Infrared metamaterial for surface-enhanced infrared absorption spectroscopy: pushing the frontier of ultrasensitive on-chip sensing

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\textbf{ABSTRACT}

Surface-enhanced infrared absorption (SEIRA) spectroscopy is a powerful technique that overcomes the issue of low molecular absorption cross-sections in infrared spectroscopy. Due to the collective oscillations of electrons in the infrared regime, SEIRA using resonant metamaterial provides greatly enhanced (up to $10^7$) electromagnetic fields extending up to tens of nanometers from the metamaterial. The enhanced near-field enables spectroscopic analysis and ultrasensitive on-chip sensing of molecules. This interesting characteristic has aroused widespread attention from researchers to SEIRA technology, and various SEIRA-based sensing applications have been continuously emerging. Optimization of the signal enhancement to obtain high sensing performance is the developing main thread of SEIRA technology. In this Review, we provide a basic understanding of SEIRA’s sensing mechanism and theoretical model. With this background, several SEIRA optimizing methods are discussed, ranging from design, materials to algorithms. Additionally, perspectives about the future development trends of SEIRA technologies are discussed.

\textbf{KEYWORDS}

Infrared metamaterial; surface-enhanced infrared absorption; sensor; ultrasensitive sensing; machine learning

1. Introduction

Infrared (IR) spectroscopy is one of the widely used spectroscopic techniques, and it is related to molecular transition moments between energy levels.\cite{1} This movement contains a lot of vibrational information linked to the chemical bonds, constituents, and configuration of the molecule. Therefore, IR spectroscopy is widely used for the identification and structural analysis of various substances.\cite{2-4} However, due to the low molecular absorption cross-sections ($10^{-20}$ cm$^2$ per molecule in the mid-IR), its detection performance is limited, especially for molecular trace detection. There are several methods to solve this issue, such as optimizing the IR source, developing ultrasensitive IR detectors, and exploiting surface-enhanced infrared absorption (SEIRA) spectroscopy. The first two approaches are effective. However, the cost of using more brilliant light sources and more sensitive detectors to achieve sensitive detection is large. SEIRA technology is a low-cost, effective, and low-noise method to improve detection performance, which was first reported by

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Hartstein et al. in 1980.\textsuperscript{[5]} They found that the infrared absorption from molecular monolayers was enhanced by a factor of 20 by using a thin film of randomly arranged Ag nanoparticles. However, since this method is not resonantly tuned to the infrared vibrations, the signal enhancement is low. Especially, compared with surface-enhanced Raman scattering (SERS),\textsuperscript{[6–9]} the SEIRA enhancement effect is not brilliant. In 1980, the enhancement factor of SEIRA is 20, and that of SERS was over $10^4$.\textsuperscript{[10]} Therefore, SEIRA did not receive widespread attention at that time and entered a period of slow development.

Metamaterials are new artificial materials engineered to have a property that is not found in naturally occurring materials.\textsuperscript{[11,12]} It has proven the ability to manipulate light at unprecedented levels and to produce various new functionalities.\textsuperscript{[13]} The SEIRA enhancement effect can be significantly improved by matching the metamaterial resonance with the respective infrared vibrations. It was first demonstrated by Neubrech et al. in 2008.\textsuperscript{[14]} They utilized a single gold nanowires nanoantenna to excite a plasmonic resonance matching the molecular infrared vibration and achieved a vibration signal enhancement of 5 orders of magnitude. Since then, many studies have been devoted to the optimization of signal enhancement as well as the application of SEIRA.\textsuperscript{[15–19]} After years of development, SEIRA has become an important vibration spectroscopy technology complementary to SERS. The advantages of SEIRA compared with SERS include: (i) SEIRA has a wider range of applications. Specifically, the strong SERS effect is mainly limited to the surface of precious metals, such as silver, gold, and copper;\textsuperscript{[20]} (ii) SEIRA-based sensors have a larger sensing depth; (iii) SEIRA has low requirements for incident light; (iv) the molecular infrared absorption cross-section ($10^{-20}$ cm$^2$ per molecule) is larger than the molecular Raman scattering cross-section ($10^{-29}$ cm$^2$ per molecule). The disadvantage of SEIRA is that the IR measurement is affected by the broad absorption peak of water. The plasmonic internal reflection technique has been proven to solve the detection issue in aqueous environments.\textsuperscript{[21]} Figure 1 shows the roadmap for the optimization and sensing application of SEIRA based on plasmonic metamaterials in recent 10 years. The fabrication process of metamaterial devices is critical for high-performance SEIRA applications. In 2012, Giessen et al. proposed a method using hole-mask colloidal nanolithography followed by tilted angle metal evaporation to fabricate large-area low-cost metamaterials (cm$^2$).\textsuperscript{[22]} Halas et al. fabricated gold cross antennas by electron beam lithography to observe the IR vibration of a self-assembled monolayer.\textsuperscript{[23]} In 2014, Neubrech et al. utilized laser interference lithography to fabricate large-area plasmonic antenna substrates for

### Nomenclature

| Abbreviation | Description                  |
|--------------|------------------------------|
| SEIRA        | Surface-enhanced infrared absorption |
| IR           | Infrared                     |
| SERS         | Surface-enhanced Raman scattering |
| TCM'T        | Temporal coupled mode theory  |
| MPA          | Metamaterial perfect absorber |
| AIN          | Aluminum nitride             |
| PDMS         | Polydimethylsiloxane         |
| ODT          | Octadecanethiol              |
| CO$_2$       | Carbon dioxide               |
| CH$_4$       | Methane                      |
| SiO$_2$      | Silicon oxide                |
| CaF$_2$      | Calcium fluoride             |
| Au           | Gold                         |
| AI           | Artificial intelligence      |
| GA           | Genetic algorithm            |
| PCA          | Principal component analysis |
| FOMs         | Figure-of-merits             |
| Q-factor     | Quality factor               |
| Ag           | Silver                       |
| Al           | Aluminum                     |
| TiN          | Titanium nitride            |
| Mo           | Molybdenum                   |
| W            | Tungsten                     |
| MgF$_2$      | Magnesium fluoride           |
| Al$_2$O$_3$  | Aluminum oxide               |
| Si           | Silicon                      |
| CeO$_2$      | Ceric dioxide                |
| Si$_3$N$_4$  | Silicon nitride             |
| ZnS          | Zinc sulphur                 |
| CMOS         | Complementary metal-oxide-semiconductor |
| GST          | Germanium antimony telluride |
| SVM          | Support vector machine       |
| DNN          | Deep neural network          |
| EF           | Enhancement factor           |
| LOD          | Limit of detection           |

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SEIRA application. Additionally, post-fabrication tuning of plasmonic resonances is reported to optimize the matching of molecular vibration and plasmon resonance. In 2015, Marini et al. fabricated a graphene-based tunable metamaterial device that was used for label-free identification of molecular vibration fingerprints. In recent years, various sensing applications based on SEIRA have emerged. In terms of physical sensors, Rinaldi et al. combined plasmonic metamaterial with a piezoelectric resonator for uncooled IR detection. In terms of chemical sensors, Halas et al. adapted a self-aligned technique to reproducibly fabricate antennas with a sub-3 nm gap and achieved the detection of 500 molecules of 4-nitrothiophenol. In terms of gas sensors, Lee et al. reported a guided resonance-based all-dielectric photonic crystal slab as SEIRA platform, which eliminate the dissipative loss and strong heating of metals and achieved ultrasensitive detection of carbon dioxide (CO$_2$). Later in 2019, the same research group (Lee et al.) designed a crooked nanoantenna based on loss engineering for ultrasensitive detection of CO$_2$. In 2020, Zhou et al. integrated metal-organic frameworks into a multi-resonant SEIRA platform for simultaneous on-chip sensing of greenhouse gases with ultralow concentrations. In terms of biosensors, Altug et al. demonstrated that deep learning empowers plasmonic metamaterial for monitoring dynamics between all major classes of biomolecules. In addition to these relative milestone research developments, there are also many other SEIRA breakthroughs in this decade.

As noted before, metamaterial-based SEIRA and its sensing applications have progressed rapidly in the past decade. Moreover, optimization of the signal enhancement to obtain high sensing performance is developing the main thread of SEIRA technology. The main purpose of this review is to present the methods of SEIRA optimization for high-performance and ultrasensitive sensing applications. First, we provide a basic understanding of SEIRA’s sensing mechanism and theoretical model. With this background, several SEIRA optimization methods are discussed, ranging from design, materials to algorithms. In the last section of this review, perspectives about the future development trends of SEIRA technologies are discussed.

2. Mechanism and model of metamaterial-based SEIRA

When infrared light is irradiated on the metamaterial, collective oscillations of electrons at a metallic surface occur, which are called plasmonic resonances. Such resonance is a mixed state of collective electronic excitations and photons localized at a metallic surface. Figure 2(a) shows the classic structure for IR plasmonic resonance, linear nanorods with micrometer lengths, and
The electromagnetic response in the infrared regime\cite{46} is highly confined around the tip of the nanoantenna. Besides, the resonance wavelength scales linearly with antenna length $L$ (Figure 2(b)).\cite{47} For a half-wave dipole antenna, the relationship between resonance wavelength and $L$ can be expressed as

$$\lambda = \frac{2L\text{na}_1}{m} + a_2$$ \hspace{1cm} (1)

where $m$ is a natural number, $n$ is the refractive index of the surrounding medium, and $a_{1,2}$ are coefficients that depend on the antenna’s geometry and material parameters. When analytes (octadecanethiol, ODT) were loaded onto the plasmonic metamaterial device and the polarization was set along the long antenna, an anti absorption peak near 3000 cm$^{-1}$ was observed in the spectrum (black curve, Figure 2(c)).\cite{14} However, when the polarization is set perpendicular to the antenna, no enhanced absorption was observed (red curve, Figure 2(c)). It proves that the ODT vibrational signal was enhanced by the nanoantenna. The enhanced vibrational strength can be extracted by a baseline correction (Figure 2(d)),\cite{48} namely dividing the spectrum of the antenna with analytes by the line shape of the bare plasmonic resonance. In the absence of analytes, the spectrum of nanoantenna is Lorentzian-type line-shape, which can be expressed as follows: \cite{49}

$$L(\omega) = \frac{\alpha}{(\omega - \omega_0)^2 + \alpha^2}$$ \hspace{1cm} (2)

where $\omega_0$ is the resonance frequency, and $\alpha$ is the resonance linewidth. When analyte molecules are loaded (Figure 2(e)),\cite{50} it becomes Fano-resonance with asymmetric line-shapes, which can be written as follows: \cite{51,52}

$$F(\omega) = A_0 + F_0 \left[ q + \frac{2(\omega - \omega_0)/\Gamma}{1 + \left[2(\omega - \omega_0)/\Gamma\right]^2} \right]$$ \hspace{1cm} (3)
where $A_0$ and $F_0$ are constant factors, $\Gamma$ is the resonance linewidth, and the Fano-parameter $q$ describes the asymmetry of the resonance. The asymmetry is the result of constructive and destructive interference between the plasmonic oscillation and molecular vibration. The plasmonic oscillation corresponds to the broad resonance of Fano-resonance, and the molecular vibration corresponds to its narrow resonance.

The coupling between the plasmonic oscillation and the molecular vibration can be described by two coupled harmonic oscillators (Figure 2(f)). Driven by incident IR light, the plasmonic resonance acts as a simple harmonic oscillation, which is called “bright mode.” On the contrary, because of the low molecular cross-section, the direct interaction between molecular vibration and far-field incident IR is small. Consequently, the molecular vibration is called “dark mode.” The dark mode is excited by coupling to the bright mode. It explains the phenomenon in Figure 2(c) that the molecular vibration is observed as a modulation in the plasmonic resonance, instead of directly appearing in the spectrum as an absorption feature.

Another mode to understand the resonant coupling is the temporal coupled-mode theory (TCMT). TCMT is an extension of the coupled harmonic oscillator model explained before. The mode consists of a single cavity coupled with inward and outward traveling waves (Figure 2(g)). The coupled-mode equations can be written as follows:

$$\frac{da}{dt} = j\omega_a a - (\gamma_{a0} + \gamma_{ae})a + \kappa_1 S_{1+} - jv b \quad (4)$$

$$\frac{db}{dt} = j\omega_b b - \gamma_{b0} b - jv a \quad (5)$$

$$S_{1-} = -S_{1+} + \kappa_1 a_2 \quad (6)$$

where $a$ and $b$ are the amplitudes of plasmonic resonance and molecular vibration, respectively. $\omega_a$ and $\omega_b$ are the center frequencies of resonance and vibration, respectively. $\gamma_{a0}$, $\gamma_{ae}$ and $\gamma_{b0}$ are intrinsic material losses, radiation losses, and molecule losses, respectively. $v$ represents the coupling constant between plasmonic resonance and molecular vibration. The aforementioned three equations describe the dynamic evolution of the resonance amplitude (Equation (4)) and the propagation of the traveling wave (Equation (6)) under the coupling of molecular vibration (Equation (5)). The coupling of molecular vibration can be understood as adding additional damping to the plasmonic resonance losses, thereby changing the ratio of external to internal damping rate. Different external to internal damping rates will result in different kinds of line shapes, including electromagnetic induced absorption and electromagnetically induced transparency.

The aforementioned two coupled harmonic oscillators and TCMT mode are mainly applicable for metallic plasmonic resonance. All-dielectric photonic crystals, which are periodic dielectric structures that either allow or forbid the propagation of electromagnetic waves of certain frequency ranges, can also be used as SEIRA devices. Such kinds of devices show a higher quality factor and weaker heating effect than metallic antennas. Instead of the collective oscillations of electrons in metallic antennas, the resonance of all-dielectric metamaterials (photonic crystals) is formed by the electric dipole modes of each individual meta-atom. The scattered field $E_{sc} = E - E_{inc}$ of all-dielectric metamaterials satisfies the Lippmann–Schwinger equation as follows:

$$E_{sc}(r) = -k^2 \int d\mathbf{r}' [\hat{e}(k, \mathbf{r}') - 1] \hat{G}_0(k, \mathbf{r}, \mathbf{r}') [E_{inc}(k, \mathbf{r}') + E_{sc}(\mathbf{r}')] \quad (7)$$

Where $k = \omega/c$, $E(\mathbf{r})$ is the total electric field, $E_{inc}(\mathbf{r})$ is a linear plane wave, $\mathbf{r}$ is the position vector, and $\hat{G}_0$ is the free space dyadic Green’s function (GF). After deriving Equation (7), the transmission $T$ can be expressed as follows:
\[ T(\omega) = \frac{T_0}{1 + q^2} \left( \frac{q + \Omega}{1 + \Omega^2} \right)^2 + T_{bg}(\omega) \]  

where \( q \) is the asymmetry parameter, \( \Omega \) is the dimensionless frequency, \( T_{bg} \) and \( T_0 \) describe the background contribution of nonresonant modes to the resonant peak amplitude and the offset, respectively. Clearly, it is a form of the classical Fano formula, indicating that the Fano-formalism mode is applicable for both plasmonic resonance and all-dielectric metamaterials.

Collectively, the Fano-formalism mode helps to understand and predict the asymmetric line-shape evolution of the SEIRA spectra using metallic antennas or all-dielectric metamaterials. Coupled harmonic oscillator mode is to visually illustrate the enhanced absorption process and the physical effects in the SEIRA system, such as electromagnetically induced transparency. TCMT reveals the influence of important parameters (including coupling constant and damping rate, etc.) on enhanced vibrational signals and IR spectrum line-shapes. These models provide effective guidance for the design and optimization of resonant metamaterials used for SEIRA. Nanostructure design strongly influences the outer optical response of plasmonic resonance, and material properties affect the inner absorption of nanoparticles and thereby the SEIRA. Additionally, machine learning algorithms can empower the SEIRA platform for multi-objective sensing applications. Therefore, we review several SEIRA optimization methods from the aspects of structural design, material choice, and machine learning algorithms in the following.

### 3. Performance optimization of SEIRA for ultrasensitive sensing

The purpose of SEIRA is to break through the limitation of the low infrared absorption cross-sections of molecules, enhance the vibration signal, and realize the ultrasensitive detection of minute amounts of analytes. Therefore, continuous improvement of the vibrational signal enhancement through SEIRA optimization is critical, which is also the developing main thread of SEIRA technology.\cite{50,63-66} Based on the existing literature researches, there are three main methods for SEIRA performance optimization, ranging from structural design, material choice, to combining machine learning algorithms.

To quantify the performance of SEIRA, a common figure-of-merits (FOMs) is needed. Enhancement factor (EF) is a commonly used FOMs in SEIRA, which relates the enhanced signal strengths to standard IR techniques. It is defined as follows:\cite{67}

\[ EF = \frac{I_{SEIRA}}{I_{REF}} \frac{N_{SEIRA}}{N_{REF}} = \frac{I_{SEIRA} N_{REF}}{I_{REF} N_{SEIRA}} \]  

where \( I_{SEIRA} \) is the enhanced signal strengths using SEIRA device, and \( I_{REF} \) is the unenhanced one using standard IR techniques. Besides, \( N_{SEIRA} \) and \( N_{REF} \) are the number of molecules in SEIRA or reference measurements, respectively.\cite{68} Limit of detection (LOD) is also an important benchmark parameter that describing the concentration/amount of the analyte corresponding to the lowest detectable signal for SEIRA-based sensors.\cite{69} Sensitivity can be defined as the response curve slope. Higher sensitivity means a larger output variable when the input is constant.\cite{29}

The absorption bandwidth is one of the important aspects that is calculated as the frequencies range with more than 90\% of the absorption maximum.\cite{70} SEIRA with both broad bandwidth and high absorption enhancement, which means that more molecular vibrations can be enhanced and detected, is ideal for sensing applications. However, it is challenging to keep high enhancement in the continuous broadband range due to the inherently narrow-band plasmonic resonances.\cite{71} One way to address this issue is to develop multiple resonant SEIRA that is individually tuned to match the characteristic vibrations of the different analytes of interest. On the other hand, SEIRA with a narrow band and high enhancement are also useful. Narrowband SEIRA with a gradually changing resonance frequency can be combined into an array for spectrometer-
less sensing application.\textsuperscript{[72]} Apart from EF, LOD, sensitivity, and bandwidth, there are also many other FOMs to characterize the performance, such as field intensity, spectral change, and quality factor (Q-factor) etc. The influence of SEIRA optimization on FOMs is discussed as follows.

3.1. Optimizing metamaterial structure design

The metamaterial pattern strongly influences the plasmonic resonance of the device and its spectral response.\textsuperscript{[73–77]} Therefore, it is an effective way to improve the EF of SEIRA by optimizing metamaterial structure design.\textsuperscript{[78,79]} Specifically, reducing the distance between the metamaterial pattern units can enhance the near-field intensity, which is attributed to the near-field interaction caused by the attractive electromagnetic force.\textsuperscript{[48]} In 2013, Aouani et al. fabricated a broadband log-periodic trapezoidal nanoantenna with a minimum gap of 20 nm between units by using the EBL method (\textit{Figure 3(a)}).\textsuperscript{[80]} It was demonstrated that the EF of SEIRA reached $0.9 \times 10^5$, and the detection of alkanethiol molecules with attomolar concentrations (<$1.2 \times 10^6$ molecules) was achieved. To further improve the EF of SEIRA, Oh et al. reported a zero-mode resonator-based SEIRA substrate composed of periodic coaxial apertures, and the minimum gap reached 7 nm by using stepper photolithography and atomic layer lithography (\textit{Figure 3(b)}).\textsuperscript{[81]} It was demonstrated that the EF of SEIRA was increased to $5 \times 10^5$ when the device was used to sense 5 nm thick silk protein film. In 2018, Gan et al. developed a SEIRA substrate with periodic strip grating structures by using atomic layer deposition processes (\textit{Figure 3(c)}).\textsuperscript{[82]} The minimum gap between adjacent gratings was 5 nm, and the EF for detecting 100 nm thick PMMA reached $8.5 \times 10^6$. Furthermore, Halas et al. proposed a self-aligned technique to fabricate bowtie-shaped nanoantennas with a minimum gap of 3 nm for ultrasensitive SEIRA application (\textit{Figure 3(d)}).\textsuperscript{[27]} It was described that the EF of SEIRA up to $10^7$ was achieved and 600 molecules of 4-NTP were successfully detected. In summary, the EF of SEIRA is enhanced by two orders of magnitude when the minimum gap is reduced from 20 to 3 nm.

Additionally, according to Babinet’s principle, nanoapertures in continuous metal films can also excite plasmonic resonance. Recently, studies have shown that nanoapertures have the ability to improve the EF of SEIRA. In 2015, Pucci et al. compared the performance of nanoslits and nanorods in SEIRA applications (\textit{Figure 3(e)}).\textsuperscript{[83]} They discovered that nanoslits obtained a larger sensing area than nanorods, which increases the EF of SEIRA by 3 times. However, the reflection of nanoslits decreases when compared with nanorods. Therefore, this optimization method is beneficial in the sensing application. The sensitivity, Q-factor, and EF of SEIRA devices can also be improved from the aspect of loss engineering of nanoantennas. In 2019, Lee et al. presented a crooked nanoantenna with a proper radiative loss for ultrasensitive gas sensing applications (\textit{Figure 3(f)}).\textsuperscript{[29]} It was demonstrated that the SEIRA enhancement factors of crooked nanoantennas were 25 times higher than that of straight nanoantennas. At the same time, Q-factor and EF were also improved, indicating the necessity of loss engineering in device design. In addition, Altug et al. reported an all-dielectric SEIRA substrate consisting of an anisotropic zigzag array with high Q-factor (\textit{Figure 3(g)}).\textsuperscript{[84]} The device was angle multiplexing and achieved the detection of a submonolayer analyte molecule in the spectrometer-less operation mode. In addition, all-dielectric SEIRA-based sensor shows a lower LOD due to its weaker heating effect than metallic antennas.\textsuperscript{[28,85]} Collectively, SEIRA performance improvement by optimizing structural design is effective, and it is still meaningful to further investigate the roles of metamaterial pattern in SEIRA performance.

3.2. Increasing near-field confinement and enhancement by constructing a perfect absorber

Strong plasmonic resonance is often accompanied by high near-field intensity and is essential for ultrasensitive SEIRA sensing applications. It can be increased by constructing a perfect
The first metamaterial perfect absorber (MPA) operating in the IR regime was demonstrated by Padilla et al. in 2010 (Figure 4(a)). MPA consists of metal metamaterial pattern, dielectric spacer, and metal ground plane. The nature of the metal-insulator-metal (MIM) resonance is the mirror dipole or quadrupole plasmonic resonance. Specifically, in a MIM dipole absorber, the electric field of the incident electromagnetic field induces electric dipoles inside the metal pattern layer, while the magnetic field generates a magnetic dipole between the pattern and the ground metal layers. The electromagnetic response of the MIM absorber can be engineered by changing the pattern geometry and the thickness of the dielectric layer. When its effective impedance matches that of free space, resonance occurs and its reflection is close to zero. Specifically, the resonant frequency, spectral linearity, and SEIRA enhancement factor can be adjusted by the thickness of the dielectric layer. In some cases, the plasmonic system in undercoupled and overcoupled can obtain higher molecular vibration enhancement. After the
IR MPA’s first emergence, Giessen et al. developed a disk-shaped narrow-band MPA with 99% absorbance for refractive index sensing (Figure 4(b)).\[92\] In 2015, Halas et al. reported a fan-shaped MPA for SEIRA detection with an enhancement factor of 10^5 (Figure 4(c)).\[93\] Compared with antennas on zinc selenide substrate,\[23\] the fan-shaped MPA had higher spatial near-field confinement. As a result, the SEIRA enhancement factor of fan-shaped MPA was 6.26 times higher than that of the fan-shaped metamaterial without a metal reflective plane. In summary, the optimization method of constructing a perfect absorber can excite larger near-field intensity, EF, and Q-factor when compared with nanoantenna without metal reflection layer.

Subsequent studies have shown that MPA has great potential in SEIRA sensing applications due to its high near-field strength. In 2016, Hui et al. combined acoustic aluminum nitride (AlN) piezoelectric acoustic wave resonator with MPA for uncooled narrowband IR detection (Figure 4(d)).\[26\] In this infrared detector, the impinging IR radiation was confined in the MPA and then changed the resonant frequency of the acoustic wave resonator. MPA is also used as a biosensor for the quantification and identification of protein, as demonstrated by Li et al. in 2019 (Figure 4(e)).\[94\] Especially, when monolayer graphene was put under the metallic antennas to tune the plasmonic resonance to match protein vibration, the sensitivity was improved. Its sensitivity was

![Image of Figure 4, Optimization of SEIRA performance by constructing a perfect absorber.](image-url)
orders of magnitude higher than that of the traditional IR spectroscopy method. In 2019, Dao et al. developed a dual-band MPA for the in situ monitoring of reaction kinetics during the poly-dimethylsiloxane (PDMS) gelation process (Figure 4(f)). As shown in the curves, the SEIRA absorption intensity of C-H and Si-CH$_3$ vibrations increased with the PDMS curing time, where C-H and Si-CH$_3$ are chemical bonds. R$_1$/R$_0$ represents the relative changes in SEIRA spectra, where R$_0$ is the initial spectrum when PDMS is loaded, and R$_1$ is the spectrum when PDMS is cured for some time. Additionally, when integrated with gas-selective-trapping polymer, MPA could be used to detect ppm level CO$_2$ gas, as demonstrated by Lee et al. in 2018 (Figure 4(g)). This MPA-based method had the advantages of low detection limit, small footprint, fast response time, and low hysteresis. Furthermore, integrating metal-organic frameworks into a multi resonant MPA enabled simultaneous on-chip sensing of greenhouse gases with ultralow concentrations (such as methane (CH$_4$) and CO$_2$), as demonstrated by Zhou et al. in 2020 (Figure 4(h)). Collectively, SEIRA performance improvement by constructing an MPA is effective, and there are many other important MPA-based applications apart from the aforementioned researches.

### 3.3. Improving the spatial overlap between analytes and enhanced near-field

Apart from near-field enhancement, the spatial overlap between the analyte and the enhanced near-field is also a significant factor for ultrasensitive SEIRA sensing applications. Better spatial overlap means more analytes are located in the enhanced near-field, resulting in higher SEIRA performance, including EF, LOD, and sensitivity. For absorptive MPA, the enhanced electromagnetic field is mainly concentrated in the dielectric spacer. Spatial overlap between the electromagnetic fields and the analytes is limited (upper panel, Figure 5(a)). One strategy to overcome this issue is to integrate the microfluidic channel with the dielectric spacer of MPA, where the channel functions as both the microfluidic channel and the spacer, as demonstrated by Chen et al. in 2016. In this configuration, the analytes in the microfluidic channel had an excellent spatial overlap with the enhanced electromagnetic field (lower panel, Figure 5(a)). For transmissive plasmonic nanostructures, one way to improve the poor spatial overlap is to add a dielectric nanopedestal between the metal pattern and the substrate, as demonstrated by Altug et al. in 2014 (Figure 5(b)). In this configuration, the full mode volume of the hot spots is available for biodetection, and the field enhancement was improved by more than 2.6 times. In short, the optimization method of improving the spatial overlap can improve the near-field coupling while keeping the field intensity constant. As a result, the FOMs including EF, LOD, and sensitivity are all improved, which is instructive for ultra-sensitive SEIRA sensing applications.

Due to its effectiveness in enhancing SEIRA performance, these strategies had been adopted in many sensing applications. In 2017, Tanaka et al. integrated a microfluidic channel with the dielectric spacer by a room-temperature bonding of silicon oxide (SiO$_2$) and calcium fluoride (CaF$_2$) (Figure 5(c)). This plasmonics-nanofluidics coupled system enabled the ultrasensitive detection of biochemical molecular in solution. In 2020, Lee et al. developed a similar nanofluidics platform by using a low-temperature interfacial heterogeneous sapphire wafer direct bonding technique (Figure 5(d)). It had advantages for in-situ dynamic monitoring of chemical molecular diffusion in solution. In addition, the excellent spatial overlap and ultra-high sensitivity also allowed this method to distinguish the subtle differences in the molecular structures, as demonstrated by Tanaka et al. in 2018 (Figure 5(e)). They utilized this platform to investigate the scaling behavior of confined molecules in the size range of tens of nanometers. In 2019, the same research group developed a plasmonics-nanofluidics platform with a vertical orientation structure that did not require a bonding process (Figure 5(f)). Since it allowed molecules to enter the hotspot concentration area, the platform had an excellent spatial overlap and achieved the butane detection of a 20 ppm concentration. Collectively, SEIRA performance enhancement
by improving the spatial overlap is effective, but the complexity and cost of the fabrication process will increase accordingly.

3.4. Choosing proper plasmonic and dielectric material

The material choice of the plasmonic device has a strong influence on the SEIRA performance. Specifically, the absorption cross-sections depend on the material properties, and the scattering cross-sections of the antenna geometry. Therefore, it is necessary to choose proper plasmonic and dielectric material for the performance optimization of SEIRA. Common plasmonic materials include gold (Au), silver (Ag), aluminum (Al), titanium nitride (TiN), molybdenum (Mo), graphene, and tungsten (W). Common dielectric materials include magnesium fluoride (MgF$_2$), CaF$_2$, aluminum oxide (Al$_2$O$_3$), silicon (Si), SiO$_2$, ceric dioxide (CeO$_2$), silicon nitride (Si$_3$N$_4$), AlN, and zinc.
sulphur (ZnS). Generally, Ag, Al, MgF₂, and Al₂O₃ are widely used as plasmonic and dielectric materials. However, choosing different plasmonic and dielectric materials make the SEIRA device feature different advantages. For instance, when Al was used as the plasmonic material, a thin self-passivating oxide layer was formed on the surface (Figure 6(a)). The oxide layer not only protected the metal pattern structure but also simplified the various chemical connections of multiple functional groups on the plasmonic structure. According to Figure 6(b), choosing TiN as dielectric materials, which have high-temperature durability and large intrinsic loss over a broad range, can broaden working bandwidth and achieve broadband plasmonic absorption enhancement. W and Si₃N₄ are a good choice for SEIRA devices when it comes to adopting a full complementary metal-oxide-semiconductor (CMOS)-compatible process (Figure 6(c)), which
is necessary for reducing fabrication costs and extending the industrial application range. When Al and CeO$_2$ were used as plasmonic and dielectric materials, a large-area (m$^2$) plasmonic structure could be mass-produced in a short time using a photomask and wet etching technologies (Figure 6(d)).$^{[140]}$

Graphene is a plasmonic material whose Fermi level can be modified by applying an electrostatic field.$^{[25]}$ Therefore, it is often used for post-fabrication tuning of plasmonic resonances, thereby matching the resonance with analyte vibration for high-performance SEIRA. For instance, Manjavacas et al. developed a graphene nanodisk array and utilized the tunability of graphene for ultrasensitive pixel SEIRA sensing (Figure 6(e)).$^{[144]}$ By tuning the plasmonic resonance of each pixel in the array, both the vibrational spectrum of molecules and their spatial location were detected. Additionally, post-fabrication tuning can also be realized by using phase change material as the dielectric material of SEIRA. In 2015, Tittl et al. prepared a germanium antimony telluride (GST) phase-change material and used it as the dielectric material (Figure 6(f)).$^{[145]}$ When the GST-based device was heated above the crystallization temperature, a significant redshift occurred due to the phase change of GST between amorphous and crystalline, thereby achieving a maximum overlap between the resonance and the vibration. Apart from the properties of the materials themselves, the thermal expansion coefficient is also an important factor to consider when choosing proper plasmonic and dielectric materials. In 2017, Lee et al. investigated this issue by comparing the thermal stress and pattern morphology of Mo-AlN and Mo-SiO$_2$. After high-temperature annealing, significant reflow of the thin oxide layer was observed in the Mo-SiO$_2$-based device (Figure 6(g)),$^{[131]}$ whereas no such damage was observed in the Mo-AlN-based device, which is attributed to the better thermal expansion coefficient matching of Mo-AlN. Compared with common hard materials, nanoantennas on flexible substrates such as Kapton film enabled a high absorptivity of $>90\%$ over a wide angular range, as shown in Figure 6(h).$^{[146]}$ The flexibility of this sensor was friendly to wearable devices, which makes it potential for applications in the field of human-machine interaction. It is demonstrated that polyethylene terephthalate and PMDS are also a good flexible substrate material.$^{[147,148]}$ Collectively, the material choice should be considered comprehensively according to the application requirements of SEIRA and the properties of the materials themselves.

3.5. Combining machine learning algorithm

Artificial Intelligence (AI) is a powerful driving force to promote a new revolution in science and technology.$^{[149–154]}$ Machine learning enhanced sensing is an important branch of AI and greatly improves the ability of sensors to obtain information.$^{[155–159]}$ Machine learning algorithms can also simplify the complex design and increase the types of detection targets. A genetic algorithm (GA) is a machine learning algorithm based on the concepts of evolution and natural selection. The GA was demonstrated to simplify the complex design of metamaterial structures and to achieve the rapid automatic design by Mosallaei et al. in 2018.$^{[160]}$ By means of adaptive optimization, digitized-binary elements constituted a binary pattern metamaterial, and its spectral response is close to the design goal (Figure 7(a)). In 2019, Gao et al. proposed a micro-genetic algorithm for the performance optimization of plasmonic metamaterial (Figure 7(b)).$^{[161]}$ The micro-GA replaced the mutation step in traditional GA with the repopulation step, which achieved faster convergence with a smaller initial population group. Additionally, Padilla et al. utilized a deep neural network algorithm for the design of all-dielectric metamaterial.$^{[162]}$ It is demonstrated that the method they proposed, called termed fast forward dictionary search, significantly increase the viability in the complex design of all-dielectric metamaterial devices (Figure 7(c)).

Apart from realizing the rapid automatic design, the machine learning algorithm can also increase the types of detection targets. For instance, a principal component analysis (PCA)
algorithm was used to extract and classify vibrational data of different analyte molecular. According to the PCA clusters of different analytes, glucose and fructose were successfully identified from their mixed aqueous solutions (Figure 7(d)). A further combination between SEIRA and algorithms for the identification of more analytes was demonstrated by Crozier et al. in
In this work, support vector machine (SVM) classifiers were adopted to directly analyze the spectra and determine the chemical species. It is described that five analytes were successfully distinguished after the training of ML classifiers, and the minimum concentration was 10 ppm (Figure 7(e)). In terms of biosensing, Altug et al. achieved the label-free, ultrasensitive, and real-time monitoring of four major classes of biomolecules by using a deep neural network (DNN)-enhanced infrared plasmonic biosensor (Figure 7(f)). Collectively, machine learning enhanced sensing simply the complex design as well as increase the types of targets that the SEIRA-based sensor simultaneously detect.

4. Summary and outlook

The past few decades have witnessed the rapid development of metamaterial-based SEIRA technology from a fundamental effect to various practical applications. Since the first SEIRA demonstration, a series of theories have been developed to give intuitive physical insights into SEIRA spectroscopy, such as Fano-resonance theory, coupled harmonic oscillators, and TCMT. Meantime, nanofabrication technology is also constantly developed to be advanced, highly accurate, and low-cost. On the basis of this theoretical knowledge and advanced nanofabrication methods, various SEIRA-based sensing applications, including physical sensors, chemical sensors, and biosensors, have been continuously emerging. To further improve the sensing performance, many efforts have been invested in the optimization of SEIRA performance, ranging from structural design, material choice, to combining machine learning algorithms. Thanks to these efforts, SEIRA-based sensors have been greatly improved in terms of sensing methods, sensing performance (sensitivity, detection limit etc.), and the amount and species of analytes. However, there are still some challenges for the development and sensing applications of SEIRA: (i) low-cost and large-area fabrication. It is desired for SEIRA to overcome this issue and develop towards practical industrial applications; (ii) continuously optimizing SEIRA enhancement and further improving the sensing performance by developing new and effective approaches; (iii) combining brilliant light source, sensitive detector, and SEIRA technology to further improving the detection limit; (iv) further developing ultra-broadband and ultra-narrowband SEIRA with high absorption enhancement; (v) in-situ and ultrasensitive detection of trace amount of analytes, for instance, detecting trace amount of gases and protein in their native liquid environment; (vi) developing more efficient algorithms suitable for SEIRA sensing applications. By overcoming these issues, the metamaterial-based SEIRA would have potential opportunities to be an alternative to some traditional sensing technologies and empower sensing applications in the fields of medical detection, environmental monitoring, and the Internet of Things.

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