Midinfrared Spectroscopic Analysis of Aqueous Mixtures Using Artificial-Intelligence-Enhanced Metamaterial Waveguide Sensing Platform

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ABSTRACT: As miniaturized solutions, mid-infrared (MIR) waveguide sensors are promising for label-free compositional detection of mixtures leveraging plentiful absorption fingerprints. However, the quantitative analysis of liquid mixtures is still challenging using MIR waveguide sensors, as the absorption spectrum overlaps for multiple organic components accompanied by strong water absorption background. Here, we present an artificial-intelligence-enhanced metamaterial waveguide sensing platform (AIMWSP) for aqueous mixture analysis in the MIR. With the sensitivity-improved metamaterial waveguide and assistance of machine learning, the MIR absorption spectra of a ternary mixture in water can be successfully distinguished and decomposed to single-component spectra for predicting concentration. A classification accuracy of 98.88% for 64 mixing ratios and 92.86% for four concentrations below the limit of detection (972 ppm, based on 3σ) with steps of 300 ppm are realized. Besides, the mixture concentration prediction with root-mean-squared error varying from 0.107 vol % to 1.436 vol % is also achieved. Our work indicates the potential of further extending this sensing platform to MIR spectrometer-on-chip aiming for the data analytics of multiple organic components in aqueous environments.

KEYWORDS: mid-infrared spectroscopy, waveguide sensors, artificial intelligence, metamaterial, mixture analysis

Building upon artificial intelligence (AI) and the Internet of Things (IoT), industry 4.0 is a revolutionized concept for upgrading and transforming manufacturing technologies to realize intelligent factories in the future. Meanwhile, wastewater monitoring, as one crucial aspect in industry 4.0, and the demand for various types of miniaturized sensors, such as chem/biosensors for in situ and real-time monitoring of wastewater quality, are ever-increasing. Over the years, chem/biosensors have grown rapidly along with the variety of sensing mechanisms being developed, such as electrochemistry sensors, mechanical sensors, and optical sensors. Among these, nanophotonic waveguides provide a cost-effective solution for miniaturized sensor applications due to the high compactness and versatility from the increasing levels of integration, which also benefits other photonic devices, such as the nanophotonic waveguide-based spectrometer.

Relying on the mature technical platform of near-infrared (NIR) spectroscopy, the NIR waveguide sensor has become the mainstream direction in the development of on-chip optical sensing applications. Most of the NIR waveguide sensors utilize the change of refractive index (RI) induced by the appearance of the analyte for sensing analysis, as the change of RI will cause the shift of the resonant (or interference) peak in the waveguide sensor, as shown in Figure 1a. The end point measurement of peak shift from the NIR waveguide sensor enables high-sensitivity chem/biosensing, however, the ability of specific detection for the NIR waveguide sensor without using specific receptors is still lacking. Recently, the nanoantenna operating in the mid-
Figure 1. Overview of the AIMWSP. (a−c) Comparison of (a) NIR and (b) MIR waveguide sensor work mechanisms with (c) our AIMWSP. Based on the absorbance change in the spectrum containing richer information, the AIMWSP uses machine learning for complex mixture sensing analysis (MRR: microring resonator, MZI: Mach–Zehnder interferometer). (d, e) Schematic illustration of AIMWSP. (d) The mid-IR absorption spectrum of the aqueous mixture collected by the MWS is processed by (e) machine learning for two sensing functions: the CNN is for recognizing concentration combinations, while the MLP regressor is used for mixture spectrum decomposition.
infrared (MIR) region for on-chip chem/biosensing has attracted much research interest.\textsuperscript{30–34} Thanks to the numerous spectroscopic fingerprints of molecules in the MIR\textsuperscript{35–38} together with sensitivity enhancement from the nanoantenna such as surface-enhanced infrared absorption, the existence of different analytes will be directly reflected in the significant intensity change at the particular wavelength in the spectrum (Figure 1b), enabling label-free and nondestructive sensing\textsuperscript{39} and fluid\textsuperscript{40} or gas monitoring.\textsuperscript{41,42} Despite this superiority, the scheme for a fully integrated nanoantenna sensing system implemented on a single chip is still absent. In contrast, the previous successful demonstrations of MIR waveguide sensors for trace gas\textsuperscript{43–45} or liquid\textsuperscript{46,47} detection and the integrated MIR laser or photodetector on a waveguide\textsuperscript{48–52} allow the waveguide platform to become the most promising candidate for achieving the on-chip integrated sensing system\textsuperscript{53} in the future.

As a common sensing scenario, mixture analysis is of great importance in various sensing applications. Although the MIR waveguide sensor can leverage the specific fingerprints of diverse molecules for analyte recognition, the quantitative analysis of complex liquid mixture components in the MIR remains challenging, as the superposition of absorption from multiple substances may affect the absorbance at the absorption peak of interest (Figure 1b), not to mention the strong water absorption background. Even though a MIR lab-on-a-chip\textsuperscript{54} is demonstrated for monitoring bovine serum albumin in heavy water (D\textsubscript{2}O) instead of in water (H\textsubscript{2}O) to evade the intrinsic strong water absorption, the water environment is still the most common and crucial sensing background that cannot be avoided and needs to be investigated. In recent years, metamaterials as a useful tool in designing various photonic devices with improved efficiency, including the tunable actuators\textsuperscript{55,56} metalenses,\textsuperscript{57} and meta-waveguides,\textsuperscript{58} have also been applied to the waveguide gas sensor\textsuperscript{59,60} due to the flexibility in controlling mode profile and effective RI for tuning sensitivity.\textsuperscript{61} With the proper design of the metamaterial-based waveguide sensor, it is possible to promote sensitivity in limited space for fulfilling the miniaturized requirement while avoiding excessive attenuation from water. Besides, for the analysis methods used in quantification of liquid mixtures, one strategy is to simultaneously use the change of both the real and imaginary parts of complex refractive index originating from the introduction of a mixture (ethanol and toluene in cyclohexane),\textsuperscript{62} and the other approach is by virtue of the profile of the spectrum (e.g., number of absorption peaks) to differentiate analytes and determine the component concentration (ethanol in ethanol/acetonitrile compounds) by calculating the intensity ratio at two wavelengths.\textsuperscript{63} Nevertheless, these liquid mixture sensing demonstrations based on MIR waveguide sensors primarily use a simple mixture like the binary compound without using water as solvent and only focus on one or two specific wavelength points for concentration quantification. Therefore, it is desired to develop a waveguide sensing platform that takes full advantage of the spectrum information for analyzing more complicated mixtures, especially in water environments.

In the past few years, the thriving of machine learning\textsuperscript{64} has offered great potential for many research fields ranging from data science\textsuperscript{65,66} to engineering applications.\textsuperscript{67–69} Multifarious types of the classic algorithm, such as principal component analysis\textsuperscript{70} (PCA) and support vector machines (SVM),\textsuperscript{71} have been adopted in several optical sensors for multicomponent analysis.\textsuperscript{72–75} For example, the combination of an infrared nanoantenna and PCA was reported for the classification of a glucose/fructose solution in different concentrations.\textsuperscript{72} However, although mixtures in arbitrary mixing ratios can be identified using this PCA-based nanoantenna with the mixture spectrum as input, the individual spectrum response of each component with respective concentrations is still missing. Furthermore, the available wavelength range in the MIR waveguide sensor is relatively narrower as compared with the nanoantenna, and how to efficiently leverage the mixture spectrum in a limited range is still one of the obstacles to achieving accurate mixture analysis in waveguide sensors. Fortunately, the multilayer perceptron (MLP) creates the opportunity to solve these two problems. Recently, Li et al. demonstrated an MLP regressor-enabled NIR ring sensor\textsuperscript{76} for decomposing the resonant spectrum that records the resonant peak shift over time. Compared with the resonant spectrum, the absorption spectrum contains more distinctive information about the molecule and is the main characteristic leveraged in the MIR region. By executing the MLP regressor in a MIR waveguide sensor to perform mixture spectrum decomposition, it is possible to not only uncover the absorption spectrum of pure components buried in the mixture spectra in a limited wavelength range but also determine the individual component concentrations by fully leveraging the absorption spectrum of pure components in the targeted spectral region.

In this paper, we present an AI-enhanced metamaterial waveguide sensing platform (AIMWSP) for aqueous mixture analysis in the MIR (Figure 1c). By careful design of the waveguide geometry on the silicon-on-insulator (SOI) platform, the subwavelength grating (SWG)\textsuperscript{77,78} metamaterial is utilized to increase the waveguide sensor sensitivity in a small footprint. A polydimethylsiloxane (PDMS) chamber is bonded on the chip surface to form the microfluidic channel and confine the sensing length within only 2 mm. Two sensing functions, spectral recognition and decomposition of a ternary mixture consisting of acetone, isopropyl alcohol (IPA), and glycerin in the water solution, are realized by AIMWSP: First, the convolution neural network (CNN) is employed to recognize the absorption spectra of mixtures with 64 predefined mixing ratios, and a classification accuracy of 98.88% is achieved. Additionally, spectra of four glycerin solutions with concentrations (e.g., 300 ppm) below the limit of detection (LoD, 972 ppm) are discriminated with an accuracy of 92.86%. Going one step further, we executed the MLP regressor on the 64 mixture spectra for spectrum decomposition and concentration prediction. The mixture concentration prediction based on the precise decomposed spectrum of each component, namely, decomposed pure forms, also brings about accurate prediction results, with 62% of the prediction values within 0.5 vol % root-mean-squared error (RMSE) and more than 81% of prediction values within 1 vol % RMSE. Overall, the proposed AIMWSP provides a feasible and efficient solution for mixture recognition as well as quantification in the waveguide sensing technique and indicates the potential of incorporating the miniaturized optical sensors and machine learning for the realization of MIR spectrometer-on-a-chip\textsuperscript{79} (MIRSOC) in the IoT sensing system.

RESULTS AND DISCUSSION

Operation Mechanisms and Design Principle of the AIMWSP. The working principle of the AIMWSP for aqueous
mixture spectrum analysis is illustrated in Figure 1d,e. The metamaterial waveguide sensor (MWS) covered by the PDMS chamber is immersed in the liquid mixture. Two stainless steel 90° bent tubes are inserted into the PDMS chamber as the inlet and outlet of the liquid. The input MIR light coupled by the grating coupler propagates in the waveguide and interacts with the analyte. By sweeping the input wavelength, the MIR output spectrum, which contains the spectral information on the mixture, can be acquired from the output grating coupler. After the sensing data collection, the CNN and MLP regressor are introduced for the following mixture analysis. CNN aims to achieve the recognition of a mixture under different mixing ratios and then determine the concentration of each component in the mixture, while the MLP regressor is applied to decompose the mixture spectrum into the component spectra (pure forms) for further quantification of component concentration.

Figure 2. Design of SWG metamaterial. (a) The false colored SEM image of the SWG metamaterial (yellow: Si pillars, pink: SiO$_2$ substrate). (b, c) Simulated (b) effective index and (c) propagation loss with respect to the period ($\Lambda$) and duty cycle of MWS. The waveguide width ($W$) is kept at 1.5 $\mu$m. (d–f) The distribution of electric field magnitude in (d) the X–Y cross-section, (e) Y–Z cross-section in the gap region and (f) Y–Z cross-section in the Si pillar region. The period and duty cycle of the SWG metamaterial in the simulation are set as 0.8 $\mu$m and 0.8, respectively.

To reach the target of higher sensitivity in the small footprint and avoid adopting the complicated fabrication process, the SWG metamaterial structure, which provides a direct method for engineering the effective index of waveguide and mode profile, is utilized in the waveguide sensor. There are two main parameters for the geometry design of the SWG metamaterial: period ($\Lambda$) and duty cycle (DC), which is the ratio of the length of the Si pillar $L$ to $\Lambda$, as shown in Figure 2a. In order to prevent Bragg reflection, $\Lambda$ is designed to be smaller than the Bragg period. We designed $\Lambda \leq 800$ nm to ensure the device works in the subwavelength regime. At the same time, the effective index of the propagation mode needs to be at least higher than the index of the SiO$_2$ substrate. Otherwise, the optical mode will leak to the MIR-absorptive SiO$_2$ substrate. The three-dimensional (3D) finite difference time domain (FDTD) simulation is conducted at 3.77 $\mu$m (where the absorption peak of IPA is located) to investigate the relationship between the effective index $n_{eff}$ and propagation loss versus the parameters of the SWG metamaterial ($\Lambda$ and DC), as shown in Figure 2b,c, respectively. With a gradual increase of the effective index $n_{eff}$ resulting from the increment of larger $\Lambda$ and DC (greater than the $n_{SiO2}$), the value of propagation loss starts to decrease accordingly, because the leakage loss$^{61}$ from the absorption of SiO$_2$ is reduced as the mode is more confined in Si.

Another parameter required to consider for the SWG metamaterial is the external confinement factor $\Gamma$, which measures the degree of light–matter interactions and plays a role in Beer–Lambert’s law:

$$ T = \frac{I_{\text{analyte}}}{I_{\text{ref}}} = \exp(-\alpha \Gamma L C) \tag{1} $$

where $T$ is the transmittance, $I_{\text{analyte}}$ is the intensity of optical signal under the presence of analyte, $I_{\text{ref}}$ is the intensity of the reference signal, $\alpha$ is the absorption coefficient of the analyte, $L$ is the physical waveguide length used for sensing, and $C$ is the concentration of the analyte. Reflecting on eq 1, a larger $\Gamma$ will induce higher sensitivity of the sensor. Detailed information on external confinement factor simulation and the relationship of the external confinement factor $\Gamma$ with respect to the $\Lambda$ and DC is provided in Note S1 in the Supporting Information. Compared with the conventional strip waveguide in the same width and thickness ($\Gamma_{\text{strip}} = 8.75\%$), the metamaterial waveguide offers greater $\Gamma$ within the designed range. Considering the lithography accuracy, fabrication tolerance, and propagation loss, we choose the SWG metamaterial structure with $\Lambda = 0.8 \mu$m and DC = 0.8 for device fabrication. The electric field magnitude distribution of the selected SWG metamaterial structure is simulated to reveal the origin of the sensitivity improvement, as displayed in Figure 2d–f and Figure 1d. Modifying $\Lambda$ and DC in the FDTD simulation can induce the confinement of the electric field in the Si pillar region (Figure 2f), which further increases the effective index $n_{eff}$ and reduces the propagation loss. As shown in Figure 2b, the effective index $n_{eff}$ increases as $\Lambda$ increases due to the increased external confinement factor, which is calculated by the ratio of the magnetic field intensity in the gap to the waveguide as shown in Figure 2f. The distribution of electric field magnitude in the X–Y cross-section of the selected SWG metamaterial is investigated, which contains the spectral information on the mixture, and is further decomposed into the component spectra (pure forms) for further quantification of component concentration.
A strong electric field appears in the air gap region between the Si pillars, which is beneficial for the enhanced light-matter interaction, resulting in the improved sensitivity of the sensor. In the fabrication step, a total length of 660 μm of SWG metamaterials with two 40-μm-long mode converters are inserted into the strip waveguide considering the trade-off between the higher sensitivity and the increased propagation loss from water absorption. The PDMS chamber casting by a 3D-printing mold is bonded on the chip surface to form the microfluidic channel and provide the sensing area covering only 2 mm total waveguide length, including 660 μm SWG metamaterial.

**Binary Solution Real-Time Monitoring and Mixture Spectrum Collection.** Before the mixture sensing, the dynamics monitoring of different solutes in water is carried out to characterize the MWS. Acetone, IPA, and glycerin were chosen as the measurand and also the constituents of the mixture in the following sensing demonstration. The real-time monitoring of the MWS for acetone, IPA, and glycerin solution under different concentrations is displayed in Figure 3a−c, respectively. The time trace reveals the optical transmission change caused by the change of concentration in the case of all three analytes. The small spikes that emerge in the monitoring process are incurred by the air introduced when switching solutions. According to the real-time monitoring results, the absorbance difference between pure water and binary solution (i.e., \( \Delta \text{Absorbance} = -(\alpha_{\text{analyte}} - \alpha_{\text{water}}) FL_{\text{analyte}} \times \log_{10} \frac{I_{\text{analyte}}}{I_{\text{water}}} \)) versus the analyte concentration change is

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**Figure 3.** Real-time measurement of different binary solutions. (a−c) The dynamic monitoring of (a) acetone, (b) IPA, and (c) glycerin dissolved in water under different concentrations. (d−f) The absorbance difference between water and (d) acetone solution, (e) IPA solution, and (f) glycerin solution with respect to the analyte concentration. The sensitivity of the MWS to acetone, IPA, and glycerin is −0.0285/vol %, 0.0146/vol %, and 0.0543/vol %, respectively. (g) The comparison between strip waveguide and metamaterial waveguide on sensitivity (analyte:acetone). By replacing the 660 μm strip waveguide structure with the SWG metamaterial structure in a 2 mm strip waveguide, the sensitivity increased by 1.76 times. (h) Schematic of liquid sensing testing setup, comprising optical characterization and liquid flow control modules.
All $R^2$ values are larger than 0.99 for the linear fitting of three analytes, exhibiting the good linear response of the MWS. The sensitivity of the MWS is extracted from the slope of linear curves to be $-0.0285$, $0.0146$, and $0.0543$ per vol % for acetone, IPA, and glycerin, respectively. The negative sensitivity from the curve of acetone represents the lower absorbance of acetone compared with water. Besides, we also fabricated a strip waveguide sensor without SWG metamaterial configuration as the control group in the same chip and performed the acetone real-time monitoring in the same manner as the previous experiment. As shown in Figure 3g, with equal sensing length (2 mm), the substitution of only a 660 $\mu$m strip waveguide by the SWG metamaterial brings about enhanced sensitivity by 1.76 times, which corresponds to the external confinement factor of the SWG metamaterial, $\Gamma_{SWG}=32.52\%$. The deviation of $\Gamma_{SWG}$ between the simulation and the real device is possibly coming from the incomplete etching between the Si pillars (Note S3). In spite of this, the fabricated MWS still significantly outperforms the conventional strip waveguide sensor in sensitivity without using more complex fabrication methods and provides a feasible and simple way to attain higher sensitivity in compact footprints.

Figure 4. Convolution neural network (CNN) for mixture recognition and identification of trace liquid. (a) The visualization of a portion of mixture spectra in the training data set. The training data set consisted of 64 concentration combinations with each having 14 spectra. (b) The detailed structure of the CNN training model. (c) Comparison table for labeling mixtures under different mixing ratios (e.g., label 42 corresponding to 10 10 2, represents an aqueous solution containing 10 vol % acetone, 10 vol % IPA, and 2 vol % glycerin). (d) The bar charts of testing accuracy in identifying 64 mixtures. The classification accuracy is 98.88%. (e) The dynamic monitoring of the liquid switching process from water to 300, 600, and 900 ppm glycerin solution at 3.77 $\mu$m. (f) The normalized spectra of water and 300, 600, and 900 ppm glycerin solution in the test data set. Each class has seven test spectra. (g) The confusion map of recognizing four trace glycerin concentrations, showing a high accuracy of 92.86%.
Next, the data set of the mixture is prepared for the following liquid mixture analysis. With four concentrations given by each solute (acetone and IPA: 0:5:15 vol %, glycerin: 0:2:6 vol %), ternary mixtures with 64 mixing ratios in water solution can be obtained by mixing them with each other. In the data set collection process, which uses the testing setup shown in Figure 3h, the mixtures in different concentration combinations were sent into the sensor one by one, while water acted as the buffer and was sent into the sensor at every time interval between the injection of different mixtures. Instead of recording the intensity at a single wavelength point, which carries limited information on substance, the absorption spectrum of each mixture solution, including the buffer solution infused at every time interval, was collected by sweeping the output wavelength of the laser after the output signal from the sensor was stable. All spectra were collected with wavelengths ranging from 3.708 to 3.803 μm with a step of 1 nm. Besides, in order to eliminate various unknown and unstable factors in the dynamic measurement process as much as possible, such as mechanical vibration or drift of alignment stages or environmental perturbation that may cause variation of the sensing signal, all mixture spectra were normalized with the nearest buffer solution spectrum, which is the water spectrum recorded from the nearest interval. After that, 64 classes corresponding to 64 mixing ratios of the mixture spectra were acquired.

Convolution Neural Network for Recognition of Mixture Absorption Spectrum. Without loss of generality, 12 normalized spectra from the 64 classes of mixture spectra are plotted in Figure 4a. Although there are differences...
between various spectra, some spectra are still less distinguishable. The situation is even worse in the figure showing all 64 spectra (Figure S4). Furthermore, as the components with absorbance higher (acetone) and lower than water (IPA, glycerin) simultaneously exist in the mixture, the potential cancellation effects in absorption increase the difficulty of spectrum distinction. In recent years, machine learning has shown impressive capabilities in tasks of feature extraction and object identification. Taking into account that CNN excels at classification problems, we first introduce CNN to differentiate and classify 64 types of mixture spectra. For each mixture class, we collected 21 almost consistent spectra, and a total of \(64 \times 21\) mixture spectra were prepared for building the data set, which will feed into the neural network in the subsequent training and testing process. A one-dimensional CNN (1D-CNN) structure is leveraged to perform the mixture classification, and the detailed structure of the 1D-CNN is sketched in Figure 4b. For data division of each mixture, we will have 14 spectra for training and seven spectra for testing, forming a training data set and test data set with dimensions of \(14 \times 64\) and \(7 \times 64\), respectively. By following the one-to-one correspondence between the 64 mixing ratios and labels 1–64 indicated in Figure 4c, the input mixture spectrum is eventually classified into a specific label. The accuracy of the test data set is shown in Figure 4d. An accuracy of 98.88% in recognizing 64 classes of mixture spectra is realized. With these highly accurate results, the powerful ability of CNN as well as the reliable and stable sensing performance of MWS are verified. In addition to the 64-class mixture classification, the possibility of distinguishing concentrations lower than the LoD is also investigated with the assistance of the CNN. The LoD of glycerin is 972 ppm derived by the 3-sigma rule and the noise measurement (Note S5). In accordance with LoD value, the glycerin solution with concentrations ranging from 0 to 900 ppm with an increment of 300 ppm was measured in a similar way to that before. The dynamic measurement of the liquid converted from water to different glycerin solutions at 3.77 μm is displayed in Figure 4e. There is no clear intensity change during the liquid switching process, as expected. In addition to the real-time monitoring, the spectrum under different glycerin concentrations was also recorded, with each class collecting 21 spectra. Following the previous splitting ratio for the division of training and test data sets, a total of \(7 \times 4\) spectra are included in the test data set, as shown in Figure 4f. As all spectra were already normalized with the water background using the method mentioned before, the presented spectra are all around the straight line equal to 1 without significantly discernible features. The confusion matrix for the \(7 \times 4\) test spectra is shown in Figure 4g. With only two misclassifications, the CNN achieved a 92.86% classification accuracy for the differentiation of glycerin with concentrations lower than LoD, further demonstrating the impressive ability of CNN in unearthing subtle or concealed features, which is promising for the detection of trace amounts of gas or liquid. To confirm the presence of hidden features that are helpful for the classification, we apply the PCA to the spectrum data for feature extraction and dimension reduction. The visualization result of PCA is provided in Note S6 in the Supporting Information. Four clusters with distinguishable boundaries corresponding to the four glycerin concentrations are formed in the 3D principal components space, proving the actual existence of features that can differentiate the spectra of a glycerin solution with concentrations lower than the LoD.

**Multilayer Perceptron Regressor for Spectrum Decomposition.** In the final outcome of CNN, although the mixture recognition presents a high accuracy, the individual spectrum information on each component with corresponding concentrations, namely, the pure form of each component, is still missing. An alternative algorithm is required to mine the pure forms hidden in the mixture spectrum. Therefore, we adopted the MLP regressor to implement the spectrum decomposition to attain the pure form of constituents. Different from the CNN, which requires massive data for model learning ( \(21 \times 64\) spectra in total), the MLP regressor only needs one spectrum per label to operate correctly. By sweeping the input wavelength only one time for each mixture, \(1 \times 64\) spectra in total were recorded from additional measurements. The operation flow of the MLP regressor for spectrum decomposition is illustrated in Figure 5a–c, using the mixture comprising 5 vol % acetone, 15 vol % IPA, and 2 vol % glycerin in water solution as an example. The mixture spectrum with 96 wavelength points ( \(3.708–3.803 \mu m\) ) is sent into the regressor input layer. After being processed by two fully connected layers, the mixture spectrum will be decomposed to the spectrum of 5 vol % acetone, the spectrum of 15 vol % IPA, and the spectrum of 2 vol % glycerin and displayed in the output layer. For the training process, 48 of 64 spectra were randomly selected as the training data set, and the ground truth (expected output) was set as the cascading of three target spectra. Each target spectrum has 16 identical wavelengths and was extracted from the measured pure form of each component, forming the output vector with a dimension of \(1 \times 48\), as depicted in Figure 5b and 5c. In terms of the cost function, the mean squared error (MSE), which measures the deviation between the target spectrum (measured pure form) and predicted spectrum (decomposed pure form), is plotted as a function of the training epoch in Figure 5d. The MSE is gradually decreased to around 5 \(\times 10^{-3}\) by using the Root Mean Squared Propagation (RMSProp) Optimizer with a learning rate of 0.0005. Unlike the CNN having to experience all classes of data in the training process, the 48 mixture spectra in the training process of the MLP regressor only exhibit a subset of all concentration combinations, which means the concentration combinations carried by the 16 mixture spectra in the test data set are completely unknown to the MLP regressor. In order to precisely characterize the testing results of 16 mixture spectra, we define the decomposition error using the unit of per wavelength point (PWP), which describes the average single-point error between the predicted spectrum and the target spectrum. The single-point errors are all in absolute values before averaging. In view of the output vector of the testing spectrum containing the decomposed pure form of three components, the testing results of 16 testing spectra are shown in Figure 5e–g, corresponding to the decomposition error of the predicted spectrum of acetone, IPA, and glycerin, respectively. Most of the testing spectra realize the decomposition error below 0.05 PWP, and the average decomposition error for the 16 mixture spectra is around 0.027 PWP, suggesting a high decomposition accuracy. Additionally, the small deviation in pure form prediction also reflects the stability of the MWS for liquid mixture sensing. The testing results of acetone show a larger decomposition error because of the wider variation range of its pure forms as compared with IPA and glycerin. Moreover, as long as the spectrum of all pure forms and sufficient mixture spectra of good quality are provided to the MLP regressor, it can be
envisioned that the AIMWSP is able to tackle more complex mixture analysis tasks, such as decomposition of a quaternary or quinary mixture.

Component Concentration Prediction Using Decomposed Pure Forms. Besides the mixture spectrum decomposition, the AIMWSP can also obtain the component concentration of each mixture by leveraging the measured pure form (target spectrum) and decomposed pure form (predicted spectrum). The flowchart for predicting the component concentration is illustrated in Figure 6a. First, by applying the linear fitting function to the four measured pure forms with different concentrations, the sensitivity at the same 16 wavelength points as the predicted spectrum is received. And then, we sorted the R-square of the 16 wavelength points in order from largest to smallest and picked the top eight wavelength points in the following calculation. The information for the R-square at the eight selected wavelength points can be found in Figure S7. Next, with the spectrum values from the predicted spectrum and the sensitivity at eight selected wavelength points calculated from measured pure forms, the eight concentration values corresponding to the eight spectrum values of the predicted spectrum are able to be obtained. Finally, the prediction concentration matching with the predicted spectrum is generated by averaging the eight concentration values. The predicted concentrations of 16 × 3 predicted spectra based on 16 mixture spectra in the test data...
set are shown in Figure 6b–d, corresponding to the component concentration of acetone, IPA, and glycerin, respectively. The 1 vol % error range for the acetone and IPA (0.5:15 vol %) and the 0.4 vol % error range for the glycerin (0:2:6 vol %) are displayed to evaluate the prediction error level, as delineated in the shaded area. Thanks to the contribution of the MLP regressor in spectrum decomposition with a small difference between the measured pure form and decomposed pure form, the majority of the prediction concentration falls into the shaded area, indicating an accurate concentration prediction result relying on the decomposed pure form. Except for the single-component concentration prediction, the prediction error of concentration combination from a certain mixture is assessed through RMSE, which is commonly used in error metrics for numerical predictions. The equation of RMSE applied in our case is shown as

$$\text{RMSE}(C, \hat{C}) = \sqrt{\frac{1}{3} [(C_{\text{Ace}} - \hat{C}_{\text{Ace}})^2 + (C_{\text{IPA}} - \hat{C}_{\text{IPA}})^2 + (C_{\text{gly}} - \hat{C}_{\text{gly}})^2]}$$

(2)

where \(\hat{C}_{\text{Ace}}, \hat{C}_{\text{IPA}},\) and \(\hat{C}_{\text{gly}}\) denote the predicted component concentration of acetone, IPA, and glycerin, while \(C_{\text{Ace}}, C_{\text{IPA}},\) and \(C_{\text{gly}}\) are the corresponding true component concentrations, respectively. Figure 6e and 6f give a 3D visualization of comparing the ground truth (red spheres) with the predicted concentration combination (blue spheres) in the training data set and test data set. Ten exemplary data points are presented in each case. Evidently, the distance between ground truth and prediction is proportional to the RMSE and kept at a low degree for all 40 data points. Besides, the prediction results exhibit a comparable deviation level in the training data set and testing data set, proving our trained MLP regressor has strong generalization ability. The distribution of RMSE for 16 mixing ratios corresponding to all 16 mixture spectra in the test data set is shown in Figure 6g. The RMSE of all prediction values ranges from 0.1 vol % to 1.43 vol %, with 62.5% of the prediction values having an RMSE smaller than 0.5 vol % and more than 81% of the prediction values with RMSE lower than 1 vol %. Again, our trained MLP regressor presents an accurate decomposition of the mixture spectrum, which leads to the mixture concentration prediction with a low error value. Moreover, by adopting a larger bandwidth grating coupler\(^8\) or replacing the SOI platform with other material platforms with a broader transparency window, such as silicon-on-nitride\(^8,85\) and germanium-on-silicon\(^86,87\) a wider spectrum that covers more analytes with the specific fingerprint can be included in AIMWSP and even MIRSOC in the future for more advanced multiple organic component analysis.

**CONCLUSION**

Compared with previous waveguide sensing demonstrations that depend upon the refractive index change in the NIR or absorption change at specific wavelengths in the MIR for simple analyte detection, AIMWSP leveraged the spectrum information in the MIR to proceed with complex sensing analysis of the liquid mixture with the assistance of machine learning. The SWG metamaterial configuration enables the improvement of sensitivity without extending the length of the waveguide or enlarging the footprint of the sensor, which favorably supports the subsequent spectrum classification and decomposition executed in machine learning, as a greater distinguishability will be present in the spectrum from different classes or concentrations. By implementing two machine learning algorithms, not only the spectrum of a mixture under different mixing ratios can be successfully recognized, but also the pure form of a single component buried in the mixture spectrum can be extracted. Moving forward, as two sensing tasks are accomplished by employing two different algorithms in our MWS using spectrum input, in consideration of the swiftly developing waveguide sensor, machine learning, and on-chip photonic computation,\(^88\) we can anticipate that a compact MIRSOC with multifunctions can be realized by applying diverse machine learning algorithms on a photonic computation unit for analysis of sensing data from a miniaturized but ultrasensitive waveguide sensor in the same photonic integrated circuit.

In summary, we have demonstrated a CMOS-compatible AIMWSP for spectrum recognition and decomposition of aqueous mixtures in the MIR. The SWG metamaterial conceived for enhancing the sensitivity of the sensor in the limited space is employed. The mixture absorption spectra varying from 3.708 to 3.803 µm are collected and utilized by AIMWSP. With the help of a CNN, a classification accuracy of 98.88% is achieved for distinguishing ternary mixtures with 64 types of mixing volume ratios in the water solution, and 92.86% is obtained for the recognition of four glycerin solutions with concentrations below the LoD (972 ppm). In addition, the MLP regressor is performed for mixture spectrum decomposition. By only using 48 mixture spectra comprising 48 concentration combinations for training, the pure forms of each component can be recovered from 16 unknown mixture spectra with an average decomposition error of around 0.027 PWP. Furthermore, the quantification of mixture concentration with 81% of concentration prediction results within 1 vol % RMSE is realized based on the decomposed pure forms. By combining the advantage of the MIR waveguide sensor and machine learning, our work promises great potential for complicated aqueous mixture analysis in the intelligent waveguide sensing system and is an important step toward developing a data-driven MIRSOC for the data analytics of multiple organic components in healthcare, environmental monitoring, and extensive IoT sensing applications.

**METHODS**

**FDTD Simulation.** The simulation shown in this work is implemented using the FDTD method (Lumerical Inc.). For the simulation of the effective index of the propagation mode, one SWG metamaterial unit (Si pillar + gap) on a SiO\(_2\) substrate with Bloch boundary condition at x-boundaries and perfectly matched layer boundaries and perfectly matched layer-boundaries is built as the model. A plane wave as the light source is normally incident to the SWG metamaterial unit in the z-direction. By operating the “bandstructure” function from the analysis group to extract the phase velocity from band diagrams, we can obtain the effective index of propagation mode under a certain SWG metamaterial geometry. The mesh spacing in the x-direction is changed with period and duty cycle and set as 0.1 \(\times\) period \(\times\) (1-duty cycle) in the gap region and 0.1 \(\times\) period \(\times\) duty cycle in the Si pillar region. In the y- and z-direction, the mesh size is set as 150 and 100 nm, respectively.

**Device Fabrication.** The metamaterial waveguide sensor was fabricated on the SOI wafer with a 500 nm Si device layer. First, the waveguide pattern was defined using standard electron-beam lithography (EBL, JBX-6300FS, Jeol) using a ZEP-520A e-beam resist. Then the pattern was transferred to the Si device layer by SF\(_6\)/C\(_{6}F_{8}/Ar\) deep reactive-ion etching (DRIE, Oxford Plasmalab 100 ICP) followed by e-beam resist removal (submerging samples in PG
remover at 65 °C for 45 min). For the fabrication of the PDMS chamber, the PDMS base and agent with a mixing ratio of 10:1 were poured into the chamber mold, casting by 3D printing. After evacuating the air dissolved in the PDMS using the vacuum chamber, the PDMS chamber was placed on the hot plate at 80 °C for 1.5 h for curing and then peeled off. Then the chip and PDMS chamber were sent into an oxygen plasma reactor for surface activation. After that, with the alignment marker, the PDMS chamber was bonded on the surface of the chip under the view of the microscope. The region of the SWG metamaterial was covered by the 2 mm wide microfluidic channel, and the whole bonding process was finished in a very short time after the chip was taken out from the reactor.

**Characterization.** We used a quantum cascaded laser (MIRCat-1200, Daylight solutions) as the light source, and the polarization of the light is controlled by a low-order half-wave plate (WPLH05M-4000, Thorlabs) placed at the output of the laser. An optical chopper (Stanford Research Systems, SR560) put behind the half-wave plate is connected to a lock-in amplifier (Stanford Research Systems, SR830). Then the output of the laser is coupled to the MIR ZrF₄ fiber (P3-23Z-FC-2, Thorlabs) using a ZnSe lens. Two on-chip grating couplers are responsible for the light coupling between the device and fiber, and the output signal from device is transmitted to the photodetector (PDA20H, Thorlabs), which is also connected to the lock-in amplifier. Through the observation from the optical microscope, the location of two fibers is fine-tuned by the two 6-axis stages for accurate alignment between the fibers and grating couplers. Regarding the liquid flow control, the liquid analyte in the syringe is injected into the PDMS chamber through the PE tubing, and the flow rate is controlled by the flow rate controller (legato 110, kdScientific) where the syringe is installed. Then the liquid flowing out from the PDMS chamber is eventually dripped into the waste container. In the spectrum-collecting step, the device output signal from different wavelengths is recorded by the lock-in amplifier along with the tuning of the output wavelength of the laser. The time constant of the lock-in amplifier is set as 300 ms and can be increased for a smaller noise level.

**Machine Learning by the CNN and MLP Regressor.** The CNN models employed for the recognition of mixture absorption spectra are constructed as follows: the categorical cross-entropy function is adopted as the loss function, and the adaptive moment estimation (Adam) is utilized as the optimizer. The CNN models are developed in Python with a Keras and TensorFlow backend. For the MLP regressor used for the spectrum decomposition of a mixture, the programming framework was based on PyTorch (version 1.12.0), a Python (version 3.7.13) computing package. The prediction of the component concentrations was performed in MATLAB_R2020b.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.2c10163.

Simulation of external confinement factor; electric field distribution of the SWG metamaterial; deviation of external confinement factor in simulation and experiment; display of spectra of all concentration combinations; calculation of LoD of glycerin; visualization of PCA result for the spectrum of a glycerin solution with a concentration lower than the LoD; R-square at 8 selected wavelengths for component concentration prediction; comparison of waveguide sensing platform for liquid detection (PDF)

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**Notes**

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