Optical Chemical Barcoding Based on Polarization Controlled Plasmonic Nanopixels

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Plasmonic devices offer the possibility of passively detecting changes in local chemistry that opens up a wide range of applications from molecular sensing to monitoring water quality. Conventional plasmonics have previously shown great promise as nanoscale chemical sensors through detection of small variations in the local refractive index (RI). The motivation behind using plasmonics for these applications includes the fact that detection is entirely passive and the devices themselves can be readily miniaturized. Previously, a lack of any control over the output of these devices, has fundamentally limited their application to chemicals which produce clearly identifiable resonances within the range of detection. Here it is demonstrated that microfluidic devices, incorporating polarization-controlled plasmonic nanopixels, allow the device response to be tuned to the particular analyte of interest, anywhere within the visible spectrum. This dramatically increases the effective dynamic range and allows local variations in RI to be perceived directly as color changes by the human eye. Active control over the output of the device also enables clear differentiation between a number of different analytes, paving the way for plasmonics to be used for a wide range of real-world chemical sensing applications.

1. Introduction

The first observation of extraordinary optical transmission (EOT) through subwavelength apertures was made by Ebbesen et al. in 1998.[1] Since then, there has been considerable effort invested in understanding the properties, behavior, and responses of subwavelength apertures as highlighted in the 2010 review of Garcia-Vidal et al.[2] The rapidly increasing interest in this field is motivated by the broad range of applications for these devices, which includes color filtering[3-6] and sensing,[7-10] and the new physical phenomena, which can be explored. The availability of modern nanofabrication tools to produce even more sophisticated devices has also greatly increased the number of research areas in which subwavelength aperture arrays are having an impact. With focused ion and electron beam lithography tools, it is now feasible to produce highly complex geometries of subwavelength apertures with nanometer scale precision.

The exploitation of surface plasmon resonances and localized surface plasmon resonances (LSPRs) within subwavelength apertures and nanoparticles/structures for the detection of changes in refractive index (RI) (typically seen as wavelength shifts of several hundred nanometers per refractive index unit (RIU)) has been previously reported in the literature.[10-13] However, the majority of these studies have used devices fabricated from gold with resonances located in the red and infrared regions of the electromagnetic spectrum. One previous study using bimodal plasmonic devices for RI sensing utilized monochromatic laser light (632.8 nm) and was therefore limited to measurements of the transmitted intensity only.[10]

Here, we present a new approach to RI sensing, which works within the visible range and uses microfluidics combined with dual pitch plasmonic arrays, which have found recent application as continuously tunable color filters.[5,6,10,14-16] The key features of these new devices are as follows:

(1) Plasmonics have previously been used in a small number of cases to detect RI changes by eye.[17,18] Here, we show that the response of the device can be tuned to the particular analyte under investigation, enhancing its sensitivity. A tunable output delivers a “by eye” chemical sensor, which...
works for a wide range of different chemicals, overcoming one of the fundamental limitations on the current plasmonic-based technology.

(2) The dual-pitched arrays offer greater sensitivity. These devices couple the plasmonic resonance peaks of the EOT to separate polarization states of the incident light. Hence, they simultaneously act as both: a tunable color filter and a RI sensor, which increases their sensitivity over a wider range of the visible spectrum.

(3) Bimodal plasmonics open up new avenues for analyzing the polarization-dependant optical output of the devices, in this case the isosbestic points in the spectrum,[19] which are invariant under polarization. This is a new approach to detecting changes in the RI which provides excellent differentiation between the chemicals tested here.

The use of dual pitch plasmonic devices enables unambiguous resonance peak identification, free from the effects of cross-modal convolution, which is a significant issue when using unpolarized light. This enables additional resonance information, not normally detectable in the transmitted spectra using conventional devices to be measured. The EOT resonance peak separation is achieved via polarization control of the optical output. In addition, our results show that both the intensity and position of resonances vary as a function of RI. Hence it is essential, as is the case here, that polychromatic (rather than monochromatic[10]) light sources are used for these types of measurements.

Plasmonic devices operating within the red and infrared regime have previously been used to determine RI through measurement of the positions of resonant peaks. Extending this work to the visible regime requires the appropriate combination of aperture geometry and metal film. A common material choice for optically active plasmonic devices is silver (Ag), which supports plasmonic coupling over the whole visible range while minimizing damping. The pitch of the periodic arrays and the aperture size can be adjusted to control the position at which the resonant modes appear in the transmission spectrum. Due to the asymmetry of the plasmonic device interface, two sets of resonant modes appear in the transmission spectrum. When operating in the visible modes occur, which, in the present case, correspond to the Ag/analyte and Ag/glass interfaces.[20] The polarization sensitivity of cross-shaped apertures is exploited[5,6,10] to produce a bimodal optical transmission spectrum, which is highly sensitive to changes in RI. For our device, a microfluidic channel fabricated in polydimethyl siloxane (PDMS) was directly coupled to plasmonic nanostructures fabricated in an optically opaque Ag film. The conceptual design and schematic layout is shown in Figure 1A along with a scanning electron microscope (SEM) image of the actual device and the experimental setup (Figure 1B,C). Here, surface plasmon polariton modes are labeled as “SPP” and Wood–Rayleigh anomalies as “WA.” Combining this with simple nomenclature for the interfaces shown in Figure 1C, the SPP modes associated with the analyte and glass interfaces of the device are referred to as SPP( Ag/A ) and SPP( Ag/G ), respectively.

3. Results and Discussion
3.1. Advantages of Polarization Control

There are several key advantages to using bimodal, cross-shaped apertures as the sensor transduction mechanism for chemical sensing applications. Previous work[5,6,15] has shown that it is possible to achieve a broad range of spectral resonances with subwavelength, crossed-shaped apertures by tuning the spacing between apertures (pitch). The dispersion relation of the resonant peaks associated with the different Bloch modes for EOT in periodic arrays in metal films is defined in the first approximation by Ghaemi et al. as[21]

\[
\lambda_{\text{SPP}} \equiv \frac{P}{\sqrt{i^2 + j^2}} \sqrt{\frac{\varepsilon_2 \varepsilon_m}{\varepsilon_d + \varepsilon_m}}
\]

\[
\lambda_{\text{WA}} \equiv \frac{P}{\sqrt{i^2 + j^2}} \varepsilon_d
\]

where \(P\) represents the pitch, \(\varepsilon_m\) and \(\varepsilon_d\) are the dielectric constants of the metal and dielectric layer (in this case either the quartz or analyte) at the interface, respectively, and \(i\) and \(j\) are integers representing diffraction orders. These dispersion relations correspond to the wavelengths of the resonant modes of SPPs (\(\lambda_{\text{SPP}}\),
and WAs ($\lambda_{WA}$) and approximate the resonance wavelength of the devices, allowing them to be tuned by modifying the pitch of the apertures. The dispersion relation is also dependent on the dielectric constant of both the metal film ($\varepsilon_m$) and surrounding medium ($\varepsilon_d$). Due to the interface asymmetry, we observe resonant peaks in the measured spectra arising from both interfaces (Ag/G and Ag/A) present in the microfluidic channel.

Since the open area of the apertures is the largest along the X and Y directions of the array, these will provide the strongest coupling for the resonance peaks to occur. The use of linearly polarized light allows us to select which set of resonances the incident light will couple with. In the devices presented here, changing the polarization direction of the incident light to be aligned with the X axis (0° linear polarization) or Y axis (90° linear polarization) results in the excitation of resonances associated with the 450 and 300 nm pitches, respectively. Any other polarization leads to a resultant spectrum, which is predominantly a linear combination of the spectra at these two polarizations.[23] In Figure 2A, four main peaks can be identified with two different pairs of peaks, associated with the 90° and 0° polarization directions. In addition, there exist clearly identifiable points in the spectrum, where the transmitted intensity does not change with respect to the incident polarization angle. We refer to these points throughout the text as the isosbestic points.[19]

The peaks associated with the Ag/A interface occur at 450 and 525 nm (peaks 1 and 2), while the peaks associated with the Ag/G interface occur at 680 and 805 nm (peaks 3 and 4) for the 90° and 0° polarizations, respectively. The peak position of these resonance modes are redshifted compared to the expected positions, calculated using the dispersion relations in Equations (1) and (2). This discrepancy has been experimentally observed previously,[20,21,24,25] but its origin is still debated in the literature.[26] For example, Equations (1) and (2) do not take into account the presence of the apertures in the metal film, its roughness and intergranular composition, parameters that will alter the SPP resonances through the interactions with the LSP modes.[26] An additional source of the redshift may result from the fabrication process. Since many of these structures are fabricated using focused ion beam lithography, the redeposition of material removed during milling could contribute to local changes in the RI at the Ag/A interface.[27]

Figure 2A illustrates how polarization control enables separation of the different SPP and WA modes in the visible range. Previously, without control of the output, these modes would be too close to each other in the spectra to uniquely assign the Bloch modes.[26] This is clearly observed in the 0° polarization spectrum, as a broad shoulder from 550 to 675 nm, which is convolved with the Ag/A mode (peak 2). Figure 2B shows the spectra in Figure 2A mapped to a single point in the International Commission on Illumination (Commission international de l’Eclairage) (CIE) 1931 XY chromaticity diagram. A linear transition between the purple and green colors is observed, with intermediate values that vary as a function of the polarization direction of the incident light.[22,23] This transition corresponds to the dependence of the transmitted spectra on the contribution of the resonances from the principle X and Y axes of the array.[23] The response of this bimodal plasmonic device is well within the visible regime. In addition, its design results in two separate transmission peaks at the lower end of the spectrum, enabling the dynamic range of the sensor to be increased.

### 3.2. Color-Based Refractive Index Sensing

In this section, we demonstrate that by exploiting the bimodal output of the device, it is possible to tune the resonance frequency, increasing the effective dynamic range (0.4704 is demonstrated here) and sensitivity (435 nm RIU⁻¹ is achieved here).
observed for the 0° transition is observed between the two colors seen at 90°. For changes in RI of >0.05, a distinct color change can be observed in the device transmission by eye. This is most readily observed for the 0° polarization when comparing air, water, 1 M sucrose, and pure dimethyl Sulfoxide (DMSO), with the colors shifting from bright green through pink, indigo, and chartreuse. Since the positions of the peaks that dictate the color palette in the optical images are a function of the pitch size (Equations (1) and (2)), the color change is expected to be smaller for smaller pitch sizes. This is observed in the optical images for the 90° polarization. However, the smaller pitch size also permits detection of changes over a larger range of RIs. Although in some cases the difference in colors observed with changing analytes is quite subtle, the variations in color become more obvious if the signals are divided into their RGB channels. This is illustrated in Figure S2 in the Supporting Information.

The interpretation of the RI from transmission spectra produced by EOT plasmonic devices can be carried out using several different approaches. For example, Blanchard-Dionne et al. used a method based solely on the transmitted intensity, assigning all shifts in intensity at a given wavelength to the movement of resonance peaks. The two major limitations on previous approaches to RI-based measurements are:

1. Intensity-based measurements at a single wavelength can only be used to monitor changes in RI for a very limited number of cases.

2. Peak convolution often prevents accurate measurement of peak position and interpretation of spectral information, severely limiting the practical usefulness of plasmonic chemical sensors.

A detailed discussion and supporting data covering both these issues is provided in the Section “Intensity-Based Refractive Index Measurements,” Figure S3, and Section “Resonance Peak Convolution” in the Supporting Information. The bimodal devices presented here overcome these limitations by exploiting both the full spectral information and control over the resulting output. For example, at 90° incident polarization, it is not possible to unambiguously assign the SPP(Ag/A) resonance peak for many of the analytes (see Figure S3 in the Supporting Information). But, whereas previously this would have limited the functionality of the device, here we can simply change the incident polarization such that it can be used to characterize all the analytes investigated here.

From Figure 4, the measured RI sensitivities for the 0° and 90° polarizations are 435.5 and 313.0 nm RIU⁻¹ (WA 272.7 nm RIU⁻¹), this peak assignment is possibly a convolution of wood anomaly and higher mode resonances but is clearly associated with the analyte/Ag interface, respectively. The figure of merit (FoM) defined as the sensitivity (change in wavelength per RIU) divided by the full width at half max of the peak of the SPP Ag/A mode for 0° polarization case is 12.9. Considering the working range of the device is within the visible regime, this value is very high (approximately three times the average FoM for LSPRs in nanoparticles and four times higher than in cross-shaped islands). A final important point to note is that our results also show that using nonfunctionalized devices, it is not possible to distinguish between two different chemicals that have the same RI. This has not previously been highlighted in the literature, but as shown in the Section “Chemicals with matched RIs” and Figure S4 (Supporting Information), the response of these types of devices depends only on the RI of the local environment.
3.3. Tracking Isosbestic Points to Detect RI Changes

Previous approaches to interpreting transmission spectra from plasmonic devices use either peak position or intensity as a direct measure of changes in RI. Polarization control offers a new, more effective approach to chemical differentiation. As discussed above, convolution of resonance peaks of different modes makes peak position tracking unreliable, particularly at optical wavelengths and when the analytes vary over a large RI range. We have shown that this limitation can be overcome using polarization control by the experimenter switching between the different device modes. However, even this becomes problematic as the RI of the analyte approaches that of the substrate. In the case of biomodal plasmonic devices, however, another approach is possible for tracking RI changes, the isosbestic points.

The isosbestic points are points on the spectra where the intensity remains constant as a function of the incident polarization. These points arise because the spectra at each polarization are a linear combination of the spectra from the two principle polarization directions (0° and 90°) that have a reciprocal relationship such that as the contribution from one decreases, the other increases. If the plasmon modes excited by x- and y-polarizations are linearly independent, then the output, the electric field intensity $|E|^2$ must obey the following relation

$$|E(\theta)|^2 = |E(0^\circ)|^2 \cos^2 \theta + |E(90^\circ)|^2 \sin^2 \theta$$

where $\theta$ is the polarization angle of the incident wave. Thus, when the intensity at a given wavelength within the 0° and 90° spectra is equal, its value is invariant as a function of...
polarization. The isosbestic points can be precisely and unambiguously identified as points where the spectra associated with the different incident polarizations meet. The wavelength position and intensity values of the isosbestic points readily permit the construction of a “barcode” for each analyte studied, without relying on the fitting of particular resonance peaks.

In the present study, the data were analyzed numerically in order to extract the intensity values in the transmission spectra and wavelength of all isosbestic points automatically. This was achieved by taking the standard deviation of each wavelength for all polarizations. In order to account for the experimental signal-to-noise in the spectra, isosbestic points were identified here as locations where the standard deviation was <2% of the mean percentage transmission at each wavelength over a range of at least 5 nm. Once a region of the spectrum was identified as containing an isosbestic point, the wavelength corresponding to the minimum standard deviation within that range was selected. Using this analysis method, it was possible to analyze all data sets automatically and generate a unique barcode for different analytes tested.

**Figure 5** plots color maps of the transmission intensity as a function of polarization, illustrating the transitions that occur in these bimodal plasmonic devices as a function of RI. The numerically identified isosbestic points are highlighted in white. The corresponding spectra for pure DMSO is shown in Figure 5H for comparison with the numerically identified isosbestic points shown in Figure 5G. It is evident that these points align perfectly with the points at which all the spectra in Figure 5H intersect. This has been verified for all data sets.

With the percentage transmission and wavelength values numerically extracted, it is possible to plot a unique barcode for each of the analytes studied. **Figure 6** shows that not only the wavelength, but also the intensity of the isosbestic points varies as a function of the RI. Most of the isosbestic points redshift as the RI increases and intensity variations are observed for all isosbestic points. The combination of wavelength and intensity provides a unique set of isosbestic points for each RI measured.

This approach to the analysis has the advantage that the isosbestic points are always clearly defined and provide a unique identification of each RI. Since these points are defined by the complex internal interactions of the dual pitch plasmonic device, the position of the isosbestic points is dependent upon but not linearly related to the RI. Quantification of the local RI is therefore achieved via characterization of the device, using samples of known RI to build up a barcode reference database. This enables the unambiguous determination of the RI of any arbitrary analyte with high sensitivity.

This method of analysis is novel in approach and is unique to the bimodal polarization sensitive architecture used here. Automated analysis of the spectral output of our devices is enabled by the isosbestic analysis provided here. This in turn yields an unambiguous route to the determination and study of the local analyte RI via plasmonic sensing. Chemical barcoding offers significant advantages over traditional approaches, including...
and G) DMSO. Vertical axes for (B–G) are identical to (A).

4. Conclusions

This work has explored the application of full-spectrum, bimodal plasmonic devices combined with microfluidics for optical RI sensing. The bimodal properties of the devices enable us to tune the plasmonic resonance frequency in order to cover a broad dynamic range (0.4704 RIU) for RI measurements with high sensitivity (477 nm RIU$^{-1}$) in the visible regime. Continuous control over the device output was enabled by varying the incident polarization. Through these devices, we have demonstrated for the first time, a full-spectrum, passive detection of RI variation “by eye” using plasmonics for a wide range of different chemicals. Such a device could therefore be used to directly detect changes in local chemistry (provided this is accompanied by a change in RI) without any additional equipment required.

We have reviewed and discussed some of the issues associated with “intensity-only”- and “peak-only”-based RI measurements, and suggest an alternative approach for RI determination based on identification of the isosbestic points from bimodal plasmonic devices. This has the advantage that it avoids issues associated with the peak convolution and effectively utilizes the full-spectrum for the extraction of a unique chemical barcode for each RI. Once the device is calibrated, this approach can be used to quantify RI by comparison with a barcode “library.”

In summary, the results of this work highlight the new opportunities afforded by bimodal optical plasmonic devices for chemical sensing providing devices with threefold to fourfold improvements in the figure of merit. We also present a unique analysis method that allows for automated statistical analysis of data for the identification of RI from an unknown sample spectra. The devices presented here could be readily incorporated into platforms for RI measurements based on plasmonic effects in the visible range of the optical spectrum, making passive detection “by eye” of different analytes a practical reality.

5. Experimental Section

The plasmonic devices were fabricated in 150 nm thick Ag films. To achieve small grain sizes and promote adhesion, a 3 nm Ge seed layer was used. Both layers were deposited on precleaned quartz wafers by electron-beam evaporation (Nanochrome II, Intlvac) with a deposition rate of 3 Å s$^{-1}$. For the fabrication of the subwavelength apertures, focused ion beam (FIB) lithography (Helios Nanolab 600 Dual Beam FIB-SEM, FEI) was used with a beam current of 9.7 pA and an accelerating voltage of 30 kV. SEM images were also collected using the Helios Nanolab. Optical images were collected using an inverted optical microscope (Nikon Ti-U) with a 60× objective. Percentage transmission spectra were acquired using the same microscope, employing a spectrometer (IsoPlane SCT 320, Princeton Instruments) with a diffraction grating of 1200 lines mm$^{-1}$. All spectra were normalized with respect to the white-field illumination through the bare quartz substrate and acquired at the same polarization settings as the spectra. By defining a specific region of interest that was the same size as the patterned area, the volume of measured analyte was kept constant. Microfluidic devices with 200 μm inlet channels and a 5 mm$^2$ sensing window were defined using laser printed transparencies as photo masks for SU-8 photolithography, with the resultant devices being used as a master for PDMS casting (Silgard 184, 10:1 base to cross-linker). Refractive indices of the solutions used in this experiment were independently verified using a digital refractometer (Misco PA203). All data displayed here were binned to 1 nm for display purposes and white-field corrected (raw data can be downloaded as part of the Supporting Information).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
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