Designable spectrometer-free index sensing using plasmonic Doppler gratings

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ABSTRACT: Typical nanoparticle-based plasmonic index sensors detect the spectral shift of localized surface plasmon resonance (LSPR) upon the change of environmental index. Therefore, they require broadband illumination and spectrometers. The sensitivity and flexibility of nanoparticle-based index sensors are usually limited because LSPR peaks are usually broad and the spectral position cannot be freely designed. Here, we present a fully designable index sensing platform using a plasmonic Doppler grating (PDG), which provides broadband and azimuthal angle dependent grating periodicities. Different from LSPR, the PDG index sensor is based on the momentum matching between photons and surface plasmons via the lattice momentum of the grating. Therefore, index change is translated into the variation of in-plane azimuthal angle for photon-to-plasmon coupling, which manifests as directly observable dark bands in the reflection image. The PDG can be freely designed to optimally match the range of index variation for specific applications. In this work, we demonstrate PDG index sensors for large (n = 1.00–1.52) and small index variation (n = 1.3330–1.3650). The tiny and nonlinear index change of water-ethanol mixture has been clearly observed and accurately quantified. Since the PDG is a dispersive device, it enables on-site and single-color index sensing without a spectrometer and provides a promising spectroscopic platform for on-chip analytical applications.

Introduction Plasmonic nanoparticle-based sensors have attracted tremendous attention. The working principle is based on detecting the spectral shift of the localized surface plasmon resonance (LSPR). Since LSPR is determined by the particle shape, materials and the surrounding medium, the change in the environmental index can be quantified by measuring the spectral shift of LSPR. This kind of nanoparticle-based plasmonic sensors has found many applications, including heavy metal pollutant detection, hydrogen sensing, disease diagnosis, chemical reaction monitoring and index sensing. However, the sensitivity of nanoparticle index sensors based on LSPR is typically limited by the broad bandwidth of the LSPR peaks, which is mainly due to the intrinsically low quality factor of plasmonic resonator. To have reasonable sensitivity, LSPR based index sensors either require very large spectral shift upon particle aggregation or rely on sharp spectral features, e.g. the steep edge of Fano-like resonance of specially engineered nanostructures. Moreover, the LSPR of single nanoparticles cannot be freely designed because LSPR is an intrinsic property of the nanoparticle. Therefore, the sensitivity, i.e. the spectral shift per refractive index unit (RIU), can hardly be optimally tuned for different applications. From experimental point of view, the major drawback of LSPR based index sensors is that they require broadband illumination and a spectrometer to perform spectroscopic analysis. Although there are colorimetric sensors developed for bare-eye detection, they are more suitable for qualitative analysis rather than quantitative one, for which high-performance spectrometers are still necessary to detect the small shift of the broad LSPR peaks.

To address these issues, we propose using a plasmonic Doppler grating (PDG) as a designable index sensor, which is capable of on-site, single-color and spectrometer-free sensing. The working principle of PDGs is based on the coupling between free-space photon and surface plasmons (SPs) via the azimuthal angle dependent gratings, instead of LSPR. Typically, direct excitation of SPs by free space photons is not possible because SPs possess larger in-plane momentum than the corresponding pho-
tons. Several schemes have been developed to excite SPs at metal/dielectric boundaries, including Kretschmann-and Otto-configurations and nonlinear wave-mixing and metallic gratings. Among these strategies, metallic gratings have been extensively used and investigated because of its simplicity and well understood coupling mechanism. A grating can effectively excite SPs because it provides lattice momentum to fulfill the momentum conservation condition (Fig. 1a)

$$\frac{2\pi}{\lambda_0} n_d \sin \alpha + \frac{2m\pi}{P} = \pm \frac{2\pi}{\lambda_0} \sqrt{\varepsilon_m n_m^2 - n_d^2 \sin^2 \alpha}.$$ (1)

Here, $\alpha$ is the incident angle, $\lambda_0$ is the vacuum wavelength of the incident light, $\varepsilon_m$ is the permittivity of material, $P$ is the periodicity of the grating, $n_d$ is the refractive index of the surrounding dielectric medium and $m$ is the resonant order. Eq. (1) is the base of index sensing using plasmonic gratings as it links the refractive index of the surrounding medium ($n_d$) to the grating periodicity ($P$). Chirped gratings with one-dimensional gradient of the periodicities have been realized in single structures offer continuously varying periods to improve the feasibility for different applications. For two-dimensional chirping, we have introduced the plasmonic Doppler grating, as described in our previous work. The two-dimensional Doppler grating design enables azimuthal angle dependent chirp of the grating periodicity, which can be described as

$$P(\varphi) = \pm d \cos \varphi + \sqrt{(d/\cos \omega 2\varphi + 2\Delta r^2 - d^2)/2}.\quad (2)$$

Here, $\varphi$ is the in-plane azimuthal angle, at which free space photons effectively excite SPs. $\Delta r$ is the radius increment and $d$ is the displacement of the ring center. They are the two most important design parameters for a PDG because they determine the span and the central wavelength of the spectral window. By choosing these two design parameters, a PDG can be easily designed for optimal sensing performance for large index change or small index change. Inserting Eq. (2) into (1), the coupling wavelength can be expressed as

$$\lambda_0 = \left[ \pm d \cos \varphi \pm \sqrt{(d/\cos \omega 2\varphi + 2\Delta r^2 - d^2)/2} \right] \left( \frac{\varepsilon_m n_m^2}{\varepsilon_m + n_m^2} - n_d \sin \alpha \right).$$ (3)

Equation (3) links the refractive index of the surrounding medium ($n_d$) to the in-plane azimuthal angle ($\varphi$) for PDG index sensing. For a well-designed PDG structure (fixed $\Delta r$, $d$ and $\varepsilon_m$) illuminated by single-color light source impinging at a specific incident angle (fixed $\lambda_0$ and $\alpha$), photon-to-plasmon coupling only happens effectively along specific azimuthal angles determined by the refractive index of surrounding medium. As a result, the index change is translated into the change of in-coupling azimuthal angle, enabling on-site single-color index sensing capability of a PDG. In an experiment, the change of the in-coupling azimuthal angle can be easily observed because photon-to-plasmon coupling would manifest as dark bands in the reflection images. In the following, we demonstrate index sensing with reflection type PDGs (Fig. 1b) optimally designed for large range ($n_d = 1.00$ to $1.52$) and small range ($n_d = 1.3330$ to $1.3650$) index sensing. Experimental results are verified with the analytical model described by Eq. (3).

Figure 1. (a) A schematic illustrating photon-to-plasmon coupling via plasmonic grating. The momentum matching condition described in Eq. (1) governs the excitation of SPs, which can propagate into opposite directions depending on the resonance order $m$. (b) A schematic showing the structure of reflection type PDG index sensor and the configuration of optical characterization. (c) SEM image of a PDG fabricated on the surface of a single-crystalline gold flake ($\Delta r = 500 \text{ nm, } d = 140 \text{ nm}$) for large range index sensing. The scale bar is $2.5 \mu \text{m}$. (d) Optical setup for near-normal incident reflection imaging.

### Method and materials

**Nanofabrication** PDGs were fabricated by applying gallium focused-ion beam (FIB) milling (Helios Nanolab 600i System, FEI Company) to create grooves on the surface of chemically grown ultrasmooth single-crystalline gold flakes on a cover glass coated with an indium-tin oxide (ITO) transparent conductive layer (Fig. 1b). The ITO layer (thickness = 40 nm) helps avoid charging effect during FIB milling and scanning electron microscope (SEM) imaging. The beam current and the acceleration voltage of the FIB are 2.1 pA and 30 kV, respectively. The flakes are chemically stable and grain boundary free, making them an ideal substrate for the fabrication of high-definition plasmonic nanostructures.

### Optical measurement

The reflection images of the fabricated PDGs were recorded by a home-made optical microscope. Figure 1b illustrates the optical characterization in reflection mode. The incident illumination is a near-
normally incident white light and the reflection image is collected by an air objective with low magnification (20×) and small numerical aperture (NA = 0.4), as shown in Figure 1d. Various transparent immersion media with different refractive indexes were introduced onto the surface of PDG and covered by a second cover glass. The used media include air (n_d = 1.00), water (n_d = 1.33), ethanol (n_d = 1.36), tert-butanol (n_d = 1.39), ethylene glycol (n_d = 1.43) and microscope index matching oil (n_d = 1.52). For large range index sensing (n_d = 1.00 - 1.52), bandpass filters with 40 nm bandwidth (FKB-VIS-40, Thorlabs) were used to obtain narrow-band illumination centered at 550 nm and 650 nm. For small range index sensing on water-ethanol mixtures (n_d = 1.3330-1.3650), a 632.8 nm laser line filter was used (bandwidth = 3 nm, FL632.8-3, Thorlabs). To avoid contamination from residual immersion media, after each immersion and sensing process, the PDGs were rinsed with ethanol and deionized water and blown dry with clean pressurized nitrogen.

Results and discussions

The angle distribution of grating periodicity and thus the sensitivity can be freely designed by choosing suitable Δr and d. From azimuthal angle 0° to 180°, the periodicity changes continuously from the maximum Δr + d to the minimum Δr - d. Therefore, PDG allows application-specific optimization of the sensitivity, defined as azimuthal angle change per refractive index unit, Δφ/RIU. For example, for large index change (n_d = 1.00 to 1.52), the PDG has been designed to possess grating periodicity from 360 nm to 640 nm by choosing Δr = 500 nm and d = 140 nm. For sensing the small index variation of the water-ethanol mixture (n_d = 1.3330 to 1.3650), the PDG has been designed to “zoom-in” to this range by choosing Δr = 390 nm and d = 20 nm. The possibility to freely design and optimize the sensitivity for specific applications makes PDG a convenient and unique index sensing platform.

Figure 2a shows the reflection images of the PDG index sensor optimized for large index change. Under the coverage of six different dielectric media, the surrounding refractive index changes from 1.00 to 1.52. As can be seen in the full-color images (left column in Fig. 2a), the color distribution changes with the index. The colors seen in the reflection images are indeed complementary to those coupled into surface plasmons. Therefore, with a band-pass color filter, the SP resonances would manifest themselves as dark bands in the reflection images. For example, in the color images taken with the red filter at 650 nm (middle column in Fig. 2a), dark bands due to SP resonances with m = -1 are clearly observed for refractive index up to 1.43. For index matching oil (n_d = 1.52), the SP mode with m = -1 is no longer observable and the dark bands from the SP modes with m = +1 and m = -2 emerge. If a green filter centered at 550 nm is used, the m = -1 mode observed for the case of air (n_d = 1.00) rapidly moves out of the range of PDG as the index increases and the dark band due to m = -2 resonance emerges and changes its incoupling azimuthal angle with increasing refractive index (right column in Fig. 2a). Using our previously developed algorithm, the intensity angle distribution (Fig. 2b) can be fitted and the azimuthal angle of the SP resonances for different environmental refractive indexes can be quantitatively determined. Reflection image analysis method and fitting parameters are given in the Supporting Information. Figure 2b shows the experimentally observed (dots) and fitted (lines) angle distributions at 650 nm and 550 nm. With the fitting, the azimuthal angles of the dark bands (m = -1 resonance at 650 nm) are quantitatively determined as ±50°, ±126°, ±139°, ±195° and ±166° for surrounding index of 1.00, 1.33, 1.36, 1.39 and 1.43, respectively. By plotting the “open angle” between the two symmetric SP resonance bands (upper panel of Fig. 3a) as a function of the refractive index, calibration curves for quantitative analysis were established. Figure 3b shows the experimental data (points) together with the calibration curves obtained from analytical model for three different SP modes at two wavelengths. The experimental results are in good agreement with the theoretical prediction. The shaded areas in Fig. 3b mark the range of the in-coupling azimuthal angles due to the finite bandwidth of the illumination defined by the bandpass filters. In addition, the spread of the in-coupling angle is also determined by the intrinsic bandwidth of photon-to-plasmon coupling via gratings, which is mainly due to the polarization of the illumination relative to the grating direction, the loss of surface plasmon, and the bandwidth of illumination and the finite illumination and collection angle. These factors have been included in the analytical model to fit the intensity profiles in Fig. 2b.

Figure 2. PDG for wide range refractive index sensing. (a) Reflection images of the PDG index sensor illuminated by a nearly normal incident white light without any filter (left column) and with bandpass filters centered at 650 nm (middle column) and 550 nm (right column). Shown from the top to the bottom rows are the reflection images of a PDG covered with air (n_d = 1.00), water (n_d = 1.33), ethanol (n_d = 1.36), tert-butanol (n_d = 1.39), ethylene glycol (n_d = 1.43) and micro-
scope index matching oil ($n_d = 1.52$). The yellow and white dashed lines mark the SP resonance dark bands with $m = -1$ and $m = 2$, respectively. (b) Reflection intensity profiles obtained with the 650 nm (left) and 550 nm (right) bandpass filters. Solid lines are obtained from fitting the experimental data with the analytical model based on Fano resonance model.

Figure 3b shows an important feature of PDG index sensors, i.e. a PDG offers different SP resonances at different colors with different slopes for index sensing. This grants additional flexibility for applications. Since the slope of a calibration curve means sensitivity, one single PDG simultaneously provides various sensitivities for the user to choose. For example, SP modes with small slopes are suitable for applications involving large index change or broad spectral range. SP modes with large slopes are sensitive to small range index sensing. The users can easily choose the SP modes by changing the color of the illumination using bandpass filters. Overall, the PDG reports the variation of the surrounding refractive index as the change in azimuthal angle of the dark bands due to photon-to-plasmon coupling, similar to the pointer in a speedometer and enabling easy and direct evaluation of the surrounding index without spectrometer.

Finally, we show that a PDG can be easily designed and optimized for quantitative analysis of a tiny index change. Here, the tiny and nonlinear index change due to the formation of hydrogen bonds in water-ethanol mixture was used as the model system. When water ($n_d = 1.3330$) and ethanol ($n_d = 1.3615$) are mixed, the refractive index of the mixture solution can go up to $n_d = 1.3650$, exceeding that of pure ethanol. This is due to the intermolecular interaction between water and ethanol molecules. The nonlinear refractive index change has been broadly used to evaluate the density of the water-ethanol mixture and to indicate their mixing ratio. The peculiar enhancement of the refractive index is very small and cannot be directly observed by currently existing plasmonic index sensing platforms. However, by using special designed PDG with high sensitivity for tiny index change, it is possible to resolve and follow the index change of the mixture of ethanol and water between 1.3330 and 1.3650 and clearly observe the peculiar index enhancement.

To resolve the small index change as a function of molar ratio of ethanol ($x_{\text{EtOH}}$), the PDG index sensor has been designed to have a radius increment $\Delta r = 390$ nm and a displacement of center $d = 20$ nm. The choice of these parameters allows the PDG index sensor to have best sensitivity within the range of index variation between 1.3330 and 1.3650. To enhance the sensitivity, a laser line filter centered at 632.8 nm with a bandwidth of 3 nm is used to produce narrow band illumination. Figure 4a shows the raw reflection images of the same PDG in contact with a series of water-ethanol mixture. Dark bands are clearly observed at different azimuthal angles depending on the molar ratio of ethanol ($x_{\text{EtOH}}$). By fitting the intensity angle distribution profiles (Fig. 4b), the azimuthal angle of SP resonances and the index of each mixture solution can be precisely quantified. The indexes obtained from PDG are plotted in Fig. 4c together with experimental data from previous works using refractometer-based methods. The agreement is very good and the peculiar index enhancement due to hydrogen bonds around $x_{\text{EtOH}} = 0.5$, i.e. the index of the mixture exceeds that of pure ethanol, is also clearly observed. Table 1 summarizes the obtained indexes with errors obtained in this work and compares it with the data from Ref. 43. This example demonstrates PDG’s ability to “zoom in” to a small index window to achieve ultimate resolution in small refractive index window.

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white dashed lines mark the azimuthal angles of the SP resonant bands with $m = -1$. (b) Intensity angle distribution extracted from the reflection images in (a) at corresponding molar ratio of ethanol. Solid traces are obtained from fitting the experimental data with an analytical model based on Fano resonance model. The index of the water-ethanol mixture as a function of the molar ratio of ethanol $X_{\text{EOH}}$. Red open stars mark the data points obtained with the PDG index sensor in this work. Green crosses, grey open triangles and the violet open squares mark the data from Refs. 43, 44 and 45, respectively. The SEM image of the PDG used here is shown in the insert of (c). The scale bar is 2.5 μm.

Table 1. Summary of the open angles between SP resonance bands ($2\varphi$), refractive indexes ($n_d$), and errors in the refractive index ($\Delta n_d$) for the fitting of water-ethanol mixtures. Data from Ref. 43 are also listed for comparison.

| $X_{\text{EOH}}$ | $2\varphi$ | $n_d$ | $\Delta n_d$ | $n_d^{39}$ |
|-----------------|------------|-------|-------------|------------|
| 0.00            | 252.93     | 1.389 | ±0.00011    | 1.3330     |
| 0.05            | 255.83     | 1.3455| ±0.00014    | 1.3410     |
| 0.10            | 259.06     | 1.3528| ±0.00012    | 1.3485     |
| 0.20            | 261.32     | 1.3578| ±0.00014    | 1.3580     |
| 0.50            | 264.65     | 1.3650| ±0.00014    | 1.3650     |
| 1.00            | 261.94     | 1.3592| ±0.00011    | 1.3615     |

Conclusion We have demonstrated the design and applications of PDG index sensors for large range and small range of index change. Since the working principle of PDG index sensor is based on photon-to-plasmon coupling via azimuthal angle dependent plasmonic gratings, the sensitivity of a PDG index sensor can be easily optimized for specific applications by choosing suitable design parameters. With an optimal design, we have demonstrated the ability of PDG to quantitatively measure very small index change of water-ethanol mixture. The peculiar index enhancement in water-ethanol solution has been clearly observed and precisely quantified. Since PDG is a planar and dispersive microstructure, it can be easily integrated into microfluidic channels for on-site spectrometer-free index sensing. With surface functionalization, PDGs can also perform spectrometer-free biochemical analysis. By incorporating active controllable materials, it is also possible to actively control the optical response of a PDG. We anticipate various sensing applications using PDGs.

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Author Contributions
F.-C.L., K.-M.S. and J.-S.H. conceived the idea. F.-C.L. and K.-M.S. performed the optical measurement, numerical simulations and theoretical analysis. F.-C.L., K.-M.S. and Y.-X.H. fabricated the structures. All coauthors contributed to the data interpretation and manuscript preparation. J.P. and J.-S.H. supervised the research. # These authors contributed equally.

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Designable spectrometer-free index sensing using plasmonic Doppler gratings
Supporting Information

Designable spectrometer-free index sensing using plasmonic Doppler gratings

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Reflection Image Analysis of PDG

The reflection images are analyzed to get the intensity distribution at different azimuthal angles. These images are first spatially filtered by a mask to remove the pixels in the irrelevant region out of the structured area. The spatially filtered color images are then converted into gray scale intensity image using the standard default color space,

\[ I = 0.2989 \times R + 0.5870 \times G + 0.1140 \times B \]  \[ \text{[S1]} \]

The azimuthal angle for each pixel is determined based on the formula

\[ \varphi[i,j] = \tan^{-1}\left(\frac{-i+i_0}{j-j_0}\right) \]  \[ \text{[S2]} \]

where \( i \) and \( j \) are the pixel coordinates of the matrix, while \( i_0 \) and \( j_0 \) are the pixel coordinate at the position of the smallest ring with zero diameter. The obtained intensity profiles are then normalized to the maximum pixel value. The normalized intensity is then plotted as a function of the azimuthal angle to demonstrate the intensity angle distribution profile.

The code that used to analyze the reflection images in MATLAB is as follow:

```matlab
% load figure
color = imread('PDG-Air-650.jpg');
gray = rgb2gray(color);  % return the RGB color to gray scale
cgray = imcomplement(gray);
imtool(cgray);
% change the histogram range
% adjust ‘contrast’
% Export to workspace. Set name (‘ncgray’)
n = size(ncgray);
n1 = n(1,1);
n2 = n(1,2);
matrix = ones(n1*n2,4);
for ny = 1:n1
    for nx = 1:n2
        matrix(n2*(ny-1) + nx,1) = n2*(ny-1) + nx;
        matrix(n2*(ny-1) + nx,2) = nx;
        matrix(n2*(ny-1) + nx,3) = ny;
        matrix(n2*(ny-1) + nx,4) = ncgray(ny,nx);
    end
end
dlmwrite('PDG-Air-650.txt',matrix);
```
Reflection Intensity Profile Fitting

The azimuthal angle of the dark band is quantified by fitting the angle distribution intensity profiles with the following equation,

\[
I(\phi) = \sum_m \left( \frac{P(\phi + \gamma) - P(\phi - \gamma)}{w_m P_m} \right)^2 \cdot \frac{1}{1 + (1 - \eta)(\sin(\phi + x_0 - \gamma))^2} \cdot A_m + y_0
\]

Parameters using in Eq. S3 are listed below.

- \( I(\phi) \): reflection intensity at azimuthal angle \( \phi \), \( m \): resonance order; \( P(\phi) \): azimuthal angle-dependent periodicity; \( P(\phi_m) \): resonant grating periodicity for the \( m \)-th order resonance; \( w_m \): spectral width of the Fano resonance for the \( m \)-th order resonance; \( q_m \): asymmetry parameter for the \( m \)-th order resonance; \( b_m \): modulation damping parameter for the \( m \)-th order resonance; \( \gamma \): angle between incident light polarization and the edge of the rings; \( \eta \): degree of polarization of the excitation in the experiment; \( A_m \): amplitude of the \( m \)-th order resonance; \( y_0 \): amplitude offset; \( x_0 \): angle offset;

The fitting formula takes into account Fano-like resonance model and takes into account the broadening due to the loss of SPs, the coupling to dark modes, the degree of polarization of the illumination and the incident polarization angle with respect to the PDG grating edge. With the fitting, the resonant grating periodicity for the \( i \)-th order resonance can be precisely obtained. Consequently, the azimuthal angle of the dark bands can be precisely determined. The fitting parameters used for the experimental data in Fig. 2 in the main text are summarized in Table S1 below, respectively. The subscripts denote the order of the mode.

Table S1 Parameters for fitting reflection images (Bandpass filter centered at 550 nm, 600 nm and 650 nm) (see detail from our previous paper: Nanoscale, 2017, 9, 10811-10819.)

| Parameters | Wavelength | 550 nm | 600 nm | 650 nm |
|------------|------------|--------|--------|--------|
| \( p_m \) (nm) | \( m = -1 \) | 323.40 | 444.78 | 495.37 |
| | \( m = +1 \) | 533.21 | 557.06 | 604.59 |
| \( w_m \) (nm) | \( m = -1 \) | 183.51 | 75.90 | 69.52 |
| | \( m = +1 \) | 20.21 | 12.78 | 14.02 |
| \( A_m \) | \( m = -1 \) | 0.92 | 0.82 | 0.81 |
| | \( m = +1 \) | 0.22 | 0.05 | 0.06 |
| \( q_m \) | \( m = -1 \) | -0.15 | -0.06 | -0.058 |
| | \( m = +1 \) | -0.18 | -1 | -1.14 |
| \( b_m \) | \( m = -1 \) | 0.14 | 0.21 | 0.24 |
| | \( m = +1 \) | 0.01 | 0 | 0 |
| \( \Delta r \) (nm) | | 400 |
| \( d \) (nm) | | 200 |
| \( \kappa \) | | 0.2 |
| \( \gamma \) (°) | | 94.39 |
| \( y_0 \) | | 1.02 |

Open angle 2\( \phi \) & Coefficient of determination \( R^2 \)

| \( 2\phi \) (°) | \( m = -1 \) | 193.68 | 128.1 | 101.48 |
| | \( m = +1 \) | 79.22 | 62.72 | |
| \( R^2 \) | | 0.82 | 0.81 | 0.80 |