Resonant Dielectric Metagratings for Response Intensified Optical Sensing

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Abstract: The development of nanoscale optical sensors is desirable for a broad range of applications, including wearable medical-diagnostics, biochemical detection, and environmental monitoring. Optical detection platforms based on resonant nanostructures are the golden standard

for miniaturized footprint and high optical sensitivity. These sensors function by measuring a shift in resonance wavelength upon binding of analytes to their surface. However, such measurements are sensitive to intensity fluctuations of the illuminating source and its wavelength calibration, which limits their applicability. Here, we propose and experimentally demonstrate a novel optical sensing concept based on diffraction measurements from resonant dielectric metagratings. We show that our approach enables the direct measurement of unknown analytes with enhanced sensitivity and without need for intensity calibrations. The intensified sensitivity of our metagrating-sensor is derived from combining the resonant phenomena of the nanostructures with the tailored diffraction from the metagrating, thereby providing the highest sensitivity demonstrated to date amongst grating-based sensors. As a proof of concept, we validated the metagrating-sensor using an antibody binding assay, achieving a femtomolar-level limit of detection. Due to their high sensitivity and robust performance, the proposed metagrating sensors pave the way for novel miniaturized medical diagnostics and biosensing applications.

1. Introduction

Over the last decade, significant progress in nanofabrication, nano-characterization, and computer modeling has led to the development of miniaturized sensing devices that allow the fast and reliable detection of molecules of interest.[1-3] The small footprint of miniaturized sensing devices has increased the appeal for their use in our daily life.[4] In particular, optical sensors are attractive due to their robustness, highly sensitive nature, and their potential for use in wireless devices.[5, 6] To date, optical sensors have found a broad range of applications, including environmental monitoring, food safety, and medical diagnostics.[3, 6-8] Amongst the various optical sensing techniques in use, label-free sensing has been at the forefront of rapid and inexpensive detection paradigms.[9] Label-free sensing does not require chemical modification of the target molecule of interest, instead of using a receptor to capture the target through its binding properties.[9, 10] As high affinity and selectivity are desirable sensor properties, biomolecules such as antibodies are frequently used as receptors due to their ability to recognize and tightly bind specific targets. Once target molecules have been bound, label-free sensors must then be capable of transducing these molecular interactions into a measurable signal. In optical sensors, this transduction occurs by encoding binding events into an optical signal via waveguides,[11] micro-ring resonators,[12] optical fibers,[13] and metasurfaces.[14, 15] Amongst these platforms, optical metasurface-based sensors have thus far provided the highest potential for miniaturization as well as an accessible avenue for multiplexing of the analyte-fields.[16]

Metasurfaces are ultrathin planar arrays of resonant nanostructures made of metallic or dielectric materials that can significantly manipulate light properties.[17-19] Resonant oscillations of free electrons in metallic nanostructures lead to localized surface plasmon resonances (LSPR), which exhibit strong field enhancement on the surface. Subsequently, the oscillation currents result in increased scattering at the resonant wavelength, whose spectral position is highly sensitive to the surface refractive index. The presence of analytes on the surface of the nanostructures can alter this surface refractive index. Therefore, plasmonic systems directly enable the transduction of target binding in label-free sensing platforms.[15, 20] However, the quality factor of LSPR resonances and therefore their spectral width is relatively broad, which limits the performance of LSPR-based sensors. More recently, replacing plasmonics with dielectric metasurfaces has enabled the generation of higher quality factor resonances. Dielectric metasurfaces can exhibit much narrower resonance spectral widths, including high-Q designs.[21, 22] They further allow for a larger sensing mode volume and engineering of the field profile. As a result, dielectric metasurfaces have enabled the development of highly sensitive sensing platforms.[7, 21-23]

In both plasmonic and dielectric metasurface-based sensors, the signal obtained is derived from the measurement of the shift in resonant wavelength when analytes are in close proximity to the metasurface. Such measurements are performed either via analysis of the transmission spectra or via measurement of the change of the intensity of transmission at a fixed wavelength at the wing of the resonance. As such, the resonance shift measurements are highly sensitive to the intensity fluctuations and wavelength calibration of the input source, which limits the practical applicability of metasurface sensing outside of a laboratory setting. Therefore, there is a need to develop novel optical sensing techniques that simultaneously provide signal intensification while remaining robust against fluctuations in input source intensity and wavelength performance.

Unlike metasurface-based sensors, diffraction-grating-based sensors can directly measure the ratio of the intensities of two diffraction orders from the grating. This diffraction intensity ratio (DIR) is highly dependent on the surrounding environment. Therefore, the proximity of a target analyte to the grating leads to a change in the grating optical response, which is detected by the sensor.[24-27] Due to this ratiometric measurement, such grating-based sensors are robust to the fluctuation of light source intensity and do not require challenging background intensity-calibration of transmission or reflection spectra.[15, 20, 28, 29] To date, several grating-based diffraction sensors have been reported using different configurations such as asymmetric nanofluidic gratings,[25] sinusoidal gratings,[30] and 1D gratings.[31] However, the transduction mechanisms of these existing non-resonant grating-based sensors generally display considerably lower sensitivities in comparison to resonant metasurface-based sensors.

To address the shortcomings of these platforms, we herein propose and demonstrate a novel sensing platform that combines the advantages of both diffraction-based and resonant metasurface-based sensing. Our platform makes use of a resonant metagrating consisting of a series of dielectric nanostructures, called meta-atoms, where the individual meta-atoms exhibit a Mie-type resonance. Such resonances can scatter the waves in the forward direction while imprinting a phase in the range from 0 to 2π. Therefore, by arranging meta-atoms of different transverse dimensions and having an optimal phase discretization, one can efficiently manipulate the optical wavefront of the incident light. In particular, one can inscribe a linear phase gradient, mimicking a blazed grating, to deflect the incident light to a single diffraction order. Such a unique metagrating arrangement[32] enables maximizing the light transmitted into the first diffraction order while minimizing the light in the zeroth diffraction order in a resonant fashion.[33-36] The detection signal, measured as DIR, can therefore be significantly enhanced, which can, in turn, boost the platform's limit of detection (LOD). In addition, the resonant nature of the meta-atoms of our metagrating can significantly enhance the sensitivity of the metagrating operation to target analytes on its surface. Altogether, these factors intensify the response of our metagrating sensors, granting them exceptional and significantly improved sensitivity, relative to blazed and other grating approaches.

To validate our resonant metagrating platform, we design and fabricate two different metagrating sensors, having a large deflection angle (LDA) and a small deflection angle (SDA). We first experimentally demonstrate the refractive index (RI) sensing capability of the sensor using glycerol diluted with deionized (DI) water down to 0.5% volume/volume (v/v). The metagratings display maximum sensitivities of 752 RIU-1 and 26,266 RIU-1, for the LDA and the SDA design respectively, in the RI range of 1.331 to 1.401. Finally, we demonstrate the potential of our platform for use in label-free biosensing applications by detecting the binding of a commonly used and chemically unmodified detection antibody, anti-Mouse IgG, to a Mouse IgG target immobilized on the sensor surface. The resulting LOD for anti-Mouse IgG of ~770 fM represents, to our knowledge, the most

sensitive IgG limit of detection reported for an optical grating sensor, thus exemplifying the response intensification provided by our resonant metagrating platform.

2. Results and discussions

Our metagrating consists of a set of nanodisks of different sizes to impose a phase from 0 to 2π on the transmitted light (Figure 1a). This set of nanodisks forms the unit-cell (red dashed box), which is periodically repeated to form the metagrating. The light transmitted through the metagrating is split into different diffraction orders, where each diffraction order carries a fraction of the power from the incident beam. These fractions are determined by the phase ramp imprinted by the metagrating, which is highly sensitive to its surface refractive index, thus in turn to the presence of analytes on its surface. Since the arrangement of nanodisks mimics a perfect 0 to 2π phase ramp, the incident light is efficiently channeled to a single diffraction order unlike in other diffraction grating-based sensors where the input power is split to multiple diffraction orders.[27, 30] Changes in diffraction profiles due to analytes proximal to the grating can be magnified by simultaneously maximizing the transmission in the -1st diffraction order while minimizing the transmission zeroth order and measuring the ratio of transmittance between orders. The schematic of the DIR data set as a function of RI is shown in Figure 1b. As both intensities, I-1 and I0 depend on the RI values, the use of the DIR data set intensifies the sensing performance and enables the easy identification of the surrounding RI. This DIR signal is independent of the incident intensity, which is factored out in the ratio of power between the two diffraction orders. As a result, the metagrating optical sensor is robust to the fluctuations of the input intensity.

Figure 1. (a) Schematic of dielectric diffractive metagrating sensor where the supercell consists of nine nanodisks, and (b) Schematic of DIR = I-1/I0 data set as a function of RI.

The diffraction pattern further provides calibration of the incident light wavelength, which is often an issue when a fixed-wavelength laser is used to measure the sensing response in resonant metasurface sensors. The deflection angle from the metagrating can be calculated using the diffraction equation,

$$n_{tra}\sin\theta_{tra} = n_{inc}\sin\theta_{inc} - m\lambda/d , \quad (1)$$

where n_{inc} and n_{tra} are the refractive index of the incident and transmission medium, respectively. θ_{inc} and θ_{tra} are the incident and deflection angles, respectively, λ is the operating wavelength, m is the integer number of the diffraction order, and d is the grating (super-cell) period. The period d is known with high accuracy from the nanofabrication, therefore, the precision measurement of the deflection angle (in the air) from the metagrating provides a good calibration for the laser wavelength. Therefore, the metagrating sensor is also robust to fluctuations of the incident laser wavelength, which can often occur due to temperature or driving laser current fluctuations.

Equation 1 allows us to calculate the deflection angle for the two metagrating designs. The LDA design has periodicity d = 2,000 nm, corresponding to a diffraction angle of 18.6 ° in water (n = 1.331) at 850 nm. When using our experimental setup, the angle is measured in air (n = 1), once the light exits the microfluidic cell used for sensing, resulting in an external deflection angle of 25.2 °. For the SDA design with d = 4,500 nm, the corresponding diffraction angle is 8.2 ° in water at 850 nm (or a 10.9 ° external angle in the air). We note that in both cases, the angles are measured at a normal incidence of the input beam (θ_{inc}= 0).

2.1. Metagrating with large deflection angle

To design our metagrating, we employed nanodisks operating in the Huygens' resonant regime.[37] The Huygens' regime is achieved by spectrally overlapping the electric dipole (ED) and magnetic dipole (MD) resonances of the nanodisks, leading to a near-unity transmission along with 0 to 2π phase coverage. This overlap condition is in fact agile to the presence of analytes on the surface of the nanodisks and results in an improved metagrating sensitivity. To optimize the metagrating design, we modeled the metagrating and varied the height and periodicity of the nanodisk for operation in the near-infrared spectral range. This spectral range is advantageous for practical considerations, offering accessible laser sources (laser diodes) and simple detection using CMOS cameras. Our numerical models suggested an optimized nanodisk of 130 nm in height and a period of 500 nm, which enables Huygens' condition for operation in the near-infrared at the wavelength of 850 nm. For the metagrating design, we have used amorphous Silicon (a-Si), which is substantially transparent with a high refractive index over this spectral range (Supporting Information, Figure S1). We next performed numerical simulations where we varied the nanodisks' radii from 80 to 200 nm. Figures 2a,b show the calculated transmittance and the phase accumulation through an array of homogeneous nanodisks, respectively. Notably, at 850 nm, we achieved a transmission window with a near-unity transmission (Figure 2a) and 0 to 2π phase profile (Figure 2b). We have optimized our metagrating for operation in water as an embedding medium (n = 1.331) to match our sensing experiments. The resulting optimized LDA metagrating consists of four nanodisks with radii of 126, 138, 147, and 165 nm, as shown in Figure 2c. These nanodisk sizes provide a phase gradient from 0 to 2π with π/2 phase increments.

In order to numerically calculate the deflection angle, we investigated the far-field of the LDA metagrating using finite-difference time-domain (FDTD) simulations. For the modeling, we used a plane wave as an excitation source at the operating wavelength of 850 nm. The results of our simulations for the y-polarized incident beam are shown in Figure 2d. The metagrating causes the incident beam to deflect in the x-direction to the -1st diffraction order at a deflection angle of 18.6 ° (in water). As can be seen in Figure 2d, this diffraction order carries most of the incident light, while the 0th (transmitted) diffraction order only carries a small portion of incident beam power.

Figure 2. Numerically calculated (a) transmission and (b) phase profile for a variation of the nanodisk radius 80 nm to 200 nm with height 130 nm at a constant period of p = 500 nm for silicon-nanodisk metasurfaces embedded in a homogeneous medium with n = 1.331. The white-dashed line indicates the overlap of electric and magnetic resonances at a wavelength of 850 nm. (c) Schematic of the smaller supercell which consists of four nanodisks, which is responsible for a phase shift from 0 to 2π with π/2 phase increments. (d) The simulated far-field profile obtained by the LDA gradient metasurface resulting in a diffraction angle of 18.6 ° at 850 nm. (e) Simulated transmittance spectra for different diffraction orders. (f) Sensor response obtained as the diffraction intensity ratio of the -1st and 0th diffraction orders, together with a polynomial fit as a function of the analyte's refractive index.

To further investigate the scattering property of the LDA metagrating, we calculated the transmission spectrum (metagrating embedded in water, n = 1.331) using the finite-difference frequency-domain method (Figure 2e). For our metagrating, the maximum transmission to the -1st diffraction order was calculated to be 42%, while the light transmitted to the 0th order is 2.5%. The remaining power of the incident beam is distributed into other diffraction orders in forward and backward directions (Supporting Information, Figure S2). The observed distribution of the transmitted light to a single diffraction order is highly beneficial for diffractive sensing to maximize the measured signal, which is defined as the ratio between two diffraction orders.

To quantify the sensitivity of our diffractive sensor, we define the sensor's signal as, DIR = I-1/I0, where I-1 and I0 refer to the intensities of the -1st and 0th diffraction orders, respectively. Our metagrating minimizes I0 and maximizes I-1, thus quadratically maximizing the signal DIR. When different analytes are in close proximity to the surface of the gratings, the optimized deflection condition is disturbed, which results in both an increase of I0 and a decrease of I-1, thus amplifying the observed signal change. The resonant behavior of the metagrating further enhances its sensitivity to the change of the surrounding environment with a factor proportional to the quality factor of the resonance, which for this grating is $Q \approx 20$ (Figure 2e). In contrast, non-resonant grating exhibits a low-Q response, which will lead to minimal sensing performance due to the change of the surrounding medium.[38, 39]

To study the effect of the immediate environment on the performance of our diffraction metagrating platform we calculated full transmission spectra with different diffraction orders while varying the surrounding RI from 1.331 to 1.401 is shown in Supporting Information, Figure S2. The range of the RI is derived from the experimental conditions, corresponding to the change of the RI of a mixture of glycerol and deionized (DI) water.[40] Due to the increase of RI, the 0th and -1st diffraction order transmission spectra exhibit a redshift. As a result, the light transmitted through the 0th diffraction order increases, and the light transmitted through the -1st diffraction order decreases which leads to the downward DIR slope as shown in Figure 2f. It is also noticeable that at the higher RI values, the difference between two adjacent DIR values is reduced, and as a result, the sensor sensitivity is saturated. Furthermore, we have defined the metagrating sensitivity as $S = \Delta s/\Delta n$, where Δs=DIR1-DIR2 is the change of intensity ratio and Δn is the change of RI. As seen in Figure 2f, the LDA metagrating shows a maximum sensitivity of 762 RIU-1 in the sensing range of 1.331 to 1.401, which is higher than other diffraction sensors.[30] Figure 2f also shows the 2nd order polynomial fitting (R2 value of 0.9782) within this broad RI variation.

To verify our concept experimentally, we fabricated the LDA metagrating by electron beam lithography (EBL) combined with reactive ion etching (Methods). A schematic of the fabrication steps is also provided in Supporting Information, Figure S3. The scanning electron microscopic (SEM) image of the fabricated LDA metagrating is shown in Figure 3a. The red dashed region indicates a single supercell, which consists of four nanodisks. The fabricated sample is integrated into a microfluidic channel for analyte delivery and illuminated at normal incidence to the metagrating. We measured the transmission spectra using a homebuilt transmission setup (Supporting Information, Figure S4) using 5x and 100x objectives to discriminate between the transmission of the 0th and the other diffraction orders. These measurements provided the operating wavelength, ~850 nm, which corresponds to the minimum light transmission at the 0th diffraction order and maximum transmission at the first diffraction order (Supporting Information, Figure S5). We also measured the far-field optical properties of the LDA metagrating using a second optical setup, shown in Figure 3b. To perform the diffraction experiment, we used a laser diode with a power of ~5 mW and a central wavelength of 850 nm. The laser beam spot on the LDA metagrating is shown in Supporting Information, Figure S6. The laser power and laser operating wavelengths (±10 nm) were tuned using the power and temperature controllers, respectively (see Methods). We used a microfluidic channel to continuously flow glycerol at a range of concentrations from 0.5% to 50% v/v and maintained the flow rate at 15 µl/min with a maximum pressure of 15 psi. An image of the microfluidic system integrated with the metagrating is shown in Figure 3c.

Figure 3. Experimental large deflection angle results. (a) SEM image of the tilted fabricated LDA metagrating. (b) Experimental setup for the diffraction measurement. (c) Real image of the microfluidic system integrated with LDA metagrating. (d) Far-field profiles of the incident light with varying glycerol concentrations. (e) The line scan of diffraction intensity with varying the glycerol concentration in water up to 50% (v/v). (f) DIR signal measurement and the corresponding polynomial fitting as a function of RI of the glycerol-water mixture. Inset shows a magnified scale for the sensitivity estimation. (g) Real-time DIR response to the variation of glycerol concentration, and (h) 2nd order polynomial fitting of intensity ratio as a function of the analyte RI.

As seen in the experimentally measured far-field profiles (Figure 3d), with the rise in glycerol concentration and therefore RI,[20] the light transmission through the 0th and -1st diffraction orders increases and decreases, respectively. This is in agreement with numerical simulation results (Supporting Information, Figure S2). As further proof, we analyzed the line scans of the far-field profiles, shown in Figure 3e. In the line scan analysis, we integrated the intensity over 30 vertical pixels covering each of the individual diffraction orders to enhance the calculation accuracy and average them accordingly, confirming the observed changes in transmittance to the 0th and -1st diffraction orders. To probe the limit of detection, we gradually reduced the concentration of glycerol and experimentally demonstrated that our sensor can detect as low as 0.5% (v/v) concentration of glycerol solution in water. Subsequently, by quantifying the diffraction intensity ratio of the -1st to 0th diffraction orders, we have shown the correlation between the DIR and RI in Figure 3f. This result shows that the experimental sensitivity of the proposed sensor is 616 RIU-1, which is 19% lower than the numerically calculated value, presented in Figure 2f, i.e. 762 RIU-1. This difference might be due to several factors, including fabrication imperfections, impurities of the water medium, arbitrary scatterings of the uneven surface of the microfluidic channel, etc. Nevertheless, this sensitivity exhibits a 2nd order polynomial trend with an R2 value of 0.9782.

We next performed RI measurements using a real-time monitoring system, flowing glycerol at set concentrations for 15 minutes at a flow rate of 15 µL/min and captured the signal every 15 seconds. Between each successive glycerol concentration, DI water was flown at the same flow rate to wash the microfluidic channel and remove residual glycerol. The subsequent results for successive flow cycles, shown here as the intensity ratio between the 0th and -1st diffraction orders at glycerol concentrations from 0.5% to 50% are shown in Figure 3g (for better slope representation). Notably, our metagrating sensor exhibits a stable response over successive exposures to glycerol and washes, with the response returning to the same baseline during each wash. In addition, the correlation between the intensity ratio and refractive index is shown in Figure 3h, further validating the above results.

As our resonant metagrating sensor is based on maximizing the light at a certain diffraction order, this approach theoretically allows for further sensitivity optimization by controlling the deflection angle. In particular, earlier studies have revealed that by increasing the deflection angle, the transmission efficiency decreases, and subsequently, the diffraction efficiency diminishes significantly.[34, 35] Accordingly, we next investigated a metagrating sensor with a small deflection angle.

2.2. Metagrating with small deflection angle

Our SDA metagrating consists of nine a-Si nanodisks with radii of 126 to 200 nm as determined from the 2D transmission and phase responses shown in Figures 2a,b. The polar plot of the transmitted phase and transmission efficiency of chosen nanodisks is shown in Figure 4a. The transmission efficiency of the individual disks is close to unity, and the disks can efficiently cover the 0-2π phase

range with small discretized phase values of 2π/9. As a result, the coupling between nanodisks is more stable, which leads to beam deflection with higher efficiency. This higher efficiency indicates that the sensor response can be significantly enhanced with the use of an SDA metagrating. The simulated phase profile of the propagating waves through our SDA metagrating is shown in Figure 4b at the operating wavelength of 850 nm. The calculated deflection angle in the water environment surrounding the silicon metagrating is 8.2 degrees.

The transmission spectra of different diffraction orders are shown in Figure 4c. The SDA metagrating is able to transmit a maximum of 77% of incident light at the -1st diffraction order, which is nearly twice the transmission compared to the LDA metagrating while transmitting only 0.22% of incident light in the 0th diffraction order. The full spectra of different diffraction orders with varying analyte RI from 1.331 to 1.401 are shown in Supporting Information, Figure S7. As with the LDA metagrating, when the analyte RI increases, the light transmitted to the -1st diffraction order decreases, while the light transmitted to the 0th order increases (Figure 4d). The calculated maximum sensitivity of the SDA metagrating is therefore measured to be as high as 26,266 RIU-1 within the sensing range of 1.331 to 1.401.

Figure 4. Simulated SDA metagrating results. (a) Transmittance and phase in polar format at the operating wavelength of 850 nm. (b) Simulated phase profile obtained by the metasurface resulting in a diffraction angle of 8.2 ° at 850 nm wavelength. (c) Simulated transmittance spectra for different diffraction orders, and (f) polynomial fitting of DIR signal as a function of the analyte RI.

This sensitivity represents a 35-fold higher sensing response in comparison to the LDA sensor and a considerable increase over previously reported diffractive sensors, as shown in Table 1. We also compared our sensor's response with a conventional blazed grating that we designed using the same a-Si material and deflection angle as the SDA metagrating. The structural details of this blazed grating, as well as its transmission response in different diffraction orders due to variation of analyte RI are shown in Figure S8 of the Supporting Information. Notably, our SDA metagrating exhibits a six-fold higher sensing response compared to the conventional blazed grating.

Table 1. Performance comparisons of the reported dielectric diffraction sensors.

Characteristics	Operating wavelength	Sen. process	RI range	Sens. (RIU-1)	LOD	Ref.
		Bulk	Surface			
Porous silicon 1D grating	632nm	×	√	NA	NA	41.7nM [24]
Asymmetric optofluidic grating	635nm	√	√	1.334-1.373	2.416	NA [25]

Asymmetric Fraunhofer diffraction	532nm	√	×	1.33416-1.33406	11,000	NA	[27]
Sinusoidal relief grating (numerical work)	632nm	√	×	1.36-1.59	-557	NA	[30]
Diffractive metagrating	850nm	√	√	1.331-1.401	26,266	~770 fM	This work

We next experimentally confirmed the simulated sensitivity enhancement presented by the SDA resonant metagrating. An SEM of the fabricated SDA metagrating is shown in Figure 5a, where the red dashed area indicates a single supercell consisting of nine nanodisks. The experimental transmission spectra of different diffraction orders are shown in Figure 5b. The measured 0th diffraction order exhibited only 6% transmission, while the other (first plus higher) diffraction orders exhibited transmission of 50%. Although the simulated transmission spectra (-1st order) have a sharp dip at around 830 nm however, this is not visible in the measured transmission spectra mainly due to the lower resolution of the spectrometer. However, this particular sharp dip does not influence our results which are based on broader Mie-resonant features. Later, we performed the RI measurement using the same continuous flow microfluidic system and assay protocol mentioned above. The incident beam spot on the SDA metagrating is shown in Supporting Information, Figure S9. The incident beam spot covers fewer supercells of the metagrating, thereby justifying the larger period of the SDA in comparison to the LDA. The diffraction intensity in the different diffraction orders with the variation of glycerol concentration is shown in Figure 5c.

Figure 5. Experimental SDA metagrating results. (a) SEM image of the fabricated SDA metagrating. (b) Experimental transmission results of different diffraction orders. (c) The line scan of diffraction intensity with varying the glycerol concentration in water up to 50% (v/v), and (d) sensitivity response as a function of RI.

When the glycerol concentration is increased, light transmitting through the 0th diffraction order is increased, albeit to a lesser extent than with the LDA metagrating. Nonetheless, the intensity ratio of SDA metagrating is four times higher than the LDA metagrating. This leads to a significantly improved sensing response with a maximum sensitivity of 2,645 RIU-1 (Figure 5d), which is higher than that reported for other diffraction-based sensing approaches.[25, 30] To realize the effect of fabrication imperfections, we have shown the response in the ideal simulation case as well as with a

50% variation from the ideal simulation case (Supporting Information, Figure S10). By considering this deviation from the ideal case, our calculated maximum sensitivity becomes 4,210 RIU-1, which is comparable to the experimentally measured sensitivity. Notably, as the glycerol concentration further increases, the SDA metagrating response sharply drops (Figure 5d, shaded region). This is characteristic of the optimization process undertaken to enhance the sensor's response at a target refractive index. In this design, the SDA metagrating displays its highest sensitivity at low refractive indices reflecting its use in aqueous systems. Although we have here characterized the sensor over a broad range of RIs, in practical applications, such as in biosensing, the observed RI changes tend to be small in comparison due to low analyte concentrations. These small RI changes have previously proven challenging to detect with less sensitive platforms.[2] However, the acute sensitivity of our platform at aqueous RIs makes it suitable for the detection of analytes at these low concentrations, which is a desirable application of optical sensors. We have also investigated the oblique incidence effect on the proposed metagratings, where SDA metagrating exhibits a stable response compared to the LDA metagrating (Supporting Information, Figure S11). To exemplify such unique biosensing capability in the final part of our work we investigated the SDA metagrating as a compact biosensor of IgG antibodies.

2.3. Functionalization and biosensing measurement

The high sensitivity of the SDA metagrating response to refractive index changes seen above indicates that the resonant metagratings are well suited for biosensing applications. In such applications, the capture of a biomolecule at the sensor surface induces a change in the local refractive index relative to that of the bulk solution. Therefore, while the sensing principle remains the same as above, biosensing, in addition, requires the selective capture and detection of the target biomolecule from an often complex medium. To validate our SDA metagrating sensors for biosensing applications, we next verified its capacity to detect the binding of anti-Mouse IgG antibodies, which are commonly used detection antibodies for biosensor benchmarking trials and for signal enhancement in immuno-sensors. The resulting antibody binding measurements should therefore provide a metric for both our sensors' capacity to detect the binding of a detection antibody to its target as well as their sensitivity to the capture of moderately-sized biomolecules by surface-immobilized antibodies.

Figure 6. (a) Schematic illustration of surface functionalization for selective biosensing of anti-Mouse IgG. (b) Experimentally measured transmission for the zeroth-order diffraction during the different binding steps. (c) A plot of the average intensity ratio vs. anti-Mouse IgG concentration in the range of 5×10-13 to 50×10-6 g/mL (3.1 fM to 312 nM). Each point is an average of three trials with error bars representing the standard deviation. The red curve represents a four-parameter logistic fit with the shaded area showing a detection range from 3×10-10 g/mL to 6.5×10-9 g/mL (IC20 to IC80).

To simulate a stable test system, we immobilized a primary antibody (Mouse IgG) onto the dielectric metagrating using silicon to amine/sulfhydryl coupling strategy (Methods, Figure 6a). After confirming stable Mouse IgG immobilization (Figure 6b), we performed an anti-Mouse IgG binding assay by measuring the diffraction intensity ratio between the 0th and -1st diffraction orders at a range of analyte concentrations from 5×10-13 to 5×10-6 g/mL (3.1 fM to 31 nM), shown in Figure 6c. The resulting sensor response was fitted with the four-parameter logistic fit, shown with a red curve in Figure 6c. From the fitted model, the assay's LOD (IC10) was calculated to be 123 pg/mL (~770 fM)

with a detection range (calculated as IC20 to IC80) of 3×10-10 g/mL to 6.5×10-9 g/mL and a dynamic range of roughly 80%. Notably, these results are comparable to the reported affinities of tight-binding antibodies,[41] suggesting that our sensing platform can be used to transduce most immunoassays. It is therefore also likely that the measured LOD is bounded by antibody binding affinity rather than by platform sensitivity. In addition, while many biomolecular targets of interest are smaller than antibodies, the dynamic range observed for antibody binding suggests that the binding of smaller bio-molecules could still be accurately detected, especially if detection antibodies are used to enhance the signal obtained. As such, these results demonstrate that SDA metagratings are suitable for use in optical biosensing.

3. Conclusion

In this work, we designed and experimentally validated a novel label-free optical sensing platform that uses resonant dielectric metagratings. These metagratings can transduce changes in local RI caused by the presence of an analyte of interest into an optical signal with extremely high sensitivity in comparison to existing optical sensing platforms while remaining insensitive to fluctuations in the input light source. Here, we investigated two metagrating designs that exhibit different deflection angles and found that LDA and SDA metagratings show maximum sensitivities of 752 and 26,266 RIU-1, respectively, in the RI range of 1.331 to 1.401, which is equivalent to a glycerol concentration of 0.5% to 50% in water. These sensors have also been shown to be capable of detecting a change in RI as small as 0.0003 (0.5% (v/v) glycerol). To further demonstrate the suitability of our metagrating sensors to real-world optical sensing applications, we verified the SDA metagrating sensor's capacity to detect biomolecular binding events using a Mouse-IgG / anti-Mouse IgG system. To our knowledge, the SDA metagrating sensor exhibited the smallest anti-Mouse IgG limit of detection yet reported of ~770 fM. In addition, they function at a single wavelength, using a ratiometric analysis rather than a time-consuming full-spectrum analysis, thus greatly simplifying their use beyond the lab bench. These results altogether demonstrate that our sensor concept presents a robust platform with significant signal amplification at low analyte concentrations, making it particularly suitable for label-free biosensing applications. Given the wide range of bioreceptors and other capture technologies that could be readily adapted for use with our platforms, this metagrating sensing platform provides a new avenue for the creation of on-demand response intensified optical sensors.

4. Methods

Numerical simulations. To optimize the individual nanodisk parameters for our metagrating, we use the Matlab-based rigorous coupled-wave analysis (RCWA) to examine the transmission properties of periodic arrays of nanodisks (Figure 2a,b). Such periodic arrays can accurately approximate the local transmission properties of a metagrating composed of gradually varying nanodisks. RCWA has been widely used for investigating the transmission properties of periodic structures due to its fast convergence and accurate calculations. RCWA is a freely available open-source software package that works in the frequency domain [....] . We have used λ/12 spatial resolution and up to 7-order Fourier harmonics in both the x and y directions, which ensures the convergence of the resonant meta-atoms. Following the nanodisk optimization process, we use Lumerical FDTD software to perform the far-field analysis for the entire metagrating with gradually varying nanodisks (Figure 2d), owing to its ability to calculate electromagnetic properties for large structures with minimal post-processing effort [Arseni papers]. A plane wave source was used with periodic boundary conditions in the x-y axis, and perfectly matched layer (PML) boundary conditions were used in the z-axis. All other numerical studies (Figures 2e,f; 4; S2; S7; S8 and S10) were carried out using CST Microwave studio in the frequency domain. A tetrahedral mesh was used for accurate numerical analysis. The waveguide ports have been used with unit cell boundary conditions to calculate the s-parameters of

the LDA and SDA metagratings. The wave propagation (Figure 4b) through the metagratings was investigated by employing a plane wave excitation source. Periodic boundary conditions were applied in the y-direction, and perfect electric conductor boundary conditions were applied in the x-direction. Additionally, open boundary conditions were used along the z-axis.

Fabrication. Metagratings were fabricated on a thick quartz glass substrate, with a thickness of 1mm. First, the substrate was cleaned with oxygen plasma. Subsequently, 130 nm thick amorphous silicon (a-Si) was deposited onto the glass substrate using a plasma-enhanced chemical vapor deposition (PECVD, Oxford PlasmaLab System 100). The thickness, as well as the optical properties of a-Si, were confirmed and measured by Ellipsometry. These parameters were used in numerical simulations. The metagrating patterns were fabricated on a-Si film through electron beam lithography (EBL) by means of ZEP 520 negative resist. After developing, we deposited 30 nm Aluminium (Al) on the sample via thermal evaporator, followed by lift-off. The Al metagrating masks were transferred into the a-silicon film by induction coupled plasma (ICP). Finally, the residual Al mask was removed by wet etching.

Experimental Setup. We have measured the transmission spectra of the fabricated gradient meta-surfaces using a home-built white-light spectroscopy setup in a confocal configuration. The sample was illuminated from the backside and NIR 5x and 100x objectives were used to capture the transmission spectra for 0th and other diffraction orders, respectively. The beam deflection measurement was carried out by the experimental set-up shown in Fig. 3b. A low-power, 5mW coherent laser diode was used as a light source. Fiber-coupled collimators were used to produce parallel beams which lead to the best possible coupling of light into and out of a fiber. A polarizer has been used to make the incident beam polarized according to the measurement requirements. The 100x objective was used to collect all the transmitted light passing through the sample. A lens has been placed in a focal distance of the objective which helps to establish a k-space measurement environment. Another additional lens is placed at a focal distance of the CCD camera to image the back focal plane in real space. The real and k-space measurement has been carried out by altering (keeping and removing) the k-space lens. In the end, a CCD camera was placed at a focal distance from the real-space measuring lens to capture the far-field images.

Sample preparation and sensing measurements. A series of glycerol (Univar AJA242) solutions were prepared from 50% (v/v) to 0.5% (v/v) by serially diluting in 18 MΩ.cm DI water with refractive index spanning a range of 1.401 to 1.3313 (Supporting Information, Figure S12).

The fabricated sample is embedded in a microfluidic chip. Our microfluidics chip supports two input channels, wherein channel 1 is for reference (DI water) and channel 2 is for the analyte of interest. We flow DI water through channel 1 to achieve a base refractive index, and then use channel 2 to induce a change in the refractive index by flowing analyte of interest. As shown in Figure 3g, we flow liquids at a rate of 15 µL/min and alternate between reference and analyte every 15 minutes. While the liquid is flowing through the channels, the data (far-field images) is continuously recorded using a CCD camera.

Surface functionalization and antibody immobilization. Functionalization involves 3 main steps: surface silanization, immobilization of the capture antibody, and blocking of any unreacted epoxide groups to prevent undesirable non-specific protein attachment (Figure 6a). Prior to functionalization, the substrate was cleaned by sonication in acetone and isopropanol followed by drying under nitrogen. The substrate was then treated with oxygen plasma (1 min at 120 W power) to enrich the surface with hydroxyl groups, followed by submerging in 1% v/v 3-Glycidyloxypropyl-trimethoxysilane (GLYMO) in anhydrous toluene for 2 hours. To remove unbound GLYMO and obtain

a uniform silane layer, the substrate was sonicated in anhydrous toluene for 30 s followed by baking for 30 minutes at 110o C. To immobilize the Mouse IgG, 100 µL of 80 µg/mL antibody solution in 10 mM sodium phosphate buffer (pH 9.5) was added to the substrate and incubated for 2 hours at room temperature followed by a thorough wash using DI water. Subsequently, the sample is incubated in a 10 mM cysteine solution in 10 mM sodium phosphate buffer (pH 9.5) for 15 minutes to destroy or block any unreacted epoxide groups. This incubation was followed by another DI water wash and drying under a nitrogen stream.

Antibody binding assay. The anti-Mouse IgG was diluted to the working concentrations (50 µg/mL, 5 µg/mL, 0.5 µg/mL, 50 ng/mL, 10 ng/mL, 5 ng/mL, 1 ng/mL, 0.5 ng/mL, 50 pg/mL, 5pg/mL, 0.5 pg/mL) using 10 mM sodium phosphate buffer (pH 7.4). Working samples were added to the substrate and incubated for 15 minutes at room temperature. Following incubation, the sample was rinsed thoroughly with DI water and dried under a nitrogen stream to remove unbound anti-Mouse IgG. The effect of nonspecific binding and the presence of contaminants in the test sample were also investigated. For further details please refer to Figure S13 in Supporting Information. Optical measurements were carried out in the dry state as three independent trials of at least five replicate measurements each. The full transmission and reflection spectra of different diffraction orders in a dry state are shown in Supporting Information, Figure S14. Due to the dry state environment, the resonant wavelength undergoes a hypsochromic shift from 850 nm to 820 nm. We, therefore, performed biosensing measurements at a wavelength of 820 nm.

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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