Subradiant Dipolar Interactions in Plasmonic Nanoring Resonator Array for Integrated Label-Free Biosensing

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ABSTRACT: With the development of advanced nanofabrication technologies over the past decade, plasmonic nanostructures have attracted wide attention for their potential in label-free biosensing applications. However, the sensing performance of nanostructured plasmonic sensors is primarily limited by the broad-line-width features with low peak-to-dip signal ratio in the extinction spectra that result from strong radiative damping. Here, we propose and systematically investigate the in-plane and out-of-plane dipolar interactions in an array of plasmonic nanoring resonators that are from the spatial combination of classic nanohole and nanodisk structures. Originating from the strong coupling of the dipolar modes from parent nanohole and nanodisk structures, the subradiant lattice plasmon resonance in the nanoring resonator array exhibits narrow-line width spectral features with high peak-to-dip signal ratio and strong near-field electromagnetic enhancement, making it an ideal platform for high-sensitivity chemical and biomedical sensing. We experimentally demonstrate that the plasmonic nanoring resonator array can be used for high-sensitivity refractive index sensing and real-time monitoring of biomolecular specific binding interactions at nanomolar concentration. Moreover, due to its simple normal incident illumination scheme and polarization independent optical response, we further transfer the plasmonic nanoring resonator array onto the optical fiber tip to demonstrate an integrated and miniaturized platform for label-free remote biosensing, which implies that the plasmonic nanoring resonator array may be a potential candidate for developing high performance and highly integrated photonic biosensing systems.

KEYWORDS: plasmonic nanostructure, biosensing, dipolar interaction, fiber optics, protein binding, point of care diagnostics

Localized surface plasmon resonance (LSPR) in a variety of plasmonic nanostructures, such as discrete metallic nanodisks and nanoparticles, have received significant attention for their potential in low-cost, label-free biosensors. In contrast to the conventional propagating surface plasmon based sensors relying on bulky prism-coupling mechanism, the size of nanostructured LSPR sensors can be reduced to the micrometer scale. This makes them very attractive for the design of portable devices for point-of-care testing (POCT) application. In contrast to the centralization and increased efficiency in laboratory diagnostics, POCT shortens the time of transport and preparation of clinical samples and biochemical-test results are rapidly available at the point of care. But unfortunately, the sensing performance of LSPR sensor is always limited by the broad-line width features with low peak-to-dip signal ratio in the extinction spectra resulting from strong radiative damping, which significantly limits the intensity of localized electromagnetic fields around the isolated nanostructures. Hence, the quest to suppress the radiative damping is essential in the research field of plasmonic biosensing. Recent works have suggested that by carefully engineering plasmonic nanostructures, such as concentric nanocavity and closely packed nanoparticle cluster, higher localized electromagnetic fields and narrower line-shape can be achieved for subradiant plasmon resonance, which in principle can be used to improve the sensing performance. Another effective approach to manipulate plasmon line width spectral features of nanostructures is to assemble them into an array. Because optical energy scattered by one nanostructure unit cell will be captured by neighboring nanostructure as plasmon instead of decaying as free-space propagating light, the array exhibits completely different optical responses from those of an isolated nanostructure. Recently, it has been demonstrated that strongly coupled one- and two-dimensional nanostructure arrays can produce narrow lattice plasmon resonance by suppressing radiative losses. Therefore,

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nanostructure arrays supporting subradiant lattice plasmon resonance have emerged as a powerful photonic platform for sensing applications.

Here, we develop a novel, high-sensitivity label-free biosensing platform based on a plasmonic nanoring resonator array (PNRA), which is constructed from the spatial combination of nanohole and nanodisk arrays. Based on coupled dipole theory, the in-plane and out-of-plane strong coupling of the dipolar modes from parent nanohole and nanodisk structures in PNRA generates a sharp subradiant lattice plasmon resonance with an extremely narrow line width (~7 nm), a high peak-to-dip signal ratio (0.7), and high refractive index sensitivity (~545 nm RIU⁻¹). The PNRA device are utilized here to experimentally achieve high sensitivity microfluidic refractive index sensing and real-time monitoring of biomolecular interaction between Ribonuclease B (RNase B) and Concanavalin A (Con A) protein molecules at ultralow concentrations. Importantly, compared to previous works that use complicated angular illuminations and specific polarizations to excite high-order guide modes in metamaterials or optical Fano resonances in nanostructures for sensing, the subradiant fundamental lattice plasmon resonance in PNRA can be excited by using normally incident randomly polarized light and generates a stable spectral lineshape with a high peak-to-dip signal ratio around the resonant wavelength. This implies that our device is able to be efficiently probed where the incident and reflected light are efficiently collected by the same optical path. As a proof-of-concept demonstration, we successfully transfer the PNRA onto the tip of an optical fiber for further miniaturization and integration. The sensing performance of optical fiber sensor with PNRA confirms it as a robust tool for remotely detecting biomolecules interaction.

■ RESULTS

Fabrication and Characterization of PNRA. The schematic diagram of the designed PNRA biosensor is depicted in Figure 1a. The structure can be regarded as the spatial combination of simple nanohole and nanodisk arrays arranged in a hexagonal lattice, where the gap between nanohole and nanodisk forms a nanoring. Due to the axial symmetry of the structure, the optical properties of PNRA are independent of the polarization direction of the normally incident light. The reflectance spectrum of the structure is investigated using finite-difference time-domain (FDTD) algorithm. The structural parameters are as follows: periodicity $P$ = 640 nm, inner radius $r$ = 150 nm, outer radius $D$ = 240 nm, and the thickness of Au film is 100 nm. The top surface of the PNRA is covered with a medium having a refractive index (RI) of 1.331 to match that of the aqueous solution in experiment. The calculated reflectance spectrum is plotted in Figure 1b (blue solid line), where the two resonance dips can be observed at wavelengths of $\lambda_1$ = 758 nm and $\lambda_2$ = 838 nm. The reflectance dip at $\lambda_1$ has a full-width at half-maximum (fwhm) line width of ~7 nm, which results in a quality factor (Q-factor) that reaches ~108. The reflectance dip at $\lambda_2$ has ~14 nm fwhm and ~60 Q-factor (see Methods for details on the extraction of fwhm and Q-factor).

Inset of Figure 1a shows the top-down scanning electron microscopy (SEM) image of the fabricated sample. Before the optical measurements, the top surface of the PNRA is immersed in an aqueous solution with a polydimethylsiloxane (PDMS) flow cell. The fabricated structure is illuminated with a randomly polarized normally incident white light from the substrate side. The experimentally measured reflectance spectrum is depicted in Figure 1b (red solid line), where two resonance dips are also observed at the wavelengths of 750 and 838 nm. The measured fwhm and Q-factor of the resonance dip at $\lambda_1$ ($\lambda_2$) are ~15 nm (~40 nm) and ~50 (~21), respectively. The relative wider fwhm and lower Q-factors achieved in experiment can be attributed to three factors: First, surface roughness of fabricated structure is limited by the grain sizes of multicyrstalline gold film produced by vacuum coating, which introduces scattering losses. Second, the geometry parameters of the fabricated sample in experiment are slightly different from those of simulated model. For example, outer radius ($D$)
of nanoring array in experiment may be larger than that of numerical simulation. As shown in Figure S1a, we theoretically find that the line-shape of resonant wavelength \( \lambda_1 \) becomes wider with the increase of outer radius. Third, an objective lens with a numerical aperture (NA) of 0.10 is used for the spectral measurements. A nonzero NA objective results in sample excitation at oblique incidence angles, which decreases the spatial coherence among different modes and generates a wide spectral line-shape in experiment.\(^{48,49}\) The simulated and measured reflectance spectra for a different outer radius of the nanoring and using a different numerical aperture of the objective are shown in Figure S1b. Nevertheless, both the spectral line-shape and the position of the resonance dips measured in the experiment are in good agreement with those calculated using FDTD simulation. Figure 1c,d depicts electric field distribution on the top and bottom surfaces of nanoring, nanohole, and nanodisk arrays at resonant wavelengths \( \lambda_1 \) and \( \lambda_2 \), where the directions of dipolar modes are indicated by the black arrows. (e) Calculated out-of-plane normalized surface charge distributions of PNRA at resonant wavelengths \( \lambda_1 \) and \( \lambda_2 \). The top and bottom surfaces and out-of-plane are indicated by blue, green, and red planes, respectively. To clearly exhibit out-of-plane normalized surface charge distributions, Figure 2e is plotted out-of-scale compared to the actual structure size.

Figure 2. Dipolar interactions in the PNRA. (a) Calculated reflectance (absorptance) spectrum of the PNRA with periodicity \( P = 640 \) nm, inner radius \( r = 150 \) nm, outer radius \( D = 240 \) nm, and Au film thickness 100 nm. The calculated in-plane normalized surface charge distributions of the relevant modes at both top and bottom surfaces of (b) nanoring, (c) nanohole, and (d) nanodisk arrays at resonant wavelengths \( \lambda_1 \) and \( \lambda_2 \), where the directions of dipolar modes are indicated by the black arrows. (e) Calculated out-of-plane normalized surface charge distributions of PNRA at resonant wavelengths \( \lambda_1 \) and \( \lambda_2 \). The top and bottom surfaces and out-of-plane are indicated by blue, green, and red planes, respectively. To clearly exhibit out-of-plane normalized surface charge distributions, Figure 2e is plotted out-of-scale compared to the actual structure size.

Theoretical Analysis of Dipolar Interactions in PNRA.

The calculated reflectance (absorptance) spectrum of the PNRA exhibits two resonance dips (peaks) at \( \lambda_1 = 758 \) nm and \( \lambda_2 = 838 \) nm, as shown in Figure 2a. These two resonance dips can be qualitatively explained by using plasmonic hybridization theory.\(^{50−53}\) To further understand these resonances in detail, we first calculate the in-plane normalized surface charge distributions of the relevant modes at both top and bottom surfaces of nanoring, nanohole, and nanodisk arrays at resonant wavelengths \( \lambda_1 \) and \( \lambda_2 \) (Figure 2b–d). As expected, the mode distributions of PNRA are exactly the spatial superposition of the in-plane dipolar modes, respectively, from nanohole and nanodisk structures. At resonant wavelength \( \lambda_1 \), dipolar modes at the top surfaces of nanohole and nanodisk structures have opposite orientations. The antiparallel dipolar interaction reduces the total dipole momentum and minimizes the radiative damping of the PNRA system, which is a typical subradiant characterization.\(^{28,29}\) As a result, antiparallel dipolar at the top surface can effectively trap the incident light and excite subradiant lattice plasmon resonance, resulting in a large narrow-line-width absorbance peak at \( \lambda_1 \). On the other side, in-plane dipolar modes at the bottom surfaces of nanohole and nanodisk structures are oriented in the same direction at \( \lambda_1 \). The parallel dipolar interaction enhances the total dipole momentum and results in a rapid depletion of the plasmon energy. Compared with the top surface, the optical intensity at the bottom surface of a PNRA is much weaker (Figure 1c). Therefore, the enhanced optical field at the top surface for resonance wavelength \( \lambda_1 \) is sensitive to the change of ambient environment, which can be used for a sensing application.
Contrary to $\lambda_1$, the dipolar interactions at resonant wavelength $\lambda_2$ are opposite: parallel dipolar interactions occur at the top surface while antiparallel dipolar interactions occur at the bottom surface. Therefore, the optical energy is mainly localized at the bottom surface of PNRA at the wavelength of 838 nm (Figure 1d). Because the bottom surface of PNRA is glass substrate and not in contact with the microfluidics, the plasmon resonance at $\lambda_2$ cannot be used for sensing applications. Moreover, the optical field at the top surface for resonance wavelength $\lambda_2$ is immune to the ambient environment, which can serve as a self-reference channel for sensing detection.

Besides investigating the in-plane dipolar interactions, we also calculate the out-of-plane normalized surface charge distributions of PNRA at resonant wavelengths $\lambda_1$ and $\lambda_2$ as shown in Figure 2e. It can be clearly seen that at the resonant wavelengths, the normalized surface charge distributions, respectively, form an out-of-plane dipolar (quadrupolar) mode for the parent nanohole (nanodisk) structure. The out-of-plane quadrupolar mode in nanodisk array originates from the geometry-dependent dipolar interaction between large nanoparticle structures arranged in a two-dimensional array.9

Due to the interference between out-of-plane dipolar and quadrupolar modes, the PNRA exhibits a Fano-like asymmetric peak-and-dip spectral profile at resonance and strongly localizes the optical field around the structure. As shown in Figure S2, the absorption and optical field intensity at the top surface of the PNRA are much stronger than those of pure nanohole and nanodisk structures at the resonant wavelengths, which is beneficial for sensing applications. This optical field primarily overlaps with the volume containing the material to be sensed, satisfying an important criterion for development of a plasmonic sensor with high figure-of-merit (FOM).

**Sensing Performance of the PNRA.** To examine the real-time sensing performance of the PNRA as a refractive index sensor, a microchannel-based miniaturized biosensor platform is fabricated by assembling a microfluidic system on top of the PNRA. To calibrate and determine the detection limit of the sensor, sodium chloride (NaCl) solutions with refractive indices (RIs) of 1.3310, 1.3420, 1.3512, 1.3596, 1.3688, and 1.3780 are manually injected into the flow channel using a peristaltic pump at a constant flow rate of 0.2 mL/min. The RIs of the sodium chloride solutions are calibrated using an Abbe refractometer. The measured reflectance spectra of the PNRA coated with NaCl solutions of different RIs are shown in Figure 3a. As the RI of the injected solution increases, a red shift of the resonance dip around the wavelength of 750 nm occurs. For the second resonance dip around the wavelength of 838 nm, because the optical intensity localized at the bottom surface is noncontact with NaCl solutions, no variation in the measured spectrum is observed. Within the investigated RI range, the line-shape of the fundamental lattice plasmon resonance does not vary and keeps a very high peak-to-dip signal ratio, indicating a stable operation of the sensing device. The FDTD calculated reflectance spectra for an equivalent change in the bulk refractive index of the media surrounding that PNRA are shown in Figure S3a. The calculated spectral resonance line-shape and its location exhibit good agreement with the experimental results. The peak-to-dip signal contrast around the resonant wavelength, SC, defined as $SC = R_{\text{peak}} - R_{\text{dip}}$ is an important parameter associated with the signal-to-noise ratio of the sensing devices. Compared to that of nanohole and nanodisk structures (Figure S4), the SC of the PNRA structure ($\sim 0.7$) is higher in simulation and experiment thanks to the highly localized optical fields caused by the subradiant dipolar interactions. This value is several times higher than that of other nanostructured plasmonic sensors31,29,31,35,38 and will be beneficial for easily detecting and distinguishing the sensing signal from background noise.

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**Figure 3.** Evaluation of PNRA sensor device integrated with microfluidics. (a) Measured reflectance spectra of the sensor device for different refractive index of sodium chloride solutions. (b) Relationship between experimentally measured resonance dip position and the refractive index. Uncertainties in (b) are based on the standard deviations of five repeated measurements for every experimental data point. The upper and lower limits of the error bar in (b) are too small to be clearly seen. (c) Wavelength shifts of dip for different refractive index of sodium chloride solutions as a function of time. (d) The relationship between wavelength shifts normalized experiment noise (N) and refractive index change in order to evaluate the limit of detection for a PNRA.
Besides peak-to-dip signal ratio, we also analyze another three critical parameters: RI sensitivity, figure of merit (FOM), and limit of detection (LOD) to quantitatively evaluate the sensing performance of the device. RI sensitivity, $S$, is defined as the resonance wavelength shift, $\Delta \lambda$, for a change in the bulk RI, $\Delta n$ (i.e., $S = \Delta \lambda / \Delta n$). The spectral-dip location in the reflectance spectra as a function of RI is plotted in Figure 3b. A RI sensitivity of 513 nm RIU$^{-1}$ is obtained by calculating the slope of the linear-fit to the experimental results, which agrees well with the calculated sensitivity of 545 nm RIU$^{-1}$ as shown in Figure S3b. Furthermore, we respectively calculate the influence of structure parameters of nanoring array (including periodicity $P$, inner radius $r$, and outer radius $R$) on resonant wavelength $\lambda_0$ and RI sensitivity. The results have been plotted in Figure S5. These results indicate both resonant wavelength $\lambda_0$ and RI sensitivity increase linearly with increased periodicity. In order to achieve the sensing detection of PNRA structure at the visible frequency, the periodicity $P = 640$ nm is selected in the paper. With fixed structure periodicity, optimized RI sensitivity can be obtained by appropriate selection of the size of inner and outer radii. In addition, the change of inner and outer radii could also significantly influence the peak-to-dip signal ratio at the resonant wavelength $\lambda_0$. FOM, defined as $FOM = S/(2\gamma)$ (the sign $2\gamma$ refers to the fwhm of the resonance dip obtained in the Q-factor extraction), is a widely accepted metric that determines the sensitivity performance of an optical sensor, and is inversely proportional to the spectral sharpness of resonance. Experimentally measured FOM value is $\sim 35$ RIU$^{-1}$ (Figure S6), which is several times higher than the reported SPR sensor based on prism-coupling configuration$^{54}$. The FDTD calculated FOM value of $\sim 78$ RIU$^{-1}$ is a factor of 2 higher than the experimentally measured values due to a wider $\Delta \lambda$ obtained in experiment. In principle, the experimental FOM can be further improved by optimizing nanofabrication techniques to achieve smaller metal scattering losses, or by using a lower NA objective lens in the measurement.

In addition to the RI sensitivity and FOM, LOD is also a key parameter for characterizing the performance of a sensing device. The LOD is defined as $LOD = N/S = \Delta n/(\Delta \lambda/N)$, where $S$ is RI sensitivity and $N$ refers to the experimental spectral noise. In our experiment, $N$ is obtained by calculating the standard deviation of the experimental signal for a duration of 80 min with a time resolution of 5 s. $S$ is measured by evaluating the relationship between the signal-to-noise ratio ($S/N$) and the change of RI shown in Figure 3d, we can achieve a LOD of $\sim 1.3219 \times 10^{-4}$ RIU for our sensor device. This LOD value is comparable to that of the previously reported SPR sensor based on prism-coupling configuration$^{54}$. The LOD value is $\sim 35$ RIU$^{-1}$

**Real-Time Detection of Specific Binding between Protein Molecules.** To further demonstrate the ability of PNRA as high-performance biosensor, we perform the experiments to detect in real-time the specific binding of RNase B and Con A protein molecules in solution on the sensing surface. The specific binding of RNase B and Con A has been extensively studied as a standard affinity model for biosensors$^{55,56}$. To capture the Con A biomolecule at different concentrations, the fabricated PNRA sensor is functionalized with immobilized RNase B. The immobilization process of RNase B is depicted in Figure 4a. First, the sensing chip is cleaned with ultrapure water and ethanol. After a subsequent wash, the sensing substrate is dipped into an ethanol solution of 11-mercaptoundecanoic acid (MUA, 10 mM) at room temperature for 24 h to self-assemble an alkanethiol monolayer on the surface of gold layer. The unreacted thiol molecules are washed away by using ethanol. After drying under $N_2$ gas, a
mixed aqueous solution containing 1-ethyl-3-(3-dimethylamino-propyl) carbodiimide hydrochloride (EDC, 0.55 M) and N-hydroxysuccinimide (NHS, 0.5 M) is used for 30 min at 4 °C to activate the alkanethiol monolayer on the gold surface. Then, the sensing chip is rinsed with deionized water and dried under N2 gas. After activating, the sensing chip is equipped with the microfluidic channel. The growth process of biomolecules on the surface of the structure is dynamically monitored in real time. 0.1 mg/mL RNase B in phosphate buffered saline (PBS) is injected into the sensor microchannel for 30 min to form a stable monomolecular layer. After the rinsing in PBS buffer, bovine serum albumin (BSA, 0.1 mg/mL) is used for 30 min to deactivate the remaining activated carboxyl sites that did not combine with the RNase B.

Different concentrations of Con A ranging from 0.02 mg/mL to 0.20 mg/mL are monitored by regenerating the biosensor surface. Figure 4b shows the wavelength changes of resonance dip \( \lambda_1 \) with a time resolution of 5 s to dynamically monitor the specific binding between RNase B and Con A. The monitoring process is depicted as follows: First, PBS solution is injected into the flow channel to obtain the baseline. Then, Con A solution is pumped to bind with RNase B on the sensing surface. Next, PBS buffer solution removes the unbound Con A molecules. Finally, the 0.8 mol/L urea solution is used to strip the surface-bound Con A molecules to effectively regenerate the sensing region, and the next concentration can be tested sequentially. As shown in Figure 4b, the baseline of our sensor chip is very stable during the measurement. Abrupt changes of the resonance wavelength after injecting Con A are observed in the sensing curves, which is attributed to the occurrence of specific binding between Con A and RNase B. The association and dissociation rate between Con A and RNase B is also calculated based on sensing curves in Figure 4b. As a contrast, the nonspecific binding between anti-IgG and RNase B does not result in the red shift of resonance wavelength, which illustrates specific binding between Con A and RNase B. To validate reliability and repeatability, each concentration of Con A is measured three times using the same sensor chip. The experiment results are summarized in Figure 4c. Determined from the experimental noise and the relationship between the wavelength response and Con A concentration, the detection limit for Con A is estimated to be 4.6 \( \mu g/mL \) (45 nM), which

Figure 5. PNRA integrated with the optical fiber for remote biosensing. (a) Schematic representation of the optical fiber sensor device with PNRA integrated on the end face of optical fiber. (b) Oblique-view SEM images of the fabricated PNRA on the optical fiber end face. Scale bar, 50 \( \mu m \). Inset at left corner is magnified SEM image. Scale bar, 1 \( \mu m \). Inset at right corner is microscope image. Scale bar, 150 \( \mu m \). (c) Experimentally measured reflectance spectra of the optical fiber sensor device for various refractive index of NaCl solutions. (d) Relationship between measured resonance dip position and the refractive index. Uncertainties are based on the standard deviations of five repeated measurements for every experimental data point. (e) Real-time specific detection of optical fiber sensor device for different concentrations of Con A. The turquoise line shows the nonspecific binding of RNase B and anti-IgG of 0.1 mg/mL. (f) Relationship between the measured wavelength position and Con A concentration. Each measurement at a given concentration is repeated three times.
indicates that the PNRA offers a high performance photonic platform for label-free biomolecular detection.

**PNRA Integrated on the Optical Fiber for Label-Free Remote Biosensing.** As we analyzed above, the subradiant dipolar interactions and lattice plasmon resonance can be excited by the normally incident randomly polarized light. Therefore, the PNRA structure is able to be transferred onto the tip of optical fiber for further integration and miniaturization. Herein we demonstrate an optical fiber biosensor by integrating the PNRA on the fiber tip as a remote biosensing platform. The schematic diagram of the designed optical fiber biosensor is depicted in Figure 5a. The structural parameters of PNRA on the fiber tip are identical to that on the quartz substrate. The designed optical fiber biosensor is fabricated by sequentially depositing 3-nm-thick Ti layer and 100-nm-thick Au film on the fine polishing end face of a 20-cm-long optical fiber (the specification of fiber: core/cladding/coating, 200/220/270 μm; NA ~ 0.22). The PNRA is patterned using FIB over a 150 μm × 150 μm area. Figure 5b shows SEM and microscope images of the fabricated sample.

To evaluate the sensing performance of optical fiber sensor integrated with PNRA, a homemade flow cell is assembled on the fiber tip. The measured reflectance spectra for the NaCl solutions with different RIs are shown in Figure 5c. The RIs and flow rate of NaCl solutions for the measurement using the optical fiber sensor are identical to that of the quartz substrate device. It can be clearly seen that resonance dip around the wavelength of 755 nm has an obvious red shift and the resonance dip around 850 nm does not vary with the increase of RIs of NaCl solutions. Compared to that of PNRA on the quartz substrate, the line-shape of the resonance dip broadens for the PNRA on the fiber tip because the fiber used in the experiment has a larger NA. The spectral-dip location around the wavelength of 755 nm as a function of RI is depicted in Figure 5d. An RI sensitivity of around 520 nm RIU−1 is obtained for the optical fiber sensor, which matches well with that of a quartz substrate device.

Finally, to determine the capability of our designed optical fiber sensor for dynamic monitoring biomolecule interactions, we performed the same experiment to detect in real-time the binding of RNase B and Con A protein molecules in fiber sensor for dynamic monitoring biomolecule interactions, which matches well with that of conventional propagating surface plasmon based sensors.23,24 Furthermore, although here we design and perform experimental demonstrations on PNRA sensor at visible frequency, its concept and sensing functionality can be easily extended to the infrared range by changing the structural parameters. It is notable that RI sensitivity of the PNRA sensor would increase for the infrared operation frequency because the electromagnetic loss within the metal layer is reduced at longer wavelength. For example, as shown in Figure 5Sa and b, when the resonance wavelength λ1 is extended to the wavelength 5000 nm, the RI sensitivity of resonance wavelength λ1 reaches up to 3800 nm RIU−1. In addition, when the resonance wavelength λ1 is adjusted from the visible to the infrared region, the line width of the resonance spectrum almost remains unchanged. Therefore, the FOM of the PNRA sensor can also be further increased at longer wavelength.

In summary, we demonstrate a PNRA device which can be used as a high-performance biosensing platform. The coupling of dipolar modes in nanohole and nanodisk arrays gives rise to a robust subradiant lattice plasmon resonance in the PNRA. The narrow spectral line width with high peak-to-dip signal ratio and strong near-field electromagnetic enhancement boost the refractive index sensitivity and FOM associated with the sensing device. In the experimental demonstrations, the PNRA not only realizes high sensitivity refractive index sensing, but also achieves real-time monitoring of biomolecular specific binding interactions at nanomolar concentrations. Compared with other plasmonic sensing devices, the PNRA does not require complicated angular illuminations and has polarization independent optical responses. Due to simple normal illumination and signal acquisition architecture, we transfer the PNRA onto the optical fiber tip and successfully achieve the integrated and remote biosensing. We envision that the PNRA may be a potential candidate for developing a high performance photonic platform for point-of-care, label-free chemical and biomedical sensing.

**METHOD**

**FDTD Simulation.** The simulations are performed based on the FDTD algorithm to obtain the reflectance spectra, electric field distribution, and charge distribution of the PNRA at normal incidence. The periodic boundary conditions are applied in both x and y direction and perfectly matched layers are used in the z direction. The grid size along the x, y, and z direction is 2 nm × 2 nm × 2 nm, respectively. The dielectric permittivity of bulk gold in the visible and near-infrared region is from Johnson and Christy.57

**Preparation of Plasmonic Nanoring Resonators Array.** First, a 3 nm Ti film and a 100 nm Au film are sputtered sequentially onto a 10 mm × 10 mm quartz substrate and on the fine polishing end face of a 20-cm-long optical fiber. The deposition rate for Ti and Au is R_{Ti} ≈ 0.016 nm/s and R_{Au} ≈ 0.05 nm/s, respectively. Then, subwavelength nanorings are fabricated by FIB milling using a dual-beam (FIB/SEM) system (Ga+ ions, 24 pA beam current, 30 keV beam energy). The end face of the optical fiber is polished in sequence using a fiber optic polishing machine with 9 μm, 3 μm, 1 μm, 0.03 μm grit emery papers.

**Q-Factor Extraction.** We use an analytical model to extract the Q-factor of the resonant dip in the PNRA. The calculated and measured spectra are fitted to an analytical model described by \( Q = \frac{a_1}{a_2} + \frac{b}{(\omega - \omega_0 + j\gamma)^2} \), where the parameters \( a_1, a_2, \) and \( b \) are constant real numbers; the sign \( j \) stands for...
imaginary unit; $\omega_0$ and $\gamma$ refer to the center resonant frequency and overall damping rate of resonance. The calculated and measured Q-factors are then determined by $Q = (\omega_0/2\gamma)$.

**Measurements of Reflectance Spectra.** For the structure with PNRA on the quartz substrate, a home-built polydimethylsiloxane (PDMS) flow cell is employed as holder of liquid solution before optical measurement. The flow cell is sandwiched between the sensing substrate and a PMMA plate. Inlet and outlet holes are drilled through the PMMA plate to connect the tubing. All reflectance spectra on the quartz substrate are taken on a UV–NIR spectrometer (HR4000, Ocean Optics, Inc.) and is displayed by a computer.

Light from a halogen lamp (HL-2000-HFSA, Ocean Optics, Inc.) is launched into one splitter end of an optical fiber jumper. The transmission spectrum is collected at the other splitter end of the fiber jumper. The transmission spectrum is collected at the other splitter end of the fiber jumper through the spectrometer (HR4000, Ocean Optics, Inc.) and is displayed by a computer. The probe is mounted in the combined end of the fiber jumper. In the above optical measurement, a peristaltic pump is used to inject sample solutions with a constant flow rate of 0.2 mL/min.

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