Loss-induced phase transition in mid-infrared plasmonic metamaterials for ultrasensitive vibrational spectroscopy

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Abstract

Metamaterials have proven their ability to possess extraordinary physical properties distinct from naturally available materials, leading to exciting sensing functionalities and applications. However, metamaterial-based sensing applications suffer from severe performance limitations due to noise interference and design constraints. Here, we propose a dual-phase strategy that leverages loss-induced different Fano-resonant phases to access both destructive and constructive signals of molecular vibration. When the two reverse signals are innovatively combined, the noise in the detection system is effectively suppressed, thereby breaking through the noise-related limitations. Additionally, by utilizing loss optimization of the plasmon-molecule coupling system, our dual-phase strategy enhances the efficiency of infrared energy transfer into the molecule without any additional fabrication complex, thereby overcoming the trade-off dilemma between performance and fabrication cost. Thanks to the pioneering breakthroughs in the limitations, our dual-phase strategy possesses an overwhelming advantage in ultrasensitive vibrational spectroscopy over traditional metamaterial technology, including strong signal strength (×4), high sensitivity (×4.2), effective noise suppression (30%), low detection limit (13 ppm), and excellent selectivity among CO2, NH3, and CH4 mixtures. This work not only opens the door to various emerging ultrasensitive detection applications, including ultrasensitive in-breath diagnostics and high-information analysis of molecular information in dynamic reactions, but also...
1 | INTRODUCTION

Infrared (IR) vibration is the basic feature of natural and artificial materials, where it shows direct linkage to the chemical bonds, constituents, and configuration of the material molecules. The detection of vibrational fingerprints is a significant path for humans to explore the nanoscale world. However, due to the low molecular absorption cross-sections of mid-IR vibrations, the effective identification needs a considerably large amount of material and a long light-matter interaction length, resulting in a bulky volume, high-energy consumption, and low performance of the detection devices. Existing research schemes dealing with the challenges include empowering the IR source, developing ultrasensitive IR detectors, and enhancing light-matter interaction. Although the first two can improve molecular detection performance, no breakthrough has been made in the core problems, namely low absorption cross-sections, and energy consumption, bulkiness, and cost are aggravated instead. In contrast, the enhancement of light-matter interaction is considered a breakthrough solution to the problem of low molecular absorption cross-sections due to its direct correlation with the interaction of photons and molecular electrons. Specifically, the IR energy is transferred to the molecular vibration through the plasmon-molecule coupling instead of relying on the direct IR absorption of the molecule. Apparently, this method is not limited by the low IR absorption cross-sections of the molecular vibration. Compared with the plasmon-molecule coupling methods such as Kerker effect, Borrmann effect, and Rabi splitting & Autler-Townes effect, Fano resonance can be observed without scathing excitation conditions and has advantages in handling with objects that have multiple resonances. Hence, it attracts wide attention. However, not all Fano resonances can achieve high-efficiency and high-intensity coupling, which is determined by the excitation method. Therefore, it is of great significance to exploit powerful optical material with a strong and efficient Fano-resonant plasmon-molecule coupling effect.

Metamaterials, the artificial sub-wavelength structures with extraordinary physical properties distinct from the intrinsic properties of naturally available materials, can locally enhance the manipulation and detection of light on ultra-small and sub-wavelength scales, thus providing unique opportunities for IR spectroscopy. Due to the nature of highly efficient interaction with light, metamaterials are considered as a prime candidate for efficiently exciting Fano resonance with high coupling strength. Metamaterial-based Fano resonance has made significant progress ranging from a fundamental effect to many interesting applications, such as dynamic reaction monitoring, hyperspectral IR chemical imaging, and biochemical molecule detection. However, it has encountered a technical bottleneck because of the limitations in signal enhancement, especially when it comes to spectroscopic advanced functions such as detecting a monolayer of molecules and monitoring trace dynamic reactions. The universal performance limitations in the metamaterial-based Fano resonance are mainly reflected in two aspects: (i) design constraints and (ii) noise-induced limitations. First of all, the Fano-resonant coupling system is a complex multi-parameter system. Its performance is subject to coupling strength, field intensity, spatial plasmon-molecule overlap, and so on. Inappropriate design of metamaterials greatly limits the overall performance of the coupling system. Second, there are many sources of noise, such as background spectral shift and metamaterial thermal noise, and so on. The noise significantly limits the sensing performance, especially in advanced detection applications.

Great efforts have been invested to break through the above limitations. In terms of design constraints, the metamaterials, that is, artificial materials, can be engineered to achieve desired properties. Approaches report that design constraint limitations can be bypassed by metamaterial structure optimization. The first method is to increase light field strength by constructing narrow gaps between adjacent metamaterial pattern units. Another structure optimization approach is to increase the spatial overlap between analytes and enhanced near-field. It is realized by undercutting the metamaterial structure or integrating nanofluidic channels with metamaterials. Additionally, there are many other optimization methods such as adding enrichment materials and constructing absorber structures.
These optimization methods significantly improve the sensitivity, but they require precise and complex fabrication steps, including photolithography, etching, and bonding processes, to build narrow gaps, nanoscale channels, and other complex structures, leading to a trade-off dilemma between performance and fabrication cost. Therefore, a new paradigm to overcome the trade-off dilemma is desirable.

Regarding the noise-induced limitations, especially the thermal noise of the metamaterial, the existing methods are limited. The possible optimization method is utilizing all-dielectric materials to form a photonic crystal slab. It works due to its features in reducing the dissipative loss and strong heating in the metals. However, when compared with metal metamaterials, all-dielectric devices suffer from the poor affinity of immobilizing some molecules, which is unfavorable for the surface functionalization in biomolecule sensing. Moreover, due to the bandgap characteristics of photonic crystals, this method suffers from the narrow operating bandwidth of the device. Therefore, simple and effective methods to break through the noise-induced limitations still present great challenges.

In this work, we present a paradigm to break through the two limitations by subtly controlling and integrating dual Fano-resonant phases. The implementation of dual Fano-resonant phases is based on the phase transition of Fano resonance achieved by tuning the loss of metamaterials. Our dual-phase strategy utilizes the low and high loss rate phases of Fano resonance to access the destructive and constructive signals of molecular vibration, respectively. When the two reverse signals are combined, the noise in the detection system is effectively suppressed, breaking through the noise-induced limitations. According to literature research, current peer research focuses on destructive signal acquisition using a single phase of Fano resonance, and our dual-phase method of breaking the limitations has not been explored (Note 1, Supporting Information). On the other hand, our dual-phase strategy is the system-level optimization of the coupled system, which enhances the efficiency of IR energy transfer into the molecule without any additional fabrication complex. Therefore, it overcomes the trade-off dilemma between performance and fabrication cost. Thanks to the pioneering breakthroughs in the limitations, our dual-phase strategy possesses an overwhelming competitive advantage in ultrasensitive vibrational spectroscopy, and demonstrates the highest level of carbon dioxide (CO₂) detection in existing mid-IR CO₂ sensors. Our work opens the door to various emerging applications, including ultrasensitive in-breath diagnostics and high-information analysis of molecular information in dynamic reactions.

2 | RESULTS AND DISCUSSIONS

2.1 | Fano-resonant dual-phase detection strategy

The commonly adopted approach to collecting vibration information is to measure molecular spectra indiscriminately. In order to improve accuracy, repeated measurements are often performed. However, the proportion of noise in the vibrational signal is constant, which makes it difficult to suppress noise. In our dual-phase strategy, the low and high loss rate phases of Fano resonance access the destructive and constructive signals of molecular vibration, respectively. The destructive information obtained at the low loss rate phase of Fano resonance is also known as the electromagnetically induced transparency (EIT), and the constructive signal captured at the high loss rate phase is called the electromagnetically induced absorption (EIA). The enhancement of the vibrational signal in different phases is at a different level, while the noise is almost the same due to the unchanged experimental setup and device. Therefore, we can utilize this fact to achieve noise suppression in dual-phase detection.

To experimentally investigate the dual-phase detection strategy, it is necessary to propose an implementation scheme to obtain different Fano-resonant phases. Metamaterial-based absorbers are plasmonic devices that consist of sandwich-like metal–insulator–metal structures. The absorption mechanism of the device is that the confined incident light is reflected and absorbed multiple times between the metal reflective layer and the metamaterial pattern. On one hand, the multiple reflections create stronger near-field enhancements than monolayer metasurfaces, making it a competitive candidate for ultra-sensitive sensing. On the other hand, the multiple reflections cause the optical behavior of the device extremely sensitive to the characteristics of the spacer including dielectric properties and thickness. Such a sensitive feature allows the device tunable to excite different Fano-resonant phases. Therefore, plasmonic devices based on metamaterial absorbers are chosen as the basic configuration. To prevent the phase conflict in the integration, the dual-phase platform must meet two requirements, including (i) the independence of the dual phases instead of offsetting or interfering with each other and (ii) the capability of being actively controllable and adjustable at the design stage of EIA and EIT. To further reduce the fabrication challenges at the wafer-scale and leverage the advanced nanofabrication technology built by the complementary metal-oxide-semiconductor (CMOS) semiconductor industry, we deploy CMOS-compatible materials and
fabrication process. Based on the above considerations, we develop a hybrid platform with two independent but spatially close detection regions (denoted as EIA-T platform), namely Region 1 and Region 2, as shown in Figure 1A. In particular, two regions are in the low and high loss rate phase of Fano resonance, respectively. The implementation of different Fano-resonant phases is based on the phase transition of Fano resonance achieved by tuning the loss of metamaterials. A cross-shaped pattern is chosen as the metamaterial structure due to its polarization-insensitive characteristics and high absorption at a wide range of incident angles (Note 2, Supporting Information).

Considering that gas detection is challenging due to its requirement of high sensitivity and low limit of detection (LOD), we select the important and common greenhouse gas, carbon dioxide (CO₂), as the detection target to investigate our dual-phase detection strategy. Polyethylenimine (PEI) is spin-coated on the surface of the plasmonic metamaterial as a gas-selective enrichment layer to functionalize the EIA-T platform. When selectively absorbed by PEI, CO₂ molecules are reversibly converted into CO₃⁻ when absorbed in selective-trapping polymer PEI. (B) The vibration changes caused by the CO₂ conversion process are detected and reflected in the spectra with different Fano-resonant phases. Specifically, the dual-phase information obtained includes destructive EIT signal and constructive EIA signal. (C) Ultra-strong molecular vibration signals are obtained when the destructive EIT and constructive EIA signals are combined, thereby breaking limitations in plasmon-molecule coupling. (D) Fano parameter q versus phase shift φ showing the molecular signal details under different phases of Fano resonance.

FIGURE 1 Fano-resonant dual-phase detection strategy. (A) Schematic representation of the dual-phase EIA-T platform for ultrasensitive dual-phase signal acquisition. The molecular vibration coupled in Region 1 of the platform is detected by the low loss rate phase of Fano resonance. Then the molecular vibration coupled in Region 2 of the platform is detected by the high loss rate phase of Fano resonance. Different Fano-resonant phases are achieved by tuning the loss of metamaterials, which is determined by the wave propagation distance, that is, thickness T₁ and T₂. In the demonstration of dual-phase strategy, trace CO₂ gas is detected, where CO₂ molecules are reversibly converted into CO₃⁻ when absorbed in selective-trapping polymer PEI. (B) The vibration changes caused by the CO₂ conversion process are detected and reflected in the spectra with different Fano-resonant phases. Specifically, the dual-phase information obtained includes destructive EIT signal and constructive EIA signal. (C) Ultra-strong molecular vibration signals are obtained when the destructive EIT and constructive EIA signals are combined, thereby breaking limitations in plasmon-molecule coupling. (D) Fano parameter q versus phase shift φ showing the molecular signal details under different phases of Fano resonance.
into CO\textsubscript{3}\textsuperscript{−}. The molecular vibration change caused by the CO\textsubscript{2} conversion process is detected by the near-field of metamaterials. The molecular vibration change in Region 1 corresponding to the low loss rate phase of the EIA-T platform is detected as a destructive EIT signal, and that in Region 2 (high loss rate phase) appears as a constructive EIA signal in the high loss rate phase of the EIA-T platform (Figure 1B). From the line shape of the spectrum, the destructive EIT signal is manifested as a decrease in the absorption spectrum near the molecular vibration peak. In contrast, the constructive EIA signal appears as an increase. When the two reversal changes are extracted based on each other, ultra-strong robust molecular vibration signals are obtained (Figure 1C). The signal strength obtained by the signal integration is higher than either side. Furthermore, it also causes an overall performance improvement including sensitivity, resolution, noise, and LOD, which will be further discussed in the later section. The formula of Fano resonance is expressed as\textsuperscript{70}

\[
\sigma(E) = D^2\left(\frac{q + \Omega}{1 + \Omega^2}\right)^2
\]

(1)

where \(E\) represents the energy, \(q = \cot(2\varphi)\) is the Fano parameter, \(\varphi\) is the phase shift of metamaterial resonance; \(\Omega = 2(E - E_0)/\Gamma\), where \(E_0\) and \(\Gamma\) are the resonance energy and width, respectively; and \(D^2 = 4\sin^2(2\varphi)\). According to the profile of Equation (1) (Figure 1D), tuning Fano parameter \(q\) to obtain different Fano-resonant phases is critical to our strategy implementation. Additionally, as the Fano-resonant phase shift increases, the signal gradually changes from an asymmetrical lineshape to a Lorentz-like symmetrical lineshape.

### 2.2 Loss-induced phase transition mechanism

Fano resonance can be investigated by using the coupled two-oscillator model where only one of the oscillators is activated. When IR light is radiated onto the metamaterials (Figure 2A), collective oscillations of electrons are excited at the surfaces and coupled with the dark loss. This Fano-resonant behavior can be modeled as the bright oscillator (orange) of the metamaterials driven by external radiation \(f(x)\) coupling rate \(\kappa\) and undergoing damping at a rate \(\gamma\) (Figure 2B). The coupling of the dark oscillator (pea green) via coupling strength \(\mu\exp(\text{i}\varphi)\) introduces another pathway of energy loss to the light-excited process. The absorption spectrum of the coupled system at resonance (\(\omega = \omega_0\)) is then calculated from the perspective of the dissipated energy as (see Note 3, Supporting Information)

\[
A(\omega_0) \approx \frac{\kappa^2\gamma_m\omega_0^2}{\mu^2\exp(2\text{i}\varphi) + \gamma_m\omega_0^2}
\]

(2)

According to Equation (2), the term \(\exp(2\text{i}\varphi)\) has a decisive influence on changing trend of the resonant absorption, which is divided into three groups. First, when \(0 < \varphi < \pi/4\) (Figure 2B-I), the coupling of the dark oscillator weakens the bright resonance of metamaterials (Figure 2B-i). From the perspective of the formula, the real part of the term \(\exp(2\text{i}\varphi)\) is a positive value. Therefore, the term \(\exp(2\text{i}\varphi)\) causes a decrease in the absorption spectrum, thereby leading to the acquisition of the destructive EIT signal. On the contrary, when \(\pi/4 < \varphi < \pi/2\), the real part of the term \(\exp(2\text{i}\varphi)\) is a negative value, and it leads to an increase in the absorption spectrum (Figure 2B-iii). The dark oscillator strengthens the resonance of the bright oscillator via coupling \(\mu\exp(\text{i}\varphi)\) (Figure 2B-III). Especially, when \(\varphi = \pi/4\) (Figure 2B-II), the real part of the term \(\exp(2\text{i}\varphi)\) is zero, which means that the movements of the two harmonic oscillators are synchronized. Therefore, the absorption change at resonance caused by the coupling of a dark oscillator is negligible (Figure 2B-ii). Collectively, the phase shift \(\varphi\) between two resonators is a crucial physical parameter for the acquisition of EIA and EIT signals.

In our strategy, we utilize the reflection of a metal layer close to the metamaterials to change the metamaterial loss and phase shift, and thereby achieve the phase transition of Fano resonance. In the absence of the metal layer, the incident light propagates through the metamaterials and the dielectric layer in sequence, and no loss change occurs during this process (see Note 4, Supporting Information). Meantime, currents in the same direction as the electric field of the incident light are induced in the metamaterial, so the resonance of metamaterials is an electric resonance. When a metal layer is added to the light propagation path, the reflected radiation interacts with the incident light, leading to the change of the metamaterial loss and phase shift (Figure 2C). Meanwhile, antiparallel currents are excited between the metamaterial and metal layer, thereby forming a magnetic dipole. The magnetic dipole makes the direction of the reflected radiation magnetic field opposite to that of the incident light, so the resonance of metamaterials in this configuration is both electric and magnetic resonance. Such resonance confines large electromagnetic energy in the intermediate spacer layer, resulting in higher spectral absorption and signal enhancement when compared with pure electric resonance.\textsuperscript{71} The confined electromagnetic energy is related to the loss and phase shift due to the time and space varying of the electromagnetic wave propagation. Therefore,
FIGURE 2  Loss-induced phase transition mechanism. (A) Schematic diagram of metamaterials irradiated by IR light. (B) Corresponding coupled harmonic oscillator model. The oscillator representing the metamaterials is driven by external radiation $f(x)$ via coupling rate $k$ and experiences damping at a rate $\gamma$, where the halo around oscillators represents the resonant intensity. When the dark damping $\gamma_m$ is coupled to the metamaterials via a coupling strength $\mu \exp(i2\phi)$, three states of Fano resonance occur: I: $0 < \phi < \pi/4$, EIT state (i); II: $\phi = \pi/4$, critical coupling (ii); and III: $\pi/4 < \phi < \pi/2$, EIA state (iii). (C) Controlling the phase transition by utilizing the reflection of a metal layer close to the metamaterials to change the metamaterial loss $\gamma$ and phase shift $\phi$. (D) The phase shift as a function of distance $T$ showing the phase transition details. (E) Current, (F) electric field, and magnetic field distribution of the metamaterials (I) without metal reflection layer, or with a metal reflection layer whose gap is (II) 500 nm, and (III) 200 nm. Points K and J are positions where the electric and magnetic fields that spatially overlap with the molecule have their maximum values, respectively. (G) The electric (upper panel) and magnetic (lower panel) field strength of the metamaterials at Points K and J as a function of MgF$_2$ thickness.
we can tune the loss and phase shift by controlling the wave propagation distance.

To explore it, we calculate the relationship between the propagation distance (dielectric thickness), the phase shift, and the loss rate. The detailed profile of thickness and phase shift is shown in Figure 2D. The phase shift varies with the dielectric thickness. The region of small thickness corresponds to the EIT phase of the Fano resonance, and the region of large thickness refers to the EIA phase. Note that EIA has a wider thickness range of phase transitions, which means the thickness tuning of EIA is more robust. Meantime, the phase shift varies with the loss rate in a similar trend (see Note 4, Supporting Information). The internal mechanism is that the change of thickness and the change of metamaterial loss have a similar effect on the phase shift. Therefore, the changing trend of the phase shift with thickness is the same as the trend with the metamaterial loss, and we define it as a loss-induced phase transition of Fano resonance. Furthermore, we simulate the current, electric, and magnetic field distributions of metamaterials under different configurations. From the perspective of current distribution (Figure 2E), circulating currents only exist in device configurations with a metal layer. The current and the magnetic dipoles increase as the decrease of dielectric layer thickness. As for the electric and magnetic field of the metamaterials (Figure 2F), EIT corresponding to 200 nm has a more compact distribution than EIA corresponding to 500 nm on the whole. Since the molecules only spatially overlap with the external electric field of the device, the sensing performance can be investigated by calculating the strength of the external electric field. Points K and J are positions where the electric and magnetic fields that spatially overlap with the molecule have their maximum values, respectively. The electric and magnetic field strengths of the EIA corresponding to 200 nm at Points K and J are nearly equal to that of the EIT (Figure 2G). According to the typical understanding, it is expected that EIT has an equal sensing performance with EIA due to its electromagnetic field strength. However, it is experimentally demonstrated that EIA has competitive advantages over EIT in the later section. By having an all-in-one sensing system, the Fano-resonant phase can be converted by controlling the wave propagation distance to obtain the EIA and EIT signals of molecular vibration. Notably, the trend in Figure 2G is not a general result obtained by an analytical solution of the electric field equations. However, the simulated variation trend of dielectric thickness versus field strength is the same for different patterns. Additionally, we can adjust the thickness according to the trend in Figure 2G to achieve a close field intensity between EIA and EIT.

### 2.3 | Performance optimization

Temporal coupled mode theory (TCMT) is a general and powerful description of coupled plasmonic systems and provides a quantitative optimization tool for the acquisition of EIA and EIT signals. The TCMT model consists of a single cavity coupled \( \omega \) with two ports representing the incoming \((S_{1+})\) and outgoing \((S_{1-})\) radiation. Compared with the harmonic oscillator model, the TCMT model mainly focuses on the spectral changes of the coupled system from the perspective of energy transfer and loss. Therefore, the loss change introduced by the analyte loading is accurately calculated and reflected in the spectrum, which makes TCMT favored for modeling the signal acquisition behavior in the coupled resonator system. Meantime, the radiative to intrinsic loss rate is a critical physical parameter regardless of phase shift between the oscillators. According to TCMT, coupled mode equations are obtained, and the absorption of metamaterials at the resonance \( (\omega = \omega_\lambda) \) can be expressed as a function of external/intrinsic damping rate \( \gamma_r/\gamma_a \) (see Note 5, Supporting Information)

\[
A_{\text{peak}} = \frac{4\gamma_r/\gamma_a}{(1+\gamma_r/\gamma_a)^2}
\]  

The profile of Equation (3) is plotted in Figure 3A. Clearly, the peak absorption of metamaterials first increases and then decreases as \( \gamma_r/\gamma_a \) reduces, and the peak absorption reaches its maximum when \( \gamma_r = \gamma_a \). It is because the system is in critical coupling when the two are equal, and the energy transfer between bright and dark modes is the most efficient. Therefore, the energy is consumed in the dark mode to the greatest extent, thereby causing the greatest absorption. To demonstrate it, the spectra of plasmonic devices with different thicknesses \( T \) (denoted as D1–D6, see Section 4 for details) are simulated, as shown in Figure 3B. Clearly, the peak absorption of the device undergoes an evolution process that first increases and then decreases, which is consistent with the trend of the peak absorption changing with the damping rate in Figure 3A. It means that the dielectric thickness \( T \) and damping \( \gamma_r,a \) are related in the TCMT model. Notably, the thickness variation of the dielectric layer will lead to a change in the resonant wavelength. According to our analysis in Note 2, Supporting Information, the resonant wavelength redshifts as the length of the cross-shaped metamaterial pattern increases and is weakly related to the width and period of the metamaterial pattern. Therefore, the pattern length is fine-tuned so that devices of different thicknesses have the same resonant wavelength to ensure that
the device resonance matches the vibration of the gas enrichments. By mapping these simulated peak absorptions to the theoretical profile (Figure 3A), the values of $\gamma_r/\gamma_a$ for D1–D6 are obtained. Combining those values with the absorption equation, the specific values of $\gamma_r$ and $\gamma_a$ are extracted (see Note 6, Supporting Information), as
plotted in Figure 3C. As observed, the increase in thickness $T$ causes an opposite changing trend between $\gamma_r$ and $\gamma_a$. After the molecular damping $\gamma_m$ is coupled ($\mu$), the enhanced molecular signals $\Delta A$ with zero detuning ($\omega_m = \omega_\lambda$) at resonance ($\omega = \omega_\lambda$) can be obtained by

$$\Delta A = \frac{4\mu^2 \gamma_r/\gamma_a \cdot (\gamma_r/\gamma_a - 1)}{\gamma_a \gamma_r \gamma_m \cdot (1 + \gamma_r/\gamma_a)^4}$$

(4)

The profile of Equation (4) is plotted in Figure 3D. When $\gamma_r/\gamma_a$ varies from 0.01 to 1, the absorption change caused by molecular coupling is negative, namely the EIT signal. Conversely, when $\gamma_r/\gamma_a$ varies from 1 to 100, the absorption change is positive, namely the EIA signal. By comparing the TCMT model and the harmonic oscillator model, we found that the two have reached the same conclusion, that is, the conversion between EIA and EIT phases can be precisely controlled by engineering the thickness of the dielectric layer. The simulated results shown in Figure 3E confirm the theoretical calculations. More specifically, as the dielectric MgF$_2$ film thickness increases from 100 to 600 nm, the enhanced molecular signal strength undergoes an evolution process that first increases and then decreases, and then repeats once again. It indicates that both EIT and EIA signals have an optimal enhancement configuration in their own region.

The next task is to find out the optimal signal configuration, mainly the optimal thicknesses of the dielectric MgF$_2$ layer and gas enrichment PEI coating layer. We simulate and obtain the mapping of the enhanced molecular signals as a function of the PEI layer thickness versus the dielectric MgF$_2$ layer thickness (Figure 3F and Section 4). Clearly, devices of a smaller dielectric thickness correspond to an EIT phase, while devices of a larger one refer to an EIA phase (right side in Figure 3F). Furthermore, a clear boundary curve between them is derived, and with the increase of the PEI thickness, the boundary first moves toward the region of larger dielectric thickness and then reaches saturation of enhancement factor near the PEI thickness of 210 nm and above (white dotted line in Figure 3F). The boundary represents a balanced state where the external loss and the internal loss are equal, and the increase in the PEI thickness causes an increase in the internal loss. Therefore, before saturation, the balance point will move in the direction of a larger external loss accordingly, namely the thicker dielectric MgF$_2$ layer. Regarding performance optimization, the region within the white circle in the region of EIT in Figure 3F represents an enhanced molecular signal of higher intensity, and the device configuration corresponding to this region will achieve excellent sensing performance. However, the influence of the PEI thickness on the sensing performance of the device has to be further highlighted. More specifically, thicker PEI certainly provides more binding sites for the gas adsorption, but it also prevents the gas molecule from entering the PEI interior. From the perspective of the spatial field intensity in the vicinity of the metamaterials (Figure 3G), it drops first, then rises, and decays rapidly after passing the metamaterial thickness. When the field intensity corresponds to 10% of the maximum field strength, the distance reaches 210 nm, where it is defined as the penetration depth. The region where PEI thickness beyond the penetration depth is not detected by the electric field of the metamaterial. It explains that the boundary in Figure 3F reaches saturation and no longer moves after the PEI thickness exceeds 210 nm. In addition, from the perspective of figure-of-merits (see Note 7, Supporting Information), the average enhancement factor of our platform reaches the maximum value of 70 at 200 nm MgF$_2$ layer in the EIT region and 100 at 500 nm MgF$_2$ layer in the EIA region, respectively, and the maximum enhancement factor in the vicinity of the metamaterial tip is 1.98 $\times$ 10$^6$. After comprehensive consideration of various factors, the final configuration of the platform is designed as a 200 nm MgF$_2$ layer for EIT signal acquisition, 500 nm MgF$_2$ layer for EIA signal acquisition, and 210 nm PEI layer as gas enrichment film on top of the MgF$_2$ layer.

### 2.4 Device fabrication and material characterization

The hybrid EIA-T platform was fabricated on a 6-in. silicon using a CMOS-compatible process, including stepper photolithography, electron beam evaporation, and ion beam etch (see the Section 4 for details). It is a kind of top-down nanofabrication using tools controlled by external experimental parameters to create nanoscale structural devices with desired shapes and properties. Compared with bottom-up methods relying on molecular or atomic assemblies, top-down SEIRA could have advantages in integrated devices with other elements such as waveguides and photonic crystals, and bottom-up SEIRA may have advantages in cost and miniaturization (Note 8, Supporting Information). Figure 4A shows the top view of scanning electron microscope (SEM) image of the fabricated metamaterials. As observed, the outline of the pattern was well-defined. To prevent the Ohmic loss of the metamaterial from affecting the damping $\gamma_r$ adjustment, the metamaterial dimensions for the EIT and EIA regions of the EIA-T platform were kept the same. The cross-sectional SEM micrographs of the EIA-T platform are shown in Figure 4B,C. Clearly, each layer of the
platform was tightly connected and quite distinct from each other. According to the optimized designs discussed in the previous section, the EIT and EIA dielectric thicknesses of the fabricated EIA-T platform were about 200 and 500 nm, respectively. Figure 4D described the atomic force microscopy (AFM) image of the enrichment layer PEI spin-coated on the EIA-T platform. As observed, the roughness of PEI was less than 10 nm, indicating the excellent thickness uniformity of the spin-coated PEI film on the device surface. Furthermore, the energy-dispersive X-ray spectroscopy (EDX) result also verified the uniform distribution of C, N elements in the coated PEI film, and the content of each element is shown in Figures 4E and S14. Then, the thickness of the spin-coated PEI film was measured by using a profilometer. By adjusting the parameters of the spin coating process (see the Section 4 for details), the desired 209 nm thick PEI film was obtained (Figure 4F).

2.5 | Experimental investigation of ultrasensitive dual-phase detection

Gas detection is one of the most challenging tasks for plasmonic sensors due to the usually extremely low concentrations in the applications, making it suitable for demonstrating the ultrasensitive dual-phase detection capabilities based on our new technology. Considering that the enrichment material plays a role of selectively enriching the target gas from a mixed sensing environment, the appropriate selection is crucial for the platform to obtain excellent gas selectivity and sensitivity. PEI is an excellent CO₂ gas-selective-trapping polymer that is often used for CO₂ adsorption and storage. Furthermore, due to its water solubility and high viscosity, it can be easily integrated with our platform through the spin-coating process as discussed in the previous section. The chemical reactions involved with the adsorption and
The desorption of CO₂ in the PEI layer are described in Figure 5A. The hard-acidic CO₂ molecules covalently react with the basic amine groups of PEI and are mainly converted into carboxyl groups \( \text{COOH} \) and bicarbonate ions \( \text{HCO}_3^- \). The reaction process is reversible, that is, the formed species can be recovered by heating, and the loss is negligible. The associated wavelength assignments for the primary by-products of the reaction path are listed in Figure 5B. The IR vibrational strengths of these by-products vary with the adsorption and desorption of CO₂ (see Note 9, Supporting Information), which is enhanced and detected by our dual-phase EIA-T platform and other common single-phase methods. Most notably, not all by-product vibrational bands are suitable as the detection target for the dual-phase EIA-T platform. There is an IR absorption overlap between the water vapors and the PEI by-products (Figure 5C). To void the interference of water vapor, the vibrational band at 7.66 μm originating from the...
conformational change in HCO$_3^-$ is chosen as the detection target for our platform. Therefore, the resonance of the dual-phase EIA-T platform coated with PEI film is also designed to be around 7.66 µm to maximize the enhancement effect.

In the demonstration of ultrasensitive dual-phase detection, the PEI functionalized EIA-T platform is placed in a gas cell with CO$_2$ concentrations changing from 0 to 1520 ppm (see Section 4 for details). The measured spectral response of the dual-phase EIA-T platform is depicted in Figure 5D. The absorption band changes that cause the CO$_2$ adsorption are significantly observed due to the coupling of plasmonic resonance and molecular vibration. Moreover, the absorption in the EIA region of the platform rose with the increase of CO$_2$ concentration, while the changing trend of the EIT region is opposite. In addition to obtaining dual-phase information, the two opposite change trends provide exciting opportunities for the platform to break the enhancement limit in vibrational spectroscopy. Specifically, the two opposite change trends are integrated through normalization and mutual reference (Figure 5E). As observed, the signal intensity of EIA is about three times larger than that of EIT, while the hybrid EIA-T platform shows a signal intensity of four times higher than that of the common single-phase method (Figure 5F). Higher signal strength allows the platform to have a larger signal varying range and more robust changes, resulting in better sensitivity and resolution. When the maximum slope of the fitting curve is defined as the sensor sensitivity, the sensitivity of the dual-phase EIA-T platform is calculated as 0.141%/ppm, which is also about four times higher than the single-phase EIT method. To the best of our knowledge, it represents the high level of existing metamaterial-based CO$_2$ sensors (see Table S7 for details). According to the data in Figure 2G, the field strength of EIA and EIT is close, but their loss rates are completely different. Therefore, the reason that the sensing performance of EIA is better than that of EIT is due to the loss rate, which means that the common conception about the relationship between electric field and sensing performance is not applicable in the coupled plasmonic system. As for the resolution, the spectral response of the platform near the atmospheric CO$_2$ concentration (400 ppm) exhibits an excellent resolution of approximately 7 ppm (Figure 5G), which is due to the larger signal varying range and lower noise level of our platform. Collectively, our dual-phase strategy obtains dual-phase information of molecular vibration, and the integration of dual-phase information further improves the detection performance including signal output intensity, sensitivity, and resolution.

As another crucial figure of merits, the detection performance of the platform is closely related to noise. The noise in our experiment includes the white noise of the measurement system and other hybrid noise of our device ($N_{\text{total}} = N_{\text{white}} + N_{\text{hybrid}}$). The total noise is measured by (i) collecting the spectra of the platform at 0 ppm CO$_2$ multiple times and (ii) then extracting the signal fluctuations of these spectra. According to the noise analysis (see Note 10, Supporting Information), the white noise $N_{\text{white}}$ is a discrete random noise caused by the measurement system and device, which is unavoidable and is mainly weakened by setting the background. However, the hybrid noise $N_{\text{hybrid}}$, caused by the environmental and device thermal changes, is proven to be reduced by our dual-phase integration strategy, which is crucial for improving LOD and also a great advantage of our method. More specifically, the noise has been reduced by nearly 30% due to the integration. By putting together the noise of the system and the output signal of the platform at low concentrations, we obtain the LOD of the platform (Figure 5H). As observed, the LOD of our hybrid dual-phase EIA-T platform reaches about 13 ppm, which is about 1.7 times lower than that of a single-phase EIT method. The breakthrough in the LOD benefits from both the large enhanced molecular signal strength and the noise suppression achieved by the dual-phase integration. Notably, the improvement is achieved entirely by our dual-phase strategy after we have reached the performance limit through various methods, including metamaterial pattern optimization, dielectric thickness optimization, and loss optimization. On the whole, thanks to all these optimization methods, in our demonstration of gas sensing, the sensing performance is greatly improved. More specifically, our work overall improves the detection limit by a factor of 30 over previously reported work. It is also attributed to the fact that our dual-phase strategy is compatible with previous optimization methods, making it promising in SEIRA design and application.

Dynamic behavior is an important part of detection performance, which reveals response time and hysteresis. Therefore, we further investigate the dynamic behavior of our dual-phase EIA-T platform. In the experiment, the real-time spectral response of the platform is recorded every 10 s, and the time interval for the measurement of the two EIT and EIA regions is about 2 s. Although our integration strategy introduces a measurement interval of 2 s, its impact on signal acquisition is basically negligible (Figure 6A). The time delay can be improved by using a microscope with the focal plane array (FPA) detector to simultaneously acquire spectra over a large area containing both EIA and EIT areas. From the perspective of the device design, it could be improved by keeping the dielectric thickness of devices the same while tuning the loss rate via structure pattern design to achieve EIA and EIT modes in two side-by-side areas. Furthermore, when
CO₂ concentrations dynamically increase from 0 to 1500 ppm, the integrated signal of our platform changes dynamically in response to changes in concentration, as shown in Figure 6B. Note that the amplitude of the change at 7.66 μm is greater than that at 6.78 μm, which is due to the smaller water vapor interference and higher enhancement effect at 7.66 μm. Meantime, it verifies the correctness of selecting 7.66 μm as the sensing band of interest. To calculate the response time and hysteresis, the spectral data at 7.66 μm is extracted and plotted in Figure 6C. When the response time is defined as the signal intensity reaching 95% of the stable value, the response time of the dual-phase EIA-T platform is about 2 min. The response time can be further improved by doping materials with a large specific surface area (metal–organic framework, graphene, etc.). The sudden drop in signal intensity every time the gas concentration changes is due to the interference caused by the flow of the injected gas, that is, the flow of the injected carrier N₂ gas induces the desorption of CO₂ on the surface of the PEI. In addition to the response time, the reversibility of the platform is also investigated. When the platform underwent
In addition, our strategy is generally applicable. With the best.

The excellent selectivity is due to the strong interaction of CO₂ with primary (R-NH₂) and secondary (R₂-NH) amines of PEI. Besides, our platform shows good long-term stability (see Note 11, Supporting Information). The performance comparison between our dual-phase EIA-T platform and some other CO₂ sensors in the mid-IR is summarized in Table S7. Thanks to our dual-phase strategy, the platform has strong competitiveness among these CO₂ sensors, especially in metamaterial-based CO₂ sensors, our performance including LOD and sensitivity is the best.

3 | CONCLUSION

We have demonstrated a dual-phase strategy to acquire dual-phase signals of molecular vibration by leveraging different Fano-resonant phases of metamaterials. The implementation of different phases relies on the Fano-resonant phase transition achieved by tuning the loss of metamaterials. It is experimentally demonstrated that dual-phase acquisition of molecular vibration information enables robust signal and noise suppression via the coupling of molecules under different resonance states. Additionally, the plasmon-molecule coupling is also optimized by the loss tuning of metamaterials to overcome the trade-off dilemma. As indicated in Table S1, our loss-induced dual-phase method is the first exploration of combining EIA and EIT phases to optimize performance.

Thanks to the dual-phase signal acquisition and the plasmon-molecule coupling optimization, substantial breakthroughs have been demonstrated in ultrasensitive high-informative vibrational spectroscopy. It shows that the signal strength and sensitivity in the CO₂ gas detection demonstration are boosted by about 1.4 times when compared with the common single-phase method, and the noise has been reduced by nearly 30%. The LOD of our strategy in CO₂ detection reaches 13 ppm, and we believe it is a milestone for IR gas sensors to achieve the high-level LOD in such a small sensing footprint (500 μm × 500 μm). In addition, our strategy is generally applicable. With proper design using CMOS-compatible materials and fabrication process, we achieved the integrated processing of our hybrid EIA-T platform in the wafer-scale fabricated devices. It shows the great feasibility of large-scale manufacturing for our designed EIA-T platform. It should be emphasized that the metamaterial gas sensing scheme in this manuscript does not conflict with the non-dispersive infrared (NDIR) sensing technology, but is an improvement and supplement for the NDIR sensing technology.

In the future, we can obtain a dual-phase signal in various classic systems such as photonic crystals, optical ring resonators, and waveguides. Furthermore, since the next generation of optical and sensing chips are developing toward high compactness and low cost, the effort could be invested to realize our dual-phase strategy in the same structures but with different polarization directions or incident angles. Additionally, the integration of bottom-up and top-down methods could have great potential to improve the detection performance of plasmonic devices. This work gains new insights into the plasmon-molecule interactions in advanced metamaterials, as well as opens the door to various emerging applications such as high-information analysis of molecular information in dynamic reactions.

4 | EXPERIMENTAL SECTION

4.1 | Numerical calculations

The spectra, electric field, and magnetic field distribution of the EIA-T platform were calculated using a finite-difference time-domain (FDTD) method (FDTD Solutions, Lumerical Inc.). A plane wave light source was chosen as the incident radiation source to drive the plasmonic system. The light source was set as elliptical polarization to be consistent with the IR microscope system. The boundary in the x- and y-directions was set to periodic boundary conditions to boost the simulation efficiency, and that in the z-direction was chosen as a perfectly matched layer (PML) boundary condition. The refractive index of MgF₂ was set as 1.38, and that of Au and Si was set according to Palik et al. The complex dielectric parameters of the PEI film used for simulation were extracted from the measured IR absorption spectra of the PEI film, and then the extracted dielectric parameters were imported into FDTD software to demonstrate their correctness (see Note 12, Supporting Information). The adhesion layer titanium (Ti) was omitted in the simulation due to its little effect of a slight increase in metal thickness on the simulated results. The vector current distributions at the metamaterial and the metal reflection layer were simulated using a 3D electromagnetic analysis software package (CST Studio Suite). The boundary condition setting
was similar to the FDTD software. Specifically, the boundary in the z-direction was set to Floquet Mode Ports, and the lateral direction used periodic boundary conditions. The incident angle was set to 0°. The dimension parameters for the simulation in Figure 2B were listed in Table S6. The simulated enhanced molecular signals in Figure 3F were the differential signal of the platform after PEI thermal desorption or adsorption of 400 ppm CO₂.

### 4.2 Nanofabrication and functionalization of the EIA-T platform

The EIA-T platform was fabricated using a CMOS-compatible process, including stepper photolithography, electron beam evaporation, and ion beam etching. The schematic diagram of processes was depicted in Note 13 (Supporting Information). Specifically, the process began with the cleaning and drying of the silicon wafer. Then, Ti (10 nm) and Au (100 nm) were sequentially deposited on the silicon surface using an evaporation system. After that, 200 nm and 500 nm thickness of MgF₂ were deposited into two separate regions by using an e-beam evaporator system. The next step is the patterning of the metamaterial. First, the PMMA photoresist was spin-coated, baked, exposed, and developed sequentially through a mid-ultraviolet step-per lithography system. Then, Ti (10 nm) and Au (100 nm) were sequentially deposited on the MgF₂ dielectric layer using the e-beam evaporator system. After that, the device was etched by an ion beam etch system. Then, the patterned two regions with different thicknesses were combined and fixed on a silicon wafer. Finally, PEI thick film was spin-coated onto the surface of the device to functionalize the platform. Specifically, the mass ratio of PEI and deionized water was 1:10, and the PEI solutions were spin-coated on devices at a speed of 4000 rpm for 1 min. After the coating, the device was placed into a vacuum drying oven at 90°C for 2 min. The ultimately achieved devices were stored in a dry storage cabinet until later use.

### 4.3 Optical measurement

We used an FT-IR spectrometer (IRTracer-100, Shimadzu) coupled to an IR microscope (AIM-900, Shimadzu) to collect the spectral data of the platform. The microscope was equipped with an HgCdTe (mercury cadmium telluride, MCT) detector cooled by liquid nitrogen, and the numerical aperture and objective were 0.4 and 15×, respectively. The signal collection region was set to 100 × 100 μm² via the knife-edge apertures. The background spectrum was obtained on the blank area of the platform without metamaterials. All data were taken at 16 scans with 4 cm⁻¹ resolution. Currently, conventional IR spectrometers are employed to provide light sources and detectors for the demonstration of our metamaterial gas sensors, making the setup heavy. The setup can be miniaturized by using a blackbody radiation source and a FPA detector. Therefore, compared with the NDIR scheme, metamaterial gas sensing chips have advantages in size, sensitivity, and detection limit, but the miniaturized IR sources and detectors supporting them are not yet fully developed.

### 4.4 Gas sensing setup and data processing

The CO₂ gas sensing setup was shown in Note 15 (Supporting Information). Specifically, the entire setup consisted of a gas controlling module, a gas mixing module, and a gas sensing module. In the gas controlling module, MFC (SAM, Horiba) with 0–10 and 0–1000 SCCM flow range was used to control the flow rate of CO₂ and N₂ gas. The flow rate was adjusted by using LabVIEW software to control the valve position of the MFC. Then, the gas out of MFC entered into the gas-mixing module to achieve uniform mixing. To ensure the accuracy of the gas-controlling module, we used an expensive commercial CO₂ gas sensor to calibrate the gas concentration. It is worth noting that we can directly connect the controlling module to the sensing module in the dynamic measurement to improve the dynamic response of the setup. After mixing, the gas mixture flowed into the gas-sensing module. In the gas-sensing module, the microscope measured the spectrum of the EIA-T platform through a barium fluoride IR window. Besides, a current-controlled heating plate was placed in the gas cell to achieve the thermal recovery of the platform. The thermal recovery temperature and time were set to 90°C and 1.5 min. The differential absorption spectrum was extracted by subtracting the reference spectrum from the measured spectrum. The spectrum of the platform before CO₂ loading gas was set as the reference spectrum. The enhanced molecular signal of the platform was extracted by $A = [(A_{EIA} - A_{EIT}) - (A_{EIA} - A_{TO})]$, where $A_{EIA}$ and $A_{EIT}$ were the measured spectra of the EIA and EIT regions, and $A_{EIA}$ and $A_{TO}$ represents the reference spectrum of the EIA and EIT regions. The fitting of enhanced molecular signal versus concentration profile in Figure 4F was performed by $y = A_1 e^{(-x/t_1)} + y_0$, where $A_1$, $t_1$, and $y_0$ were fitting parameters. The normalized field intensity was calculated by $I_{norm} = I_I/I_{max}$, where the $I_I$ and $I_{max}$ represented the field intensity and maximum field intensity obtained from the simulation.

### 4.5 Materials and apparatus

The PEI was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd (M.W. 70 000). SEM micrograph
was obtained by using a field emission SEM (Tescan Mira3 LMH, Czech Republic). The roughness of PEI film was measured by commercial AFM (Dimension Icon, Bruker Inc.). The thickness of the PEI film was measured by using an Alpha step (Alpha step-D100, Tencor Inc., Japan). The IR spectrum of PEI film was measured by an FTIR spectrometer (IRTracer-100, Shimadzu) coupled to an IR microscope (AIM-900, Shimadzu). The pattern of metamaterials was performed by a Nikon I-line stepper NSR-2205 i-12D. The etching of the Ti/Au metal layer was performed by an ion beam etching system (ADVANCED IBE-150, China). The evaporation process is performed by an electron beam evaporator (ULVAC, ei-5z).

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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REFERENCES


SUPPORTING INFORMATION
Additional supporting information can be found online in the Supporting Information section at the end of this article.

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