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Mid-infrared Nanoantennas as Ultrasensitive Vibrational Probes Assisted by Machine Learning and Hyperspectral Imaging

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ABSTRACT:

Infrared (IR) Spectroscopy has been developed for centuries and has been widely used to identify molecular structure from the massive information provided by IR fingerprint absorption, reflecting the vibration energy of the chemical bond. Due to the intrinsically weak light-matter interaction, IR spectroscopy serves low sensitivity and sizeable optical interaction length (~mm to ~cm) compared with other optical probes like Raman, florescent, and refractometry technology, which hinder the applications for ultra-sensitive biomolecular screening. Here, we reported a new type of IR spectroscopy by wavelength gradient hook nanoantenna integrated with microfluidic channel, enhancing the IR molecular absorption and bringing in refractometry function with ultrathin (~100 nm) optical interaction length. With the proof-of-concept demonstration of molecular recognition of mixed alcoholic liquids by machine learning and molecular fingerprint retrieving by hyperspectral images in one-time data acquisition, our work paves the way to advance, small-volume, real-time, ultra-sensitive, *in-vitro* biomolecular dynamic analysis in aqueous environment.

Introduction

Molecular identification of gas¹, liquid², and biomolecules³ is a fundamental requirement for various applications such as environmental monitoring, healthcare, clinical diagnosis, and biological screening. The ideal methods to identify molecules are *in-situ* detection of the chemical structures for molecules in a label-free and non-destructive manner with fast response time and high sensitivity. Optical approaches are suitable methods for molecule screening in life science thanks to remote, real-time, and sensitive detection with the aid of the development of microscopy technology. Mid-infrared (MIR) fingerprint absorption, reflecting the genetic information of molecule structures in chemical bonds and functional groups, provides natural optical probes for molecule identification. Harnessing fingerprint absorption, IR spectroscopy offers a solution for non-invasive, non-destructive, label-free, and real-time recognition and monitoring of molecules, especially in the mixture. However, traditional IR spectroscopy technology is limited by the large optical path (~mm to ~cm) due to weak light-matter interaction in MIR, hindering the sensing performance compared with other optical probes technologies such as Raman⁴, fluorescent⁵, and refractometry⁶.

To solve this problem, A. Hartstein et al. observed the enhancement of the IR absorption from molecular monolayer with thin metal overlayers in 1980, bringing the concept of surface-enhanced infrared absorption spectroscopy (SEIRAS).⁷ Furthermore, with nanofabrication technology development, artificially structured nanoantenna is proposed to enhance the IR fingerprint absorption by tailored plasmonic resonance.^{8,9} This amplification effect caused by the strong plasmon-phonon coupling between plasmonic nanoantennas (PNAs) resonance and molecular vibration was well-explained by temporal coupled-mode theory (TCMT).^{10,11} Depending on different coupling criteria, the different resonance line shape can be observed as electromagnetic

induced transparent (EIT)-like, electromagnetic induced absorption (EIA)-like or Fano-like resonance in the resonance spectrum.^{12,13} Thanks to the excellent field confinement at resonance wavelength, PNA also serves as an ultra-sensitive refractometry sensor to capture the refractive index of analytes by wavelength shifts (e.g., color change in visible light), which carries the information of physical properties of molecules.^{14,15}

Unfortunately, in the IR fingerprint region, the PNA signal of absorption changes and wavelength shifts always comes together, hindering the usage of complementary information about the physical and chemical properties of analytes for molecule identification. Machine learning (ML) is a powerful tool for separating the data from different domains to achieve enhanced pattern recognition. With the aid of machine learning, decoupling the IR fingerprint absorption and refractive index change induced by molecules has been reported for monitoring of protein dynamics¹⁶ and recognition of physiological bio-marker¹⁷. However, the molecular recognition capabilities are still limited to two specific molecules due to the narrow bandwidth and low sensitivity. To achieve global molecular identification, massive information is required for machine-learning-based recognition from PNA sensors. Consequently, high sensitivity and broadband detection range become two critical figure-of-merits (FOMs) that reflect the performance of PNA sensors.

Since the plasmon-phonon coupling is induced by a localized electric field near the PNA surface, the straightforward approach is to concentrate the molecule to the active area, which is the hot spot of the electromagnetic field. The surface enrichment strategies, including functionalized chemical bonding^{18,19}, chemical reaction²⁰, physical adsorption^{21,22}, optical trapping²³ as well as passive trapping by undercut structure²⁴ bring in the additional working requirements (e.g., chemical stimuli, temperature, pressure, pump power, etc.) for specific molecules, impeding the

system for global molecular recognition. Thus, the performance of the sensing system needs to improve by engineering the PNA structure. The intuitive way is to increase the intensity of the electric field by squeezing the gap between adjacent PNA into nanometer scale.²⁵⁻²⁷ However, the narrow gap ruins the sensing performance by a decrement in the active area and increases fabrication cost. Therefore, other approaches like hybrid 2D materials²⁸⁻³⁰ and homo/heterogeneous bonding^{31,32} are developed to bypass the fabrication using lithography of desired nanogap and to achieve a large area electromagnetic hot spots for sensing. Additionally, the loss engineering method is proposed to tune the coupling condition between PNA and molecular vibration by adjusting the loss of antenna from specific structures to achieve optimized enhancement.^{32,33}

In addition to sensitivity, the detection range is another critical FOM of PNA sensors, reflecting the number of fingerprint absorption peaks that can be captured. Thanks to the sharp resonance peaks of PNA, the enhancement becomes the maximum only when molecule fingerprint absorption peaks match with the PNA resonance, which is a very narrow bandwidth. Therefore, to detect more absorption peaks in the MIR region, multi-resonant PNA sensors are proposed to collect broadband spectrum data to recognize lipids and proteins from separate absorption wavelengths.³⁴ Nevertheless, the individual resonances of PNA by a different order of resonance modes also fails to cover the whole spectrum of IR fingerprint wavelength region from 5.5 μm to 10 μm because of the gaps between two resonance peaks.^{35,36} Therefore, to collect continuous spectral fingerprint absorption, pixelated all-dielectric nanoantenna array and tunable antenna by incident angle were proposed for ultra-broadband spectroscopic analysis for molecular barcode imaging and fingerprint absorption retrieving.^{37,38} However, the data from the different pixels are collected separately, which cannot achieve dynamic monitoring. Hyperspectral IR imaging could be an

advanced solution to solve the problems, and PNA has been used to enhance the vibrational molecular IR imaging captured by the focal plane array (FPA).³⁹ Furthermore, spectrum reconstruction by IR imaging technology is reported to retrieve wavelength shift of nanoantenna for molecular identification as refractometry microscopy with one-time data acquisition, but the performance is still limited due to the use of a monochromatic light source.⁴⁰

We proposed a novel molecular identification platform by wavelength gradient hook nanoantenna surface-enhanced infrared absorption spectroscopy (WGHNA-SEIRAS) to enhance the sensitivity and detection bandwidth of PNA based spectroscopy by engineering the loss of PNA sensor from hook nanoantenna (HNA) structure based on temporal coupled-mode theory (TCMT) and pixelating wavelength-gradient HNA building blocks. Based on WGHNA-SEIRAS, we proposed new methods to recognize three alcoholic molecules (methanol, ethanol, and isopropyl alcohol) in a mixture as a proof-of-concept demonstration by decoupling the complementary physical (refractive index) and chemical (fingerprint absorption of the chemical bond) information from IR spectrum via principal component analysis (PCA). Furthermore, with the aid of hyperspectral imaging of pixelated HNA array, we reconstructed the enhanced fingerprint absorption spectrum by one-time data acquisition from the aqueous analyte of acetone, isopropyl alcohol (IPA), and their mixture. We also integrated the WGHNA-SEIRAS platform with a microfluidic channel, solving the water absorption issue by traditional IR spectroscopy for aqueous measurement, which can be easily compatible with the biomolecular and cellular systems. Our work paves the way to achieve fast global molecular recognition by rich spectrum information from HNA-SEIRAS in non-contact, non-destructive, label-free, and miniaturized methods.

Working Principles of WGHNA-SEIRAS

The concept of WGHNA-SEIRAS platform is shown in **Fig.1**. The MIR light shines from an IR microscope and excites the plasmonic resonance of HNA on calcium difluoride (CaF₂) substrate with desired polarization state and perpendicular incidence. The transmitted or reflected light is routed to IR FPA to capture the far-field spectral response from HNA. With the plasmon-phonon coupling illustrated in **Fig.1 a**, the resonant HNA interacts with the molecular vibration at matched wavelength/frequency, thus enhancing the fingerprint absorption. Based on TCMT, we can get equations for coupling system³³(**Method 1**) and derive the transmission and reflection spectral desparation as

$$T(\omega), R(\omega) = \left| \frac{S_{t,r}}{S_{in}} \right|^2 = \left| \frac{j(\omega - \omega_0) + \gamma_{a,r} + \frac{\mu^2}{j(\omega - \omega_m) + \gamma_m}}{j(\omega - \omega_0) + (\gamma_a + \gamma_r) + \frac{\mu^2}{j(\omega - \omega_m) + \gamma_m}} \right|^2 \quad (1)$$

where ω_0 and ω_m represent the angular frequency of resonance for HNA and molecular vibration, respectively. γ_a and γ_r denote the radiative and absorptive losses of HNA, while γ_m is the absorptive loss of molecules. μ is the coupling strength between HNA and molecular vibration. From **Eq.1**, the enhanced vibration signal can be observed as electromagnetic induced transparent (EIT)-like line shape, a noticeable dip in HNA resonance when two resonance modes are well-matched ($\omega_0 = \omega_m$). The substantial enhancement of the sensing signal is observed in the change of transmission or reflection intensity compared with intrinsic molecule absorption.

To achieve a broadband response of the HNA platform, we propose two types of wavelength-gradient design by gradually changing the optical length of HNA. One is the HNA array by a gradient change in each pixel with periodic nanoantenna structures in the same scale, and the other is the HNA supercell by the gradient structure into unit cells for periodic structure, as shown in **Fig.1 d**. The respective spectrum for HNA array and supercell is demonstrated in **Fig. 1 c and e**

with the concept showing of interaction with molecules absorption peaks. The WGHNA shows the wavelength-scalable response to capture multiple fingerprint absorption peaks. With imaging processing and ML for the raw data, the fingerprint barcoding and molecule identification are achieved for array and supercell, respectively. In **Fig. 1 f**, the barcoding of molecular absorption peak is demonstrated for broadband fingerprint retrieval. The blue and green colors indicate the existence of the chemical bond, and the brightness of each pixel indicates the absorptance corresponding to the concentration of one type of chemical bond. Each pixel of the HNA array only covers a limited bandwidth near the resonance wavelengths, which gives the highest sensitivity for plasmon phonon coupling. Besides, the PCA is used to process the broadband signal from the HNA supercell to classify different types of molecules. The function of PCA is to amplify the difference of molecular spectra with massive raw data collected. As demonstrated in **Fig. 1 g**, three clusters can be observed to recognize three different molecules.

Design and Sensing Characterization of HNA

The design concept and experimental results of HNAs are shown in **Fig.2**. From **equation 5**, we observe that the T and R are related to the resonance properties of HNA, which are radiative and absorptive losses (γ_a and γ_r). The γ_a is related to the ohmic loss of plasmonic material (e.g., Au in this work) and is almost robust among different antenna structures. Therefore, the philosophy to use hook shape in PNA design is to engineer γ_r to tune the radiation from electron oscillation by inducing inverse current from short arm (L3) of HNA. The method to control radiation capability from the ratio of inverse current is merely adjusting the geometric difference (ΔL) between long arm (L1) and short arm (L3) of HNA as illustrated in **Fig.2 a**. The HNA performs a dipole resonance at resonance frequency by enhancing localized electric field intensity, thus inducing the current from one end to the other end (**Fig.2 b,c**). The connection of two arms of HNA (L2) only affects the resonance wavelength and is defined as a fixed value (400 nm) to fit the fabrication

resolution as shown in the SEM photo in **Fig.2 d**. With the decrease of ΔL , both T (**Fig.2 e**) and R (**Fig.2 f**) intensities drop, which means the antenna becomes less radiative (darker). However, the absorption signal reaches a peak value when ΔL equals $0.6 \mu\text{m}$, which means the critical coupled point ($\gamma_a = \gamma_r$) of the HNA resonator. The experiment results of resonance intensity prove the FDTD simulation observation in **Fig. 2 h-j**.

To characterize the sensing performance of each hook antenna devices, 10 nm Poly(methyl methacrylate) (PMMA) thin film is coated on top of HNA sensors. A strong resonance of the "C=O" stretching is observed at $\sim 5.8 \mu\text{m}$ in **Fig. 3**. According to TCMT results in **Eq. 1**, the sensitivity of plasmonic sensors is defined as the intensity change of resonance spectrum of transmission (ΔT) or reflection (ΔR) and is expressed as

$$\Delta T(\omega = \omega_0) = T(\omega = \omega_0) - T|_{\mu=0}(\omega = \omega_0) = \frac{2\mu^2}{\gamma_a\gamma_m} \frac{f}{(1+f)^3} \quad (2)$$

$$\Delta R(\omega = \omega_0) = R(\omega = \omega_0) - R|_{\mu=0}(\omega = \omega_0) = -\frac{2\mu^2}{\gamma_a\gamma_m} \frac{f^2}{(1+f)^3} \quad (3)$$

where μ and f denote coupling efficiency between HNA and molecular vibration as well as the ratio (γ_r / γ_a) between radiative (γ_a) and absorptive (γ_r) damping rate of the HNA, respectively. As ΔL decreases, μ remains almost unchanged because of the similar intensity of near field (Supplementary), but f decreases due to the reduced γ_r caused by the short electrical length of the antenna and the similar γ_a caused by the same antenna length ($L=L_1+L_2+L_3$), as shown in **Fig. 3 c**. The experimental results of PMMA sensing are shown in **Fig. 3 a,b**, and the extracted difference signals are plotted in **Fig. 3 d,e**. From **Fig.3 f**, we observe that the highest sensitivity of transmission mode (ΔT) comes when ΔL equals $0.6 \mu\text{m}$, while $1.2 \mu\text{m}$ (inset SEM for real HNA device) for reflection mode (ΔR), which agrees with the theoretical prediction from **Eq. 6,7** ($f=0.5$ for T and $f=2$ for R). In **Fig. 3 g,h**, a transition of line shape from Fano-like to EIT-like is observed when the resonance wavelength of HNA matching with molecular absorption wavelengths.

Besides, the highest sensitivity is achieved when the resonance wavelengths of HNA and molecules are well-matched (**Fig.3 i**). After optimization, the arm length ratio is fixed at $L_3:L_1=1:3$ to achieve the highest sensitivity at reflection mode. Therefore, to simultaneously achieve the best sensitivity and broad bandwidth, the wavelength-gradient structures are designed by gradually increasing the total length with the fixed folding degree of HNA.

Characterization of HNA Supercell and Fluidic Dynamics

The spectrum of the 16-element HNA supercell is shown in **Fig.4 a** measured by a Fourier-transform infrared (FTIR) spectroscopic microscope (**Methods 4**). The wavelength gradient response is observed from $\sim 5\ \mu\text{m}$ to $\sim 7.8\ \mu\text{m}$ with 16 HNA structures by changing the total length (L). To compare the sensing performance of WGHNA, two types of molecules (silk protein and PMMA) are separately coated on HNA supercell. **Fig.4 b** shows the sensing results of silk and PMMA on HNA supercell with the broadband response from $\sim 5.5\ \mu\text{m}$ to $8.5\ \mu\text{m}$. Multiple fingerprint absorption peaks are captured by the broadband device. The redshift of the HNA supercell spectrum is caused by the effect induced by the refractive index of analytes indicating the refractometry function of WGHNA. We further compared the sensing performance with selected HNA elements (P1, P8, and P16) from WGHNA, showing that WGHNA has a better enhancement effect of multiple absorption peaks from broad wavelength ranges, while HNA only reaches the best enhancement at narrow wavelength ranges near resonance wavelengths. Both WGHNA and HNA show the significant enhancement (3 orders of magnitude) of absorption spectrum with the direct measurement of thin-film without nanoantenna.

In addition to the proof-of-concept characteristic of thin-film, we also integrated WGHNA into a microfluidic system (**Fig. 4 d I**), which is easily compatible with biomolecular systems for molecular detection in the aqueous environment. The response of HNA supercell for water with the enhancement of OH bond absorption at $6.0\ \mu\text{m}$ is shown in **Fig.4 d II**. We also performed the

dynamic monitoring of acetone in water to mimic the real-time dynamic monitoring of metabolic in biology samples. As shown in **Fig. 4 e**, the real-time spectrum indicates the analyte change at the WGHNA surface as time goes by. Multiple fingerprint absorption peaks are captured to have rich information of chemical bond changes. (**Fig. 4 f**) By integrating the absorbance spectrum, the dynamic behavior of water and acetone can be monitored by the change of chemical bonds. The reduction of O-H bond absorptance at 2.95 μm and 6.0 μm represents the decrease of water concentration, while the increasing of C=O, C-H, C-C-C bond absorptance at 5.7 μm , 7.0 and 7.3 μm , 8.3 μm indicate the introduction of acetone molecules into the microfluidic system.

Machine Learning for Molecular Identification

To demonstrate the molecular identification properties of WGHNA, we select three types of chemically similar alcoholic liquid - methanol, ethanol, and IPA. Both of the molecules have the same functional group of hydroxy and methyl bond, resulting in similar absorption spectra in 6 μm to 9 μm wavelengths. Therefore, it is not easy to distinguish them in a mixture with a narrow bandwidth of HNA. We designed a series of experiments to compare the recognition capability of HNA and WGHNA using 1% methanol, ethanol, and IPA in water and mixture sets of each two in the same volume. With the injection of liquid from microfluidics, the response of HNA and WGHNA is plotted in **Fig. 5 a**. The apparent dips of the reflection spectrum at 6.0 μm are induced by water in both HNA and HNA supercell. The fingerprint absorption of alcoholic molecules is captured from 6.5 μm to 9 μm and is extracted from the HNA supercell spectrum in **Fig. 5 b**. Due to the low concentration of analytes, the change of reflection at absorption is small and cannot be detected without HNA. To process the small signal, we applied a second derivative to extract the characteristic of each spectrum from the HNA supercell (**Fig. 5 c**), which is widely used in traditional IR spectroscopy analysis. However, it is still difficult to distinguish clearly with the classic data processing methods from the enhanced spectrum of HNA by solely analyzing the

fingerprint absorption. Therefore, we propose a ML method using PCA to process the HNA data for extraction of multi-dimensional information from HNA, which is absorption peaks induced by vibration of the chemical bond, the wavelength shift of HNA resonance induced by the refractive index of molecules, and the intensity change of water absorption induced by loading effect of wavelength detuning.

The results of PCA processed spectra are shown in **Fig. 5 d** by dimension reduction to three principal components (PC) axes. For HNA spectra, the first PC represents the modulation of water absorption peak by loading effect of wavelength shift, and the second PC represents the wavelength shift of HNA resonance induced by refractive index of analytes. While for HNA supercell, the first and second PC is flipped in terms of data feature from the spectrum. The third PC represents the fingerprint absorption of three molecules in both the HNA and HNA supercell. The order of PC represents the degree of difference between each spectrum. In 3D PC space, each point represents the spectrum data from HNA or HNA supercell, and each cluster represents one type of molecule combination. In conclusion, with the help of PCA, the IR spectrum of HNA with different molecules can be reduced to three principal components, which indicating the three key features of loading effect, wavelength shifts, and enhanced fingerprint absorption. With the full utilization of multiple dimension information, the recognition becomes more efficient by monitoring the complementary physical (refractive index) and chemical properties (absorption fingerprints) of molecules, bring in a new degree of freedom into IR spectroscopy analysis by refractometry and plasmonic properties. Compared with previous literature that demonstrates the identification of two molecules mixture by monitoring two absorption peaks¹⁷, our work demonstrated simultaneously monitoring of 15 absorption peaks and used to identify three molecules mixture. Furthermore, with the aid of dimension reduction by PCA, the multi-

dimensional information from HNA is easily decoupled and analyzed, paving the way to achieve global molecular identification and real-time monitoring by training with deep neuron networks (DNN).

Hyperspectral Imaging of HNA Array for Fingerprint Reconstruction

Hyperspectral imaging is applied to the HNA array to retrieve the enhanced fingerprint absorption with one-time data acquisition. As shown in **Fig. 6 a-d**, the 4*4 HNA array (P1-P16) with wavelength gradient is used to capture the hyperspectral image from 4 μm (2500 cm^{-1}) to 9 μm (1111 cm^{-1}) by FPA under different analyte states (Bare, acetone, IPA and mixture). The fingerprint absorption of acetone and IPA is reflected on the hyperspectral image of HNA array at absorption wavelengths. In the mixture of Acetone and IPA, the combination of image change is observed at all absorption wavelengths. To get a better understanding of the spectral response of the HNA array, we extract the spectra of each HNA pixel in **Fig. 6 e I-III** and further calculate the difference of reflection signal induced by molecular absorption in **Fig. 6 e IV-VI**. By integrating the molecular spectra within a fixed bandwidth of each pixel (400 nm), we reconstructed the fingerprint absorption barcode of Acetone, IPA, and their mixture in **Fig. 6 f**. The darker the color of each pixel leads to the strong absorption induced by molecules. It agrees well with the fingerprint absorption of IPA and Acetone captured by traditional IR spectroscopy. The absorption peaks of IPA at 7.0 to 8.0 μm and 8.5 μm are captured by P9 to P13 and P16 (follow same orientation in **Fig. 6 a**) respectively, while the absorption peaks of acetone at 5.74 μm , 7.0 to 7.5 μm and 8.0 μm are captured by P1 to P3, P9 to P11 and P14 respectively. In the mixture sample, both absorption peaks are captures from the reconstructed imaging. The retrieved fingerprint absorption barcode of the mixture shows a combination of the barcode image between IPA and Acetone. Such rich spectral information is captured in one-time data acquisition, and the IR fingerprint absorption is enhanced by the HNA array. Compared with the similar approach

achieved by all-dielectric nanoantenna with high quality factors^{37,38}, our approach behaves smaller footprint and spatial tunability so that the whole enhanced spectra can be captured in one testing, which dramatically reduced the time for broadband fingerprint retrieving, paving the way to ultrasensitive and ultrafast molecules screening in ultra-broadband wavelength range with ultra-small volume. Although the spatial resolution is limited by the pixel of FPA (32*32 pixels) in our demonstration (4*4 HNA pixels) to avoid mutual coupling, it is easy to improve by replacing the FPA with more pixel numbers, smaller pixel area, and better detectivity (D^*).

Discussion

In this work, we propose a novel WGHNA-SEIRAS with high sensitivity and broad bandwidth for molecular identification with complementary information of physical (refractive index) and chemical (chemical bond fingerprint absorption) properties. With a demonstration of thin-film sensing of PMMA and silk protein, and microfluidic sensing of water, acetone, and acholic molecules, the WGHNA show the enormous potential of real-time broadband dynamic detection of the molecular behavior like chemical reaction and various molecular recognition. Additionally, with the aid of machine learning algorithm-PCA, the multi-dimensional rich information can be classified effectively, resulting in good pattern recognition using both spectroscopy and refractometry function from WGHNA-SEIRAS. Furthermore, leveraging FPA for hyperspectral imaging of WGHNA, the enhanced fingerprint absorption with rich information of multiple molecular vibrational peaks from broad bandwidth (from 4 μm or 2500 cm^{-1} to 9 μm or 1111 cm^{-1}) can be captured in one-time data acquisition, booting up the screening speed and recognition capability for global molecule identification. Our work brings new insights into IR spectroscopy technologies for small-volume, real-time, ultra-sensitive, *in-vitro* biomolecular dynamic analysis in the aqueous environment.

Fig.1 (a) Schematic drawing of HNA vibrational probe for molecular sensing by the interaction between plasmonic resonance and molecular vibration. The yellow color refers to the simulated electrical field near the surface of the hook antenna. The physical parameters (γ_a , γ_r , γ_m and μ) are used in TCMT modeling to express the resonance behavior of PNA and molecular vibration. (b) The spectrum of plasmonic-enhanced molecular vibration signal in reflection (R) and transmission (T) compared with intrinsic fingerprint absorption. (c) The concept drawing of spectral response of wavelength-gradient HNA array with molecular vibration fingerprints. The different curves indicate the spectrum of each pixel in the HNA array. Each HNA pixel has one periodic HNA structure and the length of HNA gradually changes among different pixels. By gradually increasing the optical length of HNA in one pixel, the optical resonant wavelength is also increasing linearly. The molecular vibration is captured by the HNA pixel which operates at the same wavelength. The enhanced absorption is marked as shadow by different color for different pixels. (d) Schematic drawing of two types of WGHNA designs – HNA array and HNA supercell. Both HNA array and supercell have the wavelength gradient nanoantenna structure. The difference is that the wavelength gradient is designed at different order of structures, which are pixel and cell levels. The HNA array has periodic HNA structure at each pixel and changes among different pixels, while the HNA supercell holds the gradient nanoantenna into one unit-cell called

supercell and repeat the supercell to form periodic structures. The inset SEM image is the top-view of HNA, and the scale bar indicates $1\mu\text{m}$. (e) The concept drawing of spectral response of wavelength-gradient HNA supercell with molecular vibration fingerprints. Example illustration of different molecular vibration fingerprints are marked in of blue, green, and red. The broadband response of supercell shows the capability to capture multiple absorption peaks. (f) The fingerprint barcoding image is processed from the HNA array pixel signal in (c). (g) Molecular recognition results from the broadband spectrum of HNA using principal component analysis (PCA) algorithm from machine learning. Each cluster indicates one type of molecule.

Fig.2 The plasmonic properties of HNA. (a) The schematic drawing of the HNA array. The polarization of incident light is aligned with the long arm of HNA. ΔL is used to characterize the folding degree of the hook antenna. (b) Simulated nearfield distribution of electric field intensity of HNA when ΔL equals $1.2\mu\text{m}$. (c) Simulated nearfield distribution of electric field polarity of HNA when ΔL equals $1.2\mu\text{m}$. The dipole resonance is generated at the resonance wavelength. (d) The SEM image of one HNA with scale bar indicating 500 nm . (e-g) the IR response spectrum as the increment of ΔL for transmission (e), reflection (f), and absorption (g). (h-i) The experimental results (points) as the increment of ΔL compared with simulation results (curves).

Fig.3 Characterization of sensing performance for HNA. (a,b) Experimental sensing spectrum of HNA with variances of ΔL for C=O stretch of PMMA. (c) Theoretical fitting of damping rate of a different folded degree from TCMT. (d-e) Extracted sensing signal of HNA with a difference with reference devices. (f) the sensitivity of the HNA sensor of transmission and reflection mode with the change of ΔL . (g) experimental sensing spectrum of HNA with variances of L for C=O stretch of PMMA. (h) Extracted sensing signal of HNA with a difference with reference devices. (i) the sensitivity of the HNA sensor of transmission and reflection mode with a change of L.

Fig.4 Broadband sensing characterization of HNA supercell by gradient increase HNA length into a unit cell and broadband monitoring of fluidic dynamics for acetone injection into the water from HNA supercell integrated with PDMS microfluidic chamber. (a) The experimental reflection spectrum of HNA by changing the length. A longer HNA leads to a longer resonant wavelength. By combining different lengths into a unit cell of the metasurface, and HNA supercell is formed with broadband resonance performance. (b) Sensing characterization of HNA supercell with the thin-film analyte of PMMA and silk protein. The fingerprint absorption peaks ranging from 5.5 μm to 9 μm are clearly captured by HNA supercell including C=O, C-H, C-O-C bond from PMMA and amide I, amide II and C-N bond from silk. (c) Comparison of sensing spectrum of PMMA and silk between HNA and HNA supercell. The HNA from P1, P8, and P16 is selected as a reference with the response to short, medium, and long-wavelength resonance, respectively. It shows HNA supercell has a good response over a broad range of wavelengths from 5.5 μm to 9 μm which HNA

only covers a narrow bandwidth near resonance wavelength for enhancement of fingerprint absorption. (d) I. Schematic drawing of an integrated microfluidic HNA supercell system for liquid sensing. The HNAs on the CaF_2 carrier chip is flip bonded to the PDMS surface with the alignment of HNAs into the microfluidic channel. The microfluidic channel is formed by a 3D printed mold and is fixed on a microscope slide. The IR light is shining from the backside of the CaF_2 chip, and reflected light is collected to monitor the far-field response of HNA supercell with different aqueous analytes. II. The response of HNAs under the water (H_2O) environment. The enhancement of the O-H bond of H_2O molecules at $6.0\ \mu\text{m}$ is observed at an enhancement factor of. Additionally, the redshift of μm from HNAs is observed to demonstrate the refractometry function of HNAs corresponding to the refractive index change of molecules. (e) The dynamic response of HNAs with respect to a different time as acetone injects into water. Each curve indicates the real-time spectrum of a mixed solvent of acetone and water, reflecting in-situ concentration information of acetone and water and dynamic change versus time. (f). Baseline-corrected absorbance spectrum at a different time at board wavelengths range from 2.5 to $3.5\ \mu\text{m}$ for O-H bond of water at $2.95\ \mu\text{m}$ and 5.5 to $9\ \mu\text{m}$ for various fingerprint peaks (O-H bond for H_2O at $6.0\ \mu\text{m}$, C=O, C-H, C-C-C bond for acetone at $5.7\ \mu\text{m}$, 7.0 and $7.3\ \mu\text{m}$, $8.3\ \mu\text{m}$, respectively). (g). The integrated absorbance of each fingerprint absorption as a function of time. As time goes by, the absorbance of O-H bond of H_2O at $2.95\ \mu\text{m}$ and $6.0\ \mu\text{m}$ decrease, indicating the concentration decrease of water molecules while the absorbance of C=O, C-H, C-C-C bond for acetone at $5.7\ \mu\text{m}$, 7.0 and $7.3\ \mu\text{m}$, $8.3\ \mu\text{m}$ increase, representing the concentration increase of acetone molecules.

Fig. 5 Machine learning demonstration of HNA spectroscopy by recognition of alcoholic molecules of methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), and IPA ($\text{C}_3\text{H}_7\text{OH}$) at a concentration of 1% in water (H_2O). (a) The response of HNA spectroscopy under different types of alcoholic molecules. The HNA only response to a narrow bandwidth near resonance wavelength at $\sim 6.5 \mu\text{m}$, while HNA supercell response to a wide bandwidth from $6 \mu\text{m}$ to $9 \mu\text{m}$. The dip at $\sim 6.0 \mu\text{m}$ represents the O-H bond of water, which is the common solvent in both cases. (b) The calculated the reflection change spectrum (i) and its second derivative (ii) of HNA supercell under different types of alcoholic molecules from $6.5 \mu\text{m}$ to $9 \mu\text{m}$, showing the fingerprint absorption peaks of each molecule and in a mixture of two types of molecules. (c) The machine learning processed a spectrum of HNA spectroscopy after dimension reduction by principal component analysis. For HNA, the 1st principle component represents the modulation effect of water absorption peaks at $6.0 \mu\text{m}$. The 2nd principle component represents the wavelength shift of HNA due to the refractive index of the analyte. The 3rd principle component represents the fingerprint absorption of molecules. While for HNA supercell, the 1st and 2nd component is flipped as the HNA case indicating the different response for refractometry and spectroscopy function. (d) The weight of scores of each spectrum in three-dimensional space after PCA for HNA(i) and HNA supercell(ii). Each cluster indicates one type of molecules and their mixtures.

Fig.6 IR fingerprint retrieval and molecules identification by hyperspectral IR imaging for HNA array. (a) Schematic illustration of wavelength gradient HNA array for hyperspectral imaging. Each pixel response to different IR wavelengths. (b) By pixelating the wavelength gradient HNA into a four by four arrangement, the hyperspectral imaging is captured by the FPA, representing the different spectrum response of each HNA pixels. P1 response shortest wavelengths ($\sim 4.67 \mu\text{m}$) and P16 response the longest wavelengths ($\sim 7.46 \mu\text{m}$). The wavelength difference is designed to

be ~200 nm to construct a linear gradient in the wavelength domain. (c) Zoom-in picture for the HNA array at four selected wavelengths (i. 4.67 μm , ii. 5.66 μm , iii. 6.88 μm , iv. 7.46 μm). The expected pixel is illuminated at a resonant wavelength while other pixels are dark. The pixel is illuminated at HNA resonance, which are 4.67 μm for P1, 5.66 μm for P6, 6.88 μm for P12, and 7.46 μm for P16. (d) The hyperspectral image of HNA array at 16 resonance wavelengths for 16 pixels under different liquid analytes conditions (Acetone, IPA and Acetone: IPA=1:1). (e) The extracted normalized reflection and difference normalized reflection spectrum of P1 to P16 under molecules of acetone (I, IV), IPA (II, V), and Acetone: IPA=1:1 (III, VI). The analytes are in the liquid phase and signals are captured by the microfluidic integrated HNA array. At the absorption wavelength of IPA (λ_{7-13} and λ_{16}) and acetone (λ_3 , λ_{7-11} and $\lambda_{14,15}$), the HNA reflection drops at the desired pixel. (f) The reconstructed fingerprint barcode image by integrating spectrum at working wavelength of each pixel for acetone (I), IPA (II), and Acetone: IPA=1:1 (III). The darker of the pixels refers to the stronger absorption of molecules. The absorption peaks of IPA at 7.0 to 8.0 μm and 8.5 μm are captured by P9 to P13 and P16 respectively, while the absorption peaks of acetone at 5.74 μm , 7.0 to 7.5 μm and 8.0 μm are captured by P1 to P3, P9 to P11 and P14 respectively. In the mixture sample, both absorption peaks are captures from the reconstructed imaging.

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Methods

TCMT modeling:

The temporal coupled-mode theory (TCMT) is used to model the coupling behavior between PNA and molecular vibration. We treat the plasmonic resonant (denoted as P) as a bright mode that is coupled to the incident light, while we treat the molecular vibration (denoted as M) as a dark mode, which coupling efficiency is much lower than PNA and can be ignored in their coupling system. Therefore, we write down the equations using TCMT as

$$\frac{dP}{dt} = j\omega_0 P - (\gamma_a + \gamma_r)P + j\mu M + \sqrt{\gamma_r} S_{in} \quad (1)$$

$$\frac{dM}{dt} = j\omega_m M - \gamma_m M + j\mu P \quad (2)$$

$$S_t = S_{in} - \sqrt{\gamma_r} P \quad (3)$$

$$S_r = \sqrt{\gamma_r} P \quad (4)$$

where P , M and ω_0 , ω_m represent the amplitude and angular frequency of resonance for HNA and molecular vibration, respectively. γ_a and γ_r denote the radiative and absorptive losses of HNA, while γ_m is the absorptive loss of molecules. μ is the coupling strength between HNA and molecular vibration. S_{in} , S_t , and S_r represent the amplitude of incident, transmitted, and reflected light,

538 respectively. Under the time-harmonic condition, the first derivative of time (d/dt) is replaced by
 539 $j\omega$, and the Eq.1 and Eq.2 can be simplified as

$$540 \quad [j(\omega - \omega_0) + (\gamma_a + \gamma_r)]P = j\mu M + \sqrt{\gamma_r}S_{in} \quad (5)$$

$$541 \quad [j(\omega - \omega_0) + \gamma_m]M = j\mu P. \quad (6)$$

542 By substituting eq. 6 to eq.5, we can eliminate M and obtain

$$543 \quad [j(\omega - \omega_0) + (\gamma_a + \gamma_r) + \frac{\mu^2}{j(\omega - \omega_0) + \gamma_m}]P = \sqrt{\gamma_r}S_{in} \quad (7)$$

544 Therefore, T and R can be expressed as

$$545 \quad T(\omega), R(\omega) = \left| \frac{S_{t,r}}{S_{in}} \right|^2 = \left| \frac{j(\omega - \omega_0) + \gamma_{a,r} + \frac{\mu^2}{j(\omega - \omega_m) + \gamma_m}}{j(\omega - \omega_0) + (\gamma_a + \gamma_r) + \frac{\mu^2}{j(\omega - \omega_m) + \gamma_m}} \right|^2 \quad (8)$$

546 The EIT-like line shape and Fano-like line shape can be expressed from **Eq.8** when $\omega_0 = \omega_m$ and
 547 $\omega_0 \neq \omega_m$, respectively. The plasmonic resonance can be easily obtained when there is no coupling
 548 effect from molecules ($\mu=0$).

$$549 \quad T(\omega) = \frac{(\omega - \omega_0)^2 + \gamma_r^2}{(\omega - \omega_0)^2 + (\gamma_a + \gamma_r)^2} \quad (9)$$

$$550 \quad R(\omega) = \frac{\gamma_a^2}{(\omega - \omega_0)^2 + (\gamma_a + \gamma_r)^2} \quad (10)$$

$$551 \quad A(\omega) = 1 - T - R = \frac{2\gamma_a\gamma_r}{(\omega - \omega_0)^2 + (\gamma_a + \gamma_r)^2} \quad (11)$$

552 **Eq. 9-11** is used to extract absorptive and radiative loss of HNA by fitting the resonance spectrum
 553 in the frequency domain from simulation (**Extended Data Fig.1**). By engineering the HNA

structure by changing ΔL with the constant L , the γ_r and γ_a can be tuned continuously, and ω_0 remains unchanged. To explore the sensing performance, we have made some assumptions to simplify **Eq.8** in order to perform the analytical operation. First, we make $\omega_0 = \omega_m$ to match the frequency of HNA and molecular vibration since the WGHNA is only designed for the molecular absorption wavelength near the HNA resonance wavelength to have the best enhancement. Second, we treat μ as a much smaller parameter compared with γ_m , γ_r , and γ_a . Therefore, we apply the difference between **Eq.9** and **Eq.8** when $\omega = \omega_0 = \omega_m$.

$$\Delta T(\omega = \omega_0) = \frac{2\mu^2}{\gamma_m} \frac{\gamma_a \gamma_r}{(\gamma_a + \gamma_r)^2 (\gamma_a + \gamma_r + \frac{\mu^2}{\gamma_m})} + \left(\frac{\mu^2}{\gamma_m}\right)^2 \frac{\gamma_r^2}{(\gamma_a + \gamma_r)^2 \left(\gamma_a + \gamma_r + \frac{\mu^2}{\gamma_m}\right)^2} \quad (12)$$

Since $\mu \ll \gamma_m$, $\frac{\mu^2}{\gamma_m}$ is a small real number close to 0. Therefore, we cancel the high order term and simplify **Eq.12** as

$$\Delta T(\omega = \omega_0) = \frac{2\mu^2}{\gamma_a \gamma_m} \frac{f}{(1 + f)^3} \quad (13)$$

where $f = \gamma_r / \gamma_a$, defining the ratio of radiative and absorptive loss. Similarly, for the reflection spectrum, we get

$$\Delta R(\omega = \omega_0) = -\frac{2\mu^2}{\gamma_a \gamma_m} \frac{f^2}{(1 + f)^3} \quad (14)$$

The negative sign in **Eq.14** indicates the opposite change in transmission and reflection spectrum induced by molecules vibration. γ_a refers to the omics loss of material; thus, it is constant in our experiment of HNA made by Au. When changing ΔL of HNA, the electrical field does not change too much among different HNA devices, so that μ is also a constant. Additionally, γ_m is also unchanged since we fix the absorption peaks of the "C=O" bond from PMMA in sensitivity

characterization. By applying the first derivative of f for **Eq.13** and **Eq.14**. We further calculate the maximum enhancement of the T and R spectrum and get the optimal condition that occurs when f equals 0.5 and 2, respectively.

FDTD simulation:

The finite-difference time-domain (FDTD) method (Lumerical FDTD¹) is performed to simulate the far-field spectrum and the nearfield distribution of plasmonic hook nanoantenna. The light source is selected as a plane-wave to simulate the incidence of light from free space. The incidence angle and polarization state are adjusted to the desired orientation to excite the bipolar mode plasmonic resonance of HNA. The refractive index of CaF₂ is set at 1.38 at wavelengths ranging from 2 μm to 10 μm . The periodic boundary at the x and y-axis (**Fig. 2 a**) is selected to simulate the effect of the periodic antenna array, and the PML boundary is chosen at the z-axis to transport light into free space. The electric field and magnetic field of HNA with different ΔL are plotted in **Extended Data Fig.2**. The electrical field distribution reflects the electric field's intensity and polarity at the resonance wavelength of nanorod and HNA devices when ΔL changes. The E^2 intensity remains the same at all devices representing the constant coupling efficiency μ . Additionally, E_x polarity indicates the bipolar resonance mode at resonance wavelength of all nanorod and HNA devices when ΔL changes. Furthermore, magnetic field distribution reflects the current orientation at resonance wavelength, indicating the nanoantenna's radiation capability. As ΔL increase, the overlap of inverse current at the short arm of HNA ruin the radiation due to the large radiative loss (γ_r). Therefore, the HNA become dark as the transmission and reflection drops.

Fabrication of HNA:

For the fabrication of HNA, electron-beam lithography (EBL, Jeol 6500FS) and lift-off process is used to pattern the nanometer scale gold structure. Before EBL, the CaF₂ chip was firstly rinsed by Acetone and IPA solutions for 1 min with sonication. After that, the chip is treated under oxygen plasma for the uniform formation of PMMA 495K A5 photoresist, which is spin-coated at 4000 rpm for 1 min. Since the conductivity of the CaF₂ chip is low, an additional E-spacer layer is spin-coated at 2000 rpm for 1 min to avoid charge accumulation during EBL. After EBL, the development with 30 s using PMMA developer (MIBK:IPA=1:3) is used to remove PMMA resist under exposure following by the cleaning with IPA for 30 s. Then electron beam evaporation (AJA International Inc.) is proceeded to deposit 80 nm thick gold on top of CaF₂ substrate and PMMA photoresist. To lift-off the nanoantenna pattern, the chip is placed in acetone for one day and rinsed by IPA. After that, the HNA chip is tested by SEM (Hitachi) and AFM (Bruker FastScan) to confirm the geometry (**Extended Data Fig.3**).

FTIR measurement:

A Fourier-transformed IR (FTIR) microscope (Agilent Cary 660) with an FTIR spectrometer (Agilent Cary 620) and HgCdTe (mercury cadmium telluride, MCT) detector is used to characterize hook nanoantenna. The background signal is collected from the CaF₂ chip using 16-32 scans at 8 cm⁻¹ resolution to compensate for the MIR gas absorption (mainly water vapor and CO₂) from the ambient. Then the sample scan is performed using 16-32 scans at 8 cm⁻¹ resolution to capture the spectral response of nanoantenna. The scanning area is adjusted to 200*200 μm² to fit the nanoantenna area. For liquid sensing, a microfluidic chamber made by PDMS is bonded to a CaF₂ chip to allow the contact of the liquid analyte with HNA, and the spectrum is captured simultaneously.

The hyperspectral images are captured by an IR focal plane array (FPA) MCT detector with 32*32 pixels. To get the IR spectrum of each pixels of the HNA array, the alignment of HNA position is performed at each data acquisitions. Due to the mutual coupling of HNA array, we cannot fit one HNA pixel to one FPA pixel to get a perfect image. Therefore, we need to fit one HNA pixel to multiple FPA pixels as shown in **Extended Data Fig.4**. We fix the pixel number of HNA array and change the pixel area. For pixel area of 40*40 μm^2 , we achieve the data acquisitions in one time (**Extended Data Fig.4 b**). For pixel area of 80*80 μm^2 , we achieve the data acquisitions in four times (**Extended Data Fig.4 c**). Compared with these two figures, a clearer square-shape imaging of HNA array is shown in the picture by 4 pixels per acquisition. This result shows that the spatial resolution of HNA array is mainly limited by pixels of FPA, which can be improved by replacing the FPA with more pixel numbers, smaller pixel area, and better detectivity (D^*).

Visualization using PCA

Principal component analysis is used in exploratory data analysis and for making predictive models. It is commonly used for dimensionality reduction by projecting each data point onto only the first few principal components to obtain lower-dimensional data while preserving as much of the data's variation as possible. To facilitate visualization of the feature space, PCA was performed in MATLAB_R2020a. In this case, a covariance matrix was computed using a factorization of singular value decomposition (SVD) for the normalized set of features from which the eigenvectors and eigenvalues were extracted. Each principal component was constructed as a linear combination of the initial features. The first three principal components were then used to display 3D scatter plots of the features.

In our experiment, we select methanol, ethanol and IPA as a proof-of-concept demonstration and dilute the liquid analytes into water with a constant volume concentration of 1%. The IR fingerprint absorption peaks of these analytes are shown in **Extended Data Fig. 5 d**. By mixing the two of three analytes, we have six different analyte states, which are 1% methanol, 1% ethanol, 1% IPA, 1% methanol + 1% ethanol, and 1% methanol + 1% IPA. To compare the device performance, we have four device configurations, which are HNA, HNA supercell, nanorod antenna (NA), NA supercell. For each analyte states and device configurations, we measure 50 spectrums used for ML. The identification results are shown in **Fig. 5 e,f** for HNA and HNA supercell and **Fig.5 e,f** for NA and NA supercell.

Extended Data Fig.1 Theoretical fitting of transmission spectrum of HNA at different ΔL using TCMT.

Extended Data Fig.2 FDTD simulation results of electric (a,b) and magnetic (c,d) field distribution of nanoantenna by different folding degree.

Extended Data Fig.3 SEM and AFM characterization of HNA.

Extended Data Fig.4 (a) Schematic illustration of 4*4 HNA array and 32*32 FPA. (b) The hyperspectral imaging of bare HNA array at 5.78 μm for HNA pixel area of 40*40 μm^2 with one data acquisition. (c) The hyperspectral imaging of bare HNA array at 5.78 μm for HNA pixel area of 80*80 μm^2 with four data acquisitions. (d) Hyperspectral imaging of HNA array at resonance wavelength of each pixels with four data acquisitions.

Extended Data Fig.5 (a) The reflection spectra of 16 HNA pixels measured by FTIR. (b) The linear fitting of resonance wavelength of HNA pixels versus total length of HNA. A good linear relationship ($R^2=0.99924$) is observed and fitted effective index is 1.203. (c) The quality factor of HNA pixels in the range of 5-8. (d) The fingerprint absorption peak of methanol, ethanol and IPA at wavelength range from 6-9 μm . (e,f) The weight of scores of each spectrum in three-dimensional space after PCA for NA(e) and NA supercell(f). Each cluster indicates one type of molecules and their mixtures.

Reporting Summary. Further information on research design is available in the Nature Research Reporting Summary linked to this article.

Data availability. The data supporting the findings of this study are available from the corresponding author on request.

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Author contributions

Z.R. and C.L. generated the design concept. Z.R. performed antenna design, fabrication, and FTIR testing. Z.Z. performed machine learning algorithm and data analysis. J.W. conducted the theoretical model and advised on fabrication and FTIR testing. C. L. supervised the project. All authors prepared the manuscript.

Competing interests

688 The authors declare no competing financial interests.

689

690 **Additional information**

691 Supplementary information is available for this paper.

692

693 **Competing interests**

694 The authors declare no competing financial interests.

Figures

Figure 1

(a) Schematic drawing of HNA vibrational probe for molecular sensing by the interaction between plasmonic resonance and molecular vibration. The yellow color refers to the simulated electrical field near the surface of the hook antenna. The physical parameters (γ_a , γ_r , γ_m and μ) are used in TCMT modeling to express the resonance behavior of PNA and molecular vibration. (b) The spectrum of plasmonic-enhanced molecular vibration signal in reflection (R) and transmission (T) compared with intrinsic fingerprint absorption. (c) The concept drawing of spectral response of wavelength-gradient HNA array with molecular vibration fingerprints. The different curves indicate the spectrum of each pixel in the HNA array. Each HNA pixel has one periodic HNA structure and the length of HNA gradually changes

among different pixels. By gradually increasing the optical length of HNA in one pixel, the optical resonant wavelength is also increasing linearly. The molecular vibration is captured by the HNA pixel which operates at the same wavelength. The enhanced absorption is marked as shadow by different color for different pixels. (d) Schematic drawing of two types of WGHNA designs – HNA array and HNA supercell. Both HNA array and supercell have the wavelength gradient nanoantenna structure. The difference is that the wavelength gradient is designed at different order of structures, which are pixel and cell levels. The HNA array has periodic HNA structure at each pixel and changes among different pixels, while the HNA supercell holds the gradient nanoantenna into one unit-cell called supercell and repeat the supercell to form periodic structures. The inset SEM image is the top-view of HNA, and the scale bar indicates 1 μm . (e) The concept drawing of spectral response of wavelength-gradient HNA supercell with molecular vibration fingerprints. Example illustration of different molecular vibration fingerprints are marked in of blue, green, and red. The broadband response of supercell shows the capability to capture multiple absorption peaks. (f) The fingerprint barcoding image is processed from the HNA array pixel signal in (c). (g) Molecular recognition results from the broadband spectrum of HNA using principal component analysis (PCA) algorithm from machine learning. Each cluster indicates one type of molecule.

Figure 2

The plasmonic properties of HNA. (a) The schematic drawing of the HNA array. The polarization of incident light is aligned with the long arm of HNA. ΔL is used to characterize the folding degree of the hook antenna. (b) Simulated nearfield distribution of electric field intensity of HNA when ΔL equals 1.2 μm . (c) Simulated nearfield distribution of electric field polarity of HNA when ΔL equals 1.2 μm . The dipole resonance is generated at the resonance wavelength. (d) The SEM image of one HNA with scale bar indicating 500 nm. (e-g) the IR response spectrum as the increment of ΔL for transmission (e), reflection (f), and absorption (g). (h-i) The experimental results (points) as the increment of ΔL compared with simulation results (curves).

Figure 3

Characterization of sensing performance for HNA. (a,b) Experimental sensing spectrum of HNA with variances of ΔL for C=O stretch of PMMA. (c) Theoretical fitting of damping rate of a different folded degree from TCMT. (d-e) Extracted sensing signal of HNA with a difference with reference devices. (f) the sensitivity of the HNA sensor of transmission and reflection mode with the change of ΔL . (g) experimental sensing spectrum of HNA with variances of L for C=O stretch of PMMA. (h) Extracted sensing signal of HNA with a difference with reference devices. (i) the sensitivity of the HNA sensor of transmission and reflection mode with a change of L .

Figure 4

Broadband sensing characterization of HNA supercell by gradient increase HNA length into a unit cell and broadband monitoring of fluidic dynamics for acetone injection into the water from HNA supercell integrated with PDMS microfluidic chamber. (a) The experimental reflection spectrum of HNA by changing the length. A longer HNA leads to a longer resonant wavelength. By combining different lengths into a unit cell of the metasurface, and HNA supercell is formed with broadband resonance performance. (b) Sensing characterization of HNA supercell with the thin-film analyte of PMMA and silk protein. The fingerprint absorption peaks ranging from 5.5 μm to 9 μm are clearly captured by HNA supercell including

C=O, C-H, C-O-C bond from PMMA and amide I, amide II and C-N bond from silk. (c) Comparison of sensing spectrum of PMMA and silk between HNA and HNA supercell. The HNA from P1, P8, and P16 is selected as a reference with the response to short, medium, and long-wavelength resonance, respectively. It shows HNA supercell has a good response over a broad range of wavelengths from 5.5 μm to 9 μm which HNA only covers a narrow bandwidth near resonance wavelength for enhancement of fingerprint absorption. (d) I. Schematic drawing of an integrated microfluidic HNA supercell system for liquid sensing. The HNAs on the CaF₂ carrier chip is flip bonded to the PDMS surface with the alignment of HNAs into the microfluidic channel. The microfluidic channel is formed by a 3D printed mold and is fixed on a microscope slide. The IR light is shining from the backside of the CaF₂ chip, and reflected light is collected to monitor the far-field response of HNA supercell with different aqueous analytes. II. The response of HNAs under the water (H₂O) environment. The enhancement of the O-H bond of H₂O molecules at 6.0 μm is observed at an enhancement factor of. Additionally, the redshift of μm from HNAs is observed to demonstrate the refractometry function of HNAs corresponding to the refractive index change of molecules. (e) The dynamic response of HNAs with respect to a different time as acetone injects into water. Each curve indicates the real-time spectrum of a mixed solvent of acetone and water, reflecting in-situ concentration information of acetone and water and dynamic change versus time. (f). Baseline-corrected absorbance spectrum at a different time at broad wavelengths range from 2.5 to 3.5 μm for O-H bond of water at 2.95 μm and 5.5 to 9 μm for various fingerprint peaks (O-H bond for H₂O at 6.0 μm , C=O, C-H, C-C-C bond for acetone at 5.7 μm , 7.0 and 7.3 μm , 8.3 μm , respectively). (g). The integrated absorbance of each fingerprint absorption as a function of time. As time goes by, the absorbance of O-H bond of H₂O at 2.95 μm and 6.0 μm decrease, indicating the concentration decrease of water molecules while the absorbance of C=O, C-H, C-C-C bond for acetone at 5.7 μm , 7.0 and 7.3 μm , 8.3 μm increase, representing the concentration increase of acetone molecules.

Figure 5

Machine learning demonstration of HNA spectroscopy by recognition of alcoholic molecules of methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), and IPA ($\text{C}_3\text{H}_7\text{OH}$) at a concentration of 1% in water (H_2O). (a) The response of HNA spectroscopy under different types of alcoholic molecules. The HNA only response to a narrow bandwidth near resonance wavelength at $\sim 6.5 \mu\text{m}$, while HNA supercell response to a wide bandwidth from 6 μm to 9 μm . The dip at $\sim 6.0 \mu\text{m}$ represents the O-H bond of water, which is the common solvent in both cases. (b) The calculated the reflection change spectrum (i) and its second derivative (ii) of HNA supercell under different types of alcoholic molecules from 6.5 μm to 9 μm , showing the fingerprint absorption peaks of each molecule and in a mixture of two types of molecules. (c) The machine learning processed a spectrum of HNA spectroscopy after dimension reduction by principal component analysis. For HNA, the 1st principle component represents the modulation effect of water absorption peaks at 6.0 μm . The 2nd principle component represents the wavelength shift of HNA due to the refractive index of the analyte. The 3rd principle component represents the fingerprint absorption of molecules. While for HNA supercell, the 1st and 2nd component is flipped as the HNA case indicating the different response

for refractometry and spectroscopy function. (d) The weight of scores of each spectrum in three-dimensional space after PCA for HNA(i) and HNA supercell(ii). Each cluster indicates one type of molecules and their mixtures.

Figure 6

IR fingerprint retrieval and molecules identification by hyperspectral IR imaging for HNA array. (a) Schematic illustration of wavelength gradient HNA array for hyperspectral imaging. Each pixel response

to different IR wavelengths. (b) By pixelating the wavelength gradient HNA into a four by four arrangement, the hyperspectral imaging is captured by the FPA, representing the different spectrum response of each HNA pixels. P1 response shortest wavelengths ($\sim 4.67\text{ }\mu\text{m}$) and P16 response the longest wavelengths ($\sim 7.46\text{ }\mu\text{m}$). The wavelength difference is designed to be $\sim 200\text{ nm}$ to construct a linear gradient in the wavelength domain. (c) Zoom-in picture for the HNA array at four selected wavelengths (i. $4.67\text{ }\mu\text{m}$, ii. $5.66\text{ }\mu\text{m}$, iii. $6.88\text{ }\mu\text{m}$, iv. $7.46\text{ }\mu\text{m}$). The expected pixel is illuminated at a resonant wavelength while other pixels are dark. The pixel is illuminated at HNA resonance, which are $4.67\text{ }\mu\text{m}$ for P1, $5.66\text{ }\mu\text{m}$ for P6, $6.88\text{ }\mu\text{m}$ for P12, and $7.46\text{ }\mu\text{m}$ for P16. (d) The hyperspectral image of HNA array at 16 resonance wavelengths for 16 pixels under different liquid analytes conditions (Acetone, IPA and Acetone: IPA=1:1). (e) The extracted normalized reflection and difference normalized reflection spectrum of P1 to P16 under molecules of acetone (I, IV), IPA (II, V), and Acetone: IPA=1:1 (III, VI). The analytes are in the liquid phase and signals are captured by the microfluidic integrated HNA array. At the absorption wavelength of IPA (λ_{7-13} and λ_{16}) and acetone (λ_3 , λ_{7-11} and $\lambda_{14,15}$), the HNA reflection drops at the desired pixel. (f) The reconstructed fingerprint barcode image by integrating spectrum at working wavelength of each pixel for acetone (I), IPA (II), and Acetone: IPA=1:1 (III). The darker of the pixels refers to the stronger absorption of molecules. The absorption peaks of IPA at 7.0 to $8.0\text{ }\mu\text{m}$ and $8.5\text{ }\mu\text{m}$ are captured by P9 to P13 and P16 respectively, while the absorption peaks of acetone at $5.74\text{ }\mu\text{m}$, 7.0 to $7.5\text{ }\mu\text{m}$ and $8.0\text{ }\mu\text{m}$ are captured by P1 to P3, P9 to P11 and P14 respectively. In the mixture sample, both absorption peaks are captures from the reconstructed imaging.