have similar THz absorption coefficients in the microporous structure. On the basis of the linear fitting slopes and measured inaccuracies of the THz absorption coefficients, the sensitivities of the microporous device for detecting the four polar gases can be obtained. The detectable molecular densities of acetone, methanol, ethanol, and ammonia vapors using the microporous gas sensor are 0.125, 1.71, 1.62, and 3.35 nmol/mm$^3$, respectively, as denoted by the blue columns in Fig. 5(b). The sensing scheme not only identifies minute concentration changes of VOC with picomolar sensitivity but also exhibits excellent discrimination for different polar VOCs.
The repeatable operation of a microporous structural gas sensor in real applications is quite important. Therefore, in situ monitoring of the acetone vapor is discussed as follows. The response and recovery of the sensor at 0.4 THz with respect to time at different concentrations of acetone vapor exposure are shown in Fig. 6. In addition to the aforementioned results of the vapor-concentration-dependent transmittance variation of the 0.4 THz wave, the response time is also modified by the vapor concentration. The acetone solution is injected at 180 s into the microfluidic channel. Thereafter, the vaporized acetone molecules fill the chamber. We observed that the sensor reaches 90% of the equilibrium response within 300 s to 500 s at the acetone concentration range of 100% to 2.5%. Meanwhile, 90% recovery is achieved in less than 15 s with adequate air flow (23 L/min) in the chamber to exhaust the adsorbed acetone vapors in the microporous structure and replace with the ambient air from the opened liquid inlet. After the removal of the stimulant vapors, the porous polymer gas sensor is recovered to indicate the reversible sensing capability. As illustrated in Fig. 6(b), the response time of the sensor to acetone vapor decreases with increasing vapor concentration, which is mainly determined by the diffusion ability of the vapor. Diffusion speed is dependent on the concentration gradient of the vapor distributed in the sample chamber. The decrease in the size of the sample chamber will speed up the vapor diffusion and further decrease the response time. Otherwise, the recovery time of the sensor is completely determined by the pumping speed and is independent of the vapor concentration [Fig. 6(c)]. i.e. The higher pumping speed (> 23 L/min) would decrease the recovery time.

4. Conclusion

We have successfully demonstrated a multilayer-stacked microporous polymer structure for sensing different types and concentrations of organic vapors in THz-frequency range. The designed THz-nose chip is experimentally demonstrated for a good performance in distinguishing four kinds of VOCs with different dipole moments, and has the estimated detection sensitivity about 7 ppm for acetone vapor sensing, corresponding to molecular density of 125 pmol/mm³. The simple micro-porous THz gas sensor has advantages including the operation in ambient atmosphere and room temperature, easy availability, portability, low cost, and low absorption loss. Additionally, the micro-porous THz gas sensor can be reversibly operated and has a reasonable response time. It is promising for the applications of environmental and industrial toxic gas sensing and medical exhaled breath detection.

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