

# Highly Sensitive Refractive Index Sensors with Plasmonic Nanoantennas—Utilization of Optimal Spectral Detuning of Fano Resonances

Martin Mesch,<sup>†</sup> Thomas Weiss,<sup>†</sup> Martin Schäferling,<sup>†</sup> Mario Hentschel,<sup>†</sup> Ravi S. Hegde,<sup>‡,§</sup> and Harald Giessen<sup>\*,†</sup>

<sup>†</sup>4<sup>th</sup> Physics Institute and Research Center SCoPE, University of Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany <sup>‡</sup>Department of Electrical Engineering, Indian Institute of Technology Gandhinagar, Palaj, Gujarat 382355, India

<sup>§</sup>Department of Electronics and Photonics, Institute of High Performance Computing, 1 Fusionopolis Way, #16-16 Connexis North, Singapore 138632

Supporting Information

**ABSTRACT:** We analyze and optimize the performance of coupled plasmonic nanoantennas for refractive index sensing. The investigated structure supports a sub- and super-radiant mode that originates from the weak coupling of a dipolar and quadrupolar mode, resulting in a Fano-type spectral line shape. In our study, we vary the near-field coupling of the two modes and particularly examine the influence of the spectral detuning between them on the sensing performance. Surprisingly, the case of matched resonance frequencies does not provide the best sensor. Instead, we find that the right amount of coupling strength and spectral detuning allows for achieving the ideal combination of narrow line width and sufficient excitation strength of the subradiant mode, and therefore results in optimized sensor performance. Our findings are confirmed by



experimental results and first-order perturbation theory. The latter is based on the resonant state expansion and provides direct access to resonance frequency shifts and line width changes as well as the excitation strength of the modes. Based on these parameters, we define a figure of merit that can be easily calculated for different sensing geometries and agrees well with the numerical and experimental results.

KEYWORDS: plasmon, sensing, coupled nanoantennas, detuning, perturbation theory, Fano resonances, resonant state expansion

In the past few years, localized surface plasmon resonances have been intensely investigated with respect to their sensing capabilities.<sup>1-9</sup> The principle of plasmonic sensors is based on the strong dependence of the resonance frequency on the dielectric environment. Even tiny changes of the material composition and, therefore, the local permittivity of the surroundings lead to resonance shifts that can be detected via optical readout. This universal mechanism can be utilized to detect a broad range of different analytes, such as gases, liquids, or biomolecules.<sup>10-15</sup> Obviously, with the ultimate goal of detecting single molecules in mind, optimization of such sensors is a major challenge in this field. Besides influences such as the material composition<sup>16,17</sup> and efficient analyte delivery,<sup>18</sup> the chosen geometry of the plasmonic nanostructures has a major impact on the sensing performance. Changing the geometry, the properties of the plasmonic resonances, as well as their interaction strength with the environment can be engineered.

Fano resonances in multiparticle systems with complex spectral features due to the interplay of different modes are of

particular interest for sensing applications.<sup>19–23</sup> The use of subradiant modes allows decreasing the line width of the generally broad and lossy dipolar plasmonic resonances. Shifts of the corresponding resonances result in significant transmittance differences at a fixed frequency due to the steep spectral slopes. Thus, such resonances are superior to the usual dipolar resonances of simple plasmonic nanostructures. However, it is crucial that the subradiant modes couple efficiently to the far field. This can be achieved by controlling the coupling of an optically active resonance with a broad resonance line width to an optically inactive mode that does not emit light to the far field by itself. The coupling strength can be controlled by adjusting the overlap of the resonant field distributions. The coupled system exhibits a sub- and a super-radiant mode, in which the radiative lifetime of the subradiant

Received: January 2, 2018 Accepted: April 30, 2018 Published: April 30, 2018

ACS Publications © 2018 American Chemical Society

modes decreases with increasing coupling strength. Gallinet et al. have studied the influence of this coupling strength and the excitation efficiency of the modes (defined as the contrast of the spectral line shape) on the sensing performance.<sup>24</sup> They investigated a system, in which a sub- and super-radiant mode are matched in resonance frequency in the weak coupling regime. They determined an ideal coupling strength for achieving the optimal sensing performance, which turned out to be close to the transition from the weak to the strong coupling regime.

In our work, we specifically analyze the spectral detuning of the involved modes. This approach extends the parameter space and allows for improvements beyond the capabilities of exploring the coupling and excitation strengths alone. We use numerical calculations as well as first-order perturbation theory to optimize the sensing performance of a Fano-resonant system. The numerical calculations have been carried out by the Fourier-modal method with adaptive spatial resolution and the scattering matrix formalism.<sup>25,26</sup> Our theory is validated by comparison with experimental measurements.

The first-order perturbation theory is based on the resonant state expansion,  $^{27-31}$  and allows for predicting resonance frequency and line width changes as a function of the refractive index in the sensing area.  $^{30-32}$  It should be emphasized that our theory differs in some aspects from previous work in this field.  $^{33-35}$  In particular, our approach is based on an analytical normalization for the resonant field distributions,  $^{30,31}$  and our perturbation equation is not restricted to resonances with a high quality factor, as shown in ref 32.

Particularly, we calculate in this work the excitation strength from a first-order perturbation theory,<sup>36</sup> which allows us to define a figure of merit that accounts for the mode sensitivity (i.e., the resonance frequency shift), the resonance line width, and the excitation strength. Our figure of merit agrees well with the numerical and experimental results for the maximum transmittance difference. It can be calculated for any resonant photonic system, thus providing a direct measure for the sensing performance that can be easily calculated, analyzed, and optimized.

## RESULTS AND DISCUSSION

An ideal system for our study is the structure depicted in Figure 1a, because it allows for good control of the single parameters, and it is well-described in the literature.<sup>37,38</sup> It consists of three gold nanoantennas repeated periodically in the x and ydirection with period of 700 nm (in each direction). At the top of the system are two parallel antennas, which are exposed to the surrounding analyte. The third antenna is separated vertically by a spacer layer of 50 nm thickness and oriented perpendicular to the top antennas. In the numerical calculations, we modeled the gold as a Drude metal with plasma frequency  $1.3024 \times 10^{16}$  rad/s and collision frequency  $1.6 \times 10^{14}$  rad/s. The lower nanoantenna is 290 nm long, 75 nm wide, and 40 nm thick. The long antenna axis is oriented in the x direction (see Figure 1a). The antenna is embedded in a polymer (refractive index n = 1.55) and located 70 nm above a substrate with refractive index n = 1.523. The fundamental plasmon resonance of this antenna can be excited by incident light linearly polarized along the long antenna axis. By symmetry breaking<sup>37</sup> it can couple to a quadrupolar mode formed in two nanoantennas on top of the polymer with dimensions of 305 nm  $\times$  75 nm  $\times$  40 nm and a horizontal



Figure 1. (a) General sensing scheme: Refractive index changes result in resonance frequency shifts that can be detected optically. The investigated structure is a periodic array (square lattice in the xy plane with period P) of coupled plasmonic nanoantennas. The unit cell consists of a layer with a single *x*-oriented nanoantenna below a spacer layer (green) and a pair of two y-oriented nanoantennas above that are in direct contact with the analyte (light and dark blue). In the considered frequency range, the layer with the single nanoantenna provides a dipolar plasmonic resonance, while the layer with the pair of nanoantennas supports a quadrupolar resonance. The coupling strength between these two resonances can be controlled by displacing the single nanoantenna in the y direction by the shift parameter s (s =0 nm is defined as the symmetric configuration with mirror symmetry in y direction), resulting in the characteristic Fano-type spectra shown in the top-right panel. (b) Spectral evolution of the transmittance at normal incidence of x-polarized plane waves for varying displacements in the case of matched resonance frequencies (for s = 0 nm) and (c) line width of the two modes. The gray shaded region denotes the regime of weak coupling.

separation of 140 nm. The quadrupolar mode is composed of the antiparallel dipole moments in the two separate antennas.

The coupling of the dipolar mode and the quadrupolar mode results in the formation of two hybridized modes that determine the optical response of the system. In the weak coupling regime with either large spectral detuning of the uncoupled modes or small spatial overlap of the modes' resonant field distributions, we obtain a sub- and a superradiant mode with a narrow and a broad line width, respectively. In contrast, the hybridization results in two modes with comparable line width in the strong coupling regime. Displacing the dipole antenna from a symmetric position allows for tuning of the coupling between the antennas in the top and bottom layer.<sup>37</sup> In the symmetric position, the dipolar and the quadrupolar modes are uncoupled, so that only the dipolar mode can be excited by far-field incidence. The resonance frequency of the quadrupolar mode correlates with the lengths of the antennas in the top layer. Adjusting the dimensions of those antennas allows for detuning the resonances with little influence on other parameters. Note that the resonant field distributions of the hybridized modes



**Figure 2.** Maximum absolute value of the normalized transmittance difference  $(|\Delta T/\Delta n|)$  derived from numerically calculated spectra for (a) varying displacement, i.e., coupling strength, in the resonance-matched case, (b) varying quadrupole length, i.e., spectral detuning of the resonances, and (c) varying displacement in the ideally detuned case. Dashed lines indicate the intersection with neighboring graphs.

consist in general of a superposition of a quadrupolar mode pattern around the antenna pair on top and a dipolar mode pattern in the vicinity of the single antenna underneath. The specific strength of the dipolar and the quadrupolar contribution depends on the quadrupole length and the displacement (see Supporting Information).

As in all plasmonic systems, the applicability as a sensor relies on the presence of a refractive index change in the vicinity of the metallic nanoantennas and its influence on the resonances, which can be monitored via the optical far-field spectrum. Modifying the refractive index of the analyte leads to a shift  $\Delta \nu$ of the spectrum, which implicates a transmittance or intensity difference  $\Delta T$  at a given frequency point. In contrast to similar structures discussed in purely theoretical studies where the analyte surrounds all antennas, our design has the advantage of a relatively straightforward experimental realizability.

In experiment, the analyte layer is several microns thick, whereas we assume a thickness of 150 nm in numerical calculations for the sake of simplicity. Previous analysis has shown that this thickness is large enough to span over the electromagnetic near-field region,<sup>30</sup> so that we can accurately predict the performance of the experimental design as a resonantly enhanced refractive index sensor. The reference refractive index of the analyte is n = 1.32, corresponding to water in the investigated frequency range.

Figure 1b,c shows the transmittance spectra and line width of the well-investigated case where the resonance frequencies of the dipolar and quadrupolar mode match in the absence of a coupling mechanism. The normally incident light is linearly polarized with the electric field oscillating parallel to the long axis of the lower antenna, i.e., along the *x* direction. In the weak coupling regime, i.e., small displacement from the symmetric position, the splitting of the modes is small, while they clearly differ in line width. This regime is suggested by Gallinet et al. for sensing applications.<sup>24</sup> For increasing displacement, which leads to an augmented overlap of the resonant near-fields and hence strong coupling, two distinct features with similar line width arise in the spectrum. In the following we will label the high frequency mode "A" and the low frequency mode "B".

As an easily accessible and experimentally relevant value, the maximum transmittance difference is plotted in Figure 2a for the case discussed above. The values are obtained by calculating two full spectra for a given refractive index n and  $n + \Delta n$ , respectively. The spectra are subsequently subtracted, normalized by  $\Delta n$ , and the maximum value for each resonance feature

is plotted over the corresponding displacement, i.e., coupling strength. A selection of transmittance curves and differences is provided in the Supporting Information. Figure 2a indicates that for both resonance features the values strongly increase in the weak coupling range, but have their optimum in the intermediate coupling range. The maximum displacement shown here corresponds to the dipole antenna sitting at the end of the quadrupole antennas.

As both resonance features behave quite similarly in this situation, we now start to detune the resonance frequency of the quadrupolar mode with respect to the dipolar mode. To keep the coupling in the intermediate range, we fix the displacement at half the distance between the symmetric case and the end of the quadrupole antenna pair (denoted as displacement factor 0.5), while varying the quadrupole antenna length. The result is depicted in Figure 2b. The dashed line at 305 nm quadrupole length represents the case of matched resonance frequencies. It is obvious that the detuning plays an important role when searching the ideal configuration for sensing applications, as the maximum transmittance difference exhibits distinct variations. When decreasing the quadrupole antenna lengths, the values strongly increase for mode A while they decrease for mode B. For longer quadrupole antenna lengths the behavior is inverted, but less pronounced. The ideal conditions are reached for a quadrupole length of 265 nm. In contrast to the coupling induced by the spatial configuration, this frequency detuning can be regarded as spectral coupling. To directly compare the case of matched resonance frequencies and the optimized case, we again sweep the displacement, with the resonance frequency of the quadrupolar mode detuned to higher frequencies (Figure 2c). We observe that the two modes now behave much more differently and provide a clearly increased transmittance difference for mode A. Moreover, this configuration is very robust against changes in the spatial arrangement, as the high transmittance difference values can be obtained in a broad range of displacement values.

As the refractive index changes in the analyte material are rather small, we can use first-order perturbation theory in order to predict the influence of the refractive index changes on the optical response of the coupled nanoantennas. The advantage of first-order perturbation theory is that we do not need to repeatedly solve Maxwell's equations for different frequencies and refractive indices. Instead, we only have to derive the relevant resonant state at complex eigenfrequency  $\nu_m$  (real part is resonance frequency, while  $-2\text{Im }\nu_m$  denotes the resonance



**Figure 3.** Results of first-order perturbation theory corresponding to Figure 2b, the case of varying quadrupole length (spectral resonance detuning). (a) Resonance frequency shift, (b) resonance line width and excitation strength, and (c) classical figure of merit (FOM, orange) as well as our FOM<sup>+</sup> including the excitation strength (black).

line width) and its normalized field distributions  $\mathbf{E}_m$ . For details on the numerical calculation of the resonant states, see ref 30 and references therein. The dependence of the refractive index change  $\Delta n$  in the analyte volume  $\mathcal{V}_a$  on the complex eigenfrequency is then approximately given by<sup>30</sup>

$$\nu_m(n+\Delta n) \approx \nu_m(n) \left[ 1 - n\Delta n \int_{\mathcal{V}_a} dV \mathbf{E}_m^2(\mathbf{r}; n) \right]$$
(1)

Strictly speaking, eq 1 is only valid at normal incidence, which is the case that we consider here. The more general case of inclined incidence is described in ref 31. The first-order perturbation theory is valid whenever the refractive index changes are small and the distance to other resonances on the complex frequency plane is sufficiently large. Furthermore, it requires a correct normalization of the resonant field distribution.<sup>27,30,31,39,40</sup> We are using here the analytical normalization derived in refs 30 and 31.

The normalization of the resonant fields implies that  $1/E_m^2(\mathbf{r};n)$  has the units of volume. As shown in the Supplemental Material of ref 30, the term  $1/E_m^2(\mathbf{r};n)$  with the correctly normalized resonant field is one-third of the so-called mode volume<sup>39,41,42</sup> averaged over all possible orientations of a dipolar emitter placed at position  $\mathbf{r}$ . It has to be emphasized that in general the mode volume is a spatially dependent quantity that depends on the orientation of the dipole moment as well as on the local field strength of the normalized field. Similarly, the mode sensitivity as the dependence of the eigenfrequency  $\nu_m$  on the refractive index change  $\Delta n$  is according to eq 1 proportional to the field strength of the correctly normalized fields in the analyte volume. This means that for achieving a large mode sensitivity, the analyte volume must include regions with large magnitude of  $\mathbf{E}_m^2(\mathbf{r};n)$ .

Let us now consider the excitation strength of a resonant state. Formally, we can decompose the total electric field inside the system of coupled nanoantennas into an incident and a scattered field.<sup>36</sup> Adapting ref 36 to our normalization, the scattered near field can be written as

$$\mathbf{E}_{\text{scat}} = \sum_{m} b_{m}(\nu) \mathbf{E}_{m}$$
(2)

 $b_{m}(\nu) = -\frac{\nu}{2(\nu - \nu_{m})}$   $\underbrace{\int_{\mathcal{V}} dV \mathbf{E}_{m}(\mathbf{r}) \cdot [\varepsilon(\mathbf{r}; \nu) - \varepsilon_{BG}(\mathbf{r}; \nu)] \mathbf{E}_{inc}(\mathbf{r}; \nu)}_{\equiv I_{m}(\nu)}$ (3)

where the incident field  $\mathbf{E}_{\rm inc}$  is a solution of Maxwell's equations for the background permittivity  $\varepsilon_{\rm BG}$  in the absence of the nanoantennas. In our case,  $\varepsilon_{\rm BG}$  consists of the substrate, the polymer surrounding the single nanoantenna, the analyte, and the superstrate. The magnitude of  $b_m$  reaches its maximum around Re  $\nu_m$ , i.e.,

$$\max|b_m(\nu)| \approx Q_m |I_m(\operatorname{Re}\nu_m)| \tag{4}$$

with the quality factor  $Q_m = \text{Re }\nu_m/2\text{Im }\nu_m$ . Therefore, we denote  $|I_m(\text{Re }\nu_m)|$  as the excitation strength of the mode.

In Figure 3a,b the parameters derived from the first-order perturbation theory are plotted for varying detuning of the quadrupole antennas. The absolute frequency shift normalized to the refractive index difference (i.e.,  $|\text{Re } \partial \nu_m / \partial n|$ ) decreases for mode A and increases for mode B for increasing quadrupole antenna length. The resonance line width and excitation strength, instead, exhibit an inverse trend. They both increase with the antenna length for mode A and decrease for mode B, yielding a sub- and a super-radiant mode.

To compare the performance of different sensing configurations, the so-called figure of merit (FOM) was introduced by Sherry et al.<sup>43</sup> It is calculated as the ratio of the sensitivity and the resonance line width. Figure 3c depicts this FOM, calculated from the values obtained by our first-order perturbation theory as orange lines. As for mode A and short quadrupole antenna lengths the sensitivity is high and the line width becomes smaller and smaller, the FOM inordinately increases. However, those high values are of no advantage as the excitation strength of the resonance also strongly decreases in this regime. Therefore, the standard FOM is not a good measure for finding the ideal sensing configuration. Gallinet et al. have also identified this issue and proposed an approach to include the contrast of the line shape into the figure of merit.<sup>44</sup> This takes into account that narrow line widths often come along with less modulation. Based on the same consideration we thus include the excitation strength in the figure of merit and calculate

with the expansion coefficient



**Figure 4.** Results of first-order perturbation theory corresponding to Figure 2c, the case of varying displacement (coupling strength). (a) Resonance frequency shift, (b) resonance line width and excitation strength, and (c) classical figure of merit (FOM, orange) as well as our FOM<sup>+</sup> including the excitation strength (black).



Figure 5. Experimental results of the optimized structure for increasing displacement (coupling strength). (a) Transmittance spectra and scanning electron microscope images of the associated structures. (b) Normalized transmittance difference. (c) Maximum values of the normalized transmittance difference plotted over the corresponding numerical calculations.

$$FOM^{+} \equiv \frac{[sensitivity] \times [excitation strength]}{[resonance linewidth]}$$
(5)

with the sensitivity being Re  $\partial \nu_m/\partial n$ . Mathematically, this definition directly follows from differentiating eq 4 with respect to *n* when assuming that the refractive index dependence of the excitation strength divided by the resonance line width is negligible. Hence, a large value of FOM<sup>+</sup> is equivalent to a strong dependence of the expansion coefficient  $b_m$  on the refractive index in the analyte volume. The FOM<sup>+</sup> is shown in Figure 3c (black lines). It exhibits a distinct maximum for both modes and perfectly resembles the behavior retrieved from the full spectral calculations (cf. Figure 2b).

The FOM<sup>+</sup> allows us to analyze the individual contributions for achieving an optimal sensing performance. First, the frequency shift is dominated by the strength of the resonant near fields in the sensing region. Analysis of the modes (Supporting Information) reveals that mode A is dominated for shorter quadrupole antenna lengths by a strong quadrupolar near-field pattern in the vicinity of the analyte material. Thus, the observed frequency shifts are large, while they decrease for longer quadrupole antenna lengths, where the near fields are dominated by the dipolar pattern around the single antenna buried in the polymer. In contrast, mode B changes its character form predominantly dipolar to quadrupolar, thus resulting in an increase of frequency shift for longer quadrupole antenna lengths.

The other two quantities entering the  $FOM^+$  are the resonance line width and the excitation strength. They behave

rather similar (see Figure 3b). This is intuitively clear, because the radiative part of the line width is related to the coupling of the resonant state to the far field, which in turn is related by reciprocity to the excitation of the resonant state. The impact of resonance line width and excitation strength on the FOM<sup>+</sup>, however, is exactly opposite: A larger excitation strength is superior for a better sensing performance and therefore increases the FOM<sup>+</sup>, while a larger line width makes the spectral feature associated with that resonance less steep and thus decreases the FOM<sup>+</sup>. The maximum of the FOM<sup>+</sup> can therefore be attributed to the following competing effects: On one hand, the resonance line width of mode A becomes smaller and the frequency shift larger for shorter quadrupole antenna length, because the character of mode A becomes more and more quadrupolar. On the other hand, this means that the dipolar contribution to this mode decreases, thus lowering the excitation strength. The maximum in FOM<sup>+</sup> and in the transmittance difference (Figure 2b) is therefore achieved due to the optimal trade-off between excitation strength, line width, and frequency shift.

The same analysis was carried out for the case of varying displacement. In contrast to the previous case, here mode A shows a much higher sensitivity and smaller line width than mode B over the entire sweep range (Figure 4a,b). The excitation strength, however, is again crucial for finding the ideal sensing configuration. Without considering it (FOM, orange lines), small displacements seem to be clearly favorable. Only due to the excitation strength, the FOM<sup>+</sup> resembles the results of the full numerical calculations (cf. Figure 2c).

Additionally, the optimized detuned structure with a quadrupole length of 265 nm was investigated experimentally. Fabrication of the samples was realized by a standard multilayer electron-beam lithography process with positive resist (PMMA) on a glass substrate. A 70 nm layer of polymer (PC403) was spin-coated and hardened prior to processing the dipole antennas (including markers for later alignment) in the first layer. Subsequently, another layer of PC403 was spincoated to flatten the surface and to ensure the vertical spacing of the layers. The quadrupole antennas, which are exposed to the analyte solutions, were then written in a second exposure process on top of the cured polymer. Precise alignment with respect to the lower layer is ensured with the aid of the previously defined markers. Five different displacements, ranging from the symmetric case to large displacements, were realized in 100  $\times$  100  $\mu$ m<sup>2</sup> sized arrays. Scanning electron microscope images (Figure 5) exemplarily depict the fabricated structures. Measurements were conducted in a FTIR spectrometer using a custom-made microfluidic silicone sensor cell, which features a 70- $\mu$ m-thick channel with inlet and outlet tubing. A constant flow of analyte solution was provided by placing a reservoir above and the outlet in a beaker below the cell. Transmittance spectra for pure water (n = 1.32) and a 1:1 mixture of water and ethylene glycol ( $n \approx 1.37$ ) were recorded with normally incident light polarized along the long axis of the lower antenna. The spectra clearly illustrate how the additional resonance evolves with increasing displacement (Figure 5a). Subtracting the corresponding spectra for the different analyte solutions exhibits the respective dispersive features (Figure 5b). For the feature at the low frequency mode, the absolute transmittance difference just increases slightly with higher displacement values. For the feature at the high frequency mode, it increases considerably with the displacement. The extracted maximum values are plotted in Figure 5c and agree well with the numerical calculations (gray lines).

# CONCLUSION

Among the variety of plasmonic structures, those exhibiting Fano resonances have an intrinsic advantage in sensing applications. Their narrow line width compared to plain dipolar resonances generally provides steeper flanks in the far-field spectra and hence larger intensity differences for small refractive index changes in the sensing volume. Still, there is a potential for further optimization. We found that besides the near-field coupling of quadrupolar and dipolar resonances, the spectral detuning between them plays an important role. With the right amount of coupling strength and spectral detuning, it is possible to find the ideal combination of narrow line width and sufficient excitation strength. First-order perturbation theory allows calculating a figure of merit that is able to predict the intensity differences retrieved from numerical calculations and experiments from the sensitivity, the resonance line width, and the excitation strength. The results are supported by good agreement between numerical calculations, perturbation theory, and measurements, all applied to the exact same system.

## ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssensors.8b00003.

Selection of transmittance curves and differences used for Figure 2 as well as some resonant electric field distributions (PDF)

## AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: h.giessen@pi4.uni-stuttgart.de.

#### ORCID 0

Thomas Weiss: 0000-0002-4991-6779

Martin Schäferling: 0000-0002-2035-0572

# Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We acknowledge financial support by Baden-Württemberg Stiftung and the Ministerium für Wissenschaft, Forschung und Kunst Baden-Württemberg, as well as ERC (ComplexPlas), BMBF, DFG, and Carl-Zeiss-Stiftung.

## REFERENCES

(1) Lazarides, A. A.; Kelly, K. L.; Jensen, T. R.; Schatz, G. C. Optical Properties of Metal Nanoparticles and Nanoparticle Aggregates Important in Biosensors. *J. Mol. Struct.: THEOCHEM* **2000**, *529*, 59–63.

(2) Mcmahon, J. M.; Henzie, J.; Odom, T. W.; Schatz, G. C.; Gray, S. K. Tailoring the Sensing Capabilities of Nanohole Arrays in Gold Films with Rayleigh Anomaly–Surface Plasmon Polaritons. *Opt. Express* 2007, *15*, 18119–18129.

(3) Anker, J. N.; Hall, W. P.; Lyandres, O.; Shah, N. C.; Zhao, J.; Van Duyne, R. P. Biosensing with Plasmonic Nanosensors. *Nat. Mater.* **2008**, *7*, 442–453.

(4) Ameling, R.; Langguth, L.; Hentschel, M.; Mesch, M.; Braun, P. V.; Giessen, H. Cavity-enhanced localized plasmon resonance sensing. *Appl. Phys. Lett.* **2010**, *97*, 253116.

(5) Mayer, K. M.; Hafner, J. H. Localized Surface Plasmon Resonance Sensors. Chem. Rev. 2011, 111, 3828–3857.

(6) Larsson, E. M.; Syrenova, S.; Langhammer, C. Nanoplasmonic Sensing for Nanomaterials Science. *Nanophotonics* 2012, *1*, 249–266.
(7) Szunerits, S.; Boukherroub, R. Sensing Using Localised Surface

Plasmon Resonance Sensors. *Chem. Commun.* **2012**, *48*, 8999–9010. (8) König, M.; Rahmani, M.; Zhang, L.; Lei, D. Y.; Roschuk, T. R.; Giannini, V.; Qiu, C.-W.; Hong, M.; Schlücker, S.; Maier, S. A. Unveiling the Correlation between Nanometer-Thick Molecular Monolayer Sensitivity and Near-Field Enhahncement and Localization in Coupled Plasmonic Oligomers. *ACS Nano* **2014**, *8*, 9188–9198.

(9) Prasad, J.; Zins, I.; Branscheid, R.; Becker, J.; Koch, A. H. R.; Fytas, G.; Kolb, U.; Sönnichsen, C. Plasmonic CoreSatellite Assemblies as Highly Sensitive Refractive Index Sensors. J. Phys. Chem. C 2015, 119, 5577–5582.

(10) Raschke, G.; Kowarik, S.; Franzl, T.; Sönnichsen, C.; Klar, T. A.; Feldmann, J.; Nichtl, A.; Kürzinger, K. Biomolecular Recognition Based on Single Gold Nanoparticle Light Scattering. *Nano Lett.* **2003**, *3*, 935–938.

(11) Buso, D.; Busato, G.; Guglielmi, M.; Martucci, A.; Bello, V.; Mattei, G.; Mazzoldi, P.; Post, M. L. Selective Optical Detection of H2 and CO with SiO2 SolGel Films Containing NiO and Au Nanoparticles. *Nanotechnology* **2007**, *18*, 475505.

(12) Kreno, L. E.; Hupp, J. T.; Van Duyne, R. P. Metal - Organic Framework Thin Film for Enhanced Localized Surface Plasmon Resonance Gas Sensing. *Anal. Chem.* **2010**, *82*, 8042–8046.

(13) Rosman, C.; Prasad, J.; Neiser, A.; Henkel, A.; Edgar, J.; Sönnichsen, C. Multiplexed Plasmon Sensor for Rapid Label-Free Analyte Detection. *Nano Lett.* **2013**, *13*, 3243–3247.

(14) Strohfeldt, N.; Zhao, J.; Tittl, A.; Giessen, H. Sensitivity Engineering in Direct Contact Palladium-Gold Nano-Sandwich Hydrogen Sensors. *Opt. Mater. Express* **2015**, *5*, 2525. (15) Mesch, M.; Zhang, C.; Braun, P. V.; Giessen, H. Functionalized Hydrogel on Plasmonic Nanoantennas for Noninvasive Glucose Sensing. *ACS Photonics* **2015**, *2*, 475–480.

(16) Jakab, A.; Rosman, C.; Khalavka, Y.; Becker, J.; Trügler, A.; Hohenester, U.; Sönnichsen, C. Highly Sensitive Plasmonic Silver Nanorods. *ACS Nano* **2011**, *5*, 6880–6885.

(17) Jeong, H.-H.; Mark, A. G.; Alarcón-Correa, M.; Kim, I.; Oswald, P.; Lee, T.-C.; Fischer, P. Dispersion and shape engineered plasmonic nanosensors. *Nat. Commun.* **2016**, *7*, 11331.

(18) Yanik, A. A.; Huang, M.; Artar, A.; Chang, T.-Y.; Altug, H. Integrated Nanoplasmonic-Nanofluidic Biosensors with Targeted Delivery of Analytes. *Appl. Phys. Lett.* **2010**, *96*, 021101.

(19) Hao, F.; Sonnefraud, Y.; Van Dorpe, P.; Maier, S. A.; Halas, N. J.; Nordlander, P. Symmetry Breaking in Plasmonic Nanocavities: Subradiant LSPR Sensing and a Tunable Fano Resonance. *Nano Lett.* **2008**, *8*, 3983–3988.

(20) Liu, N.; Weiss, T.; Mesch, M.; Langguth, L.; Eigenthaler, U.; Hirscher, M.; Sönnichsen, C.; Giessen, H. Planar Metamaterial Analogue of Electromagnetically Induced Transparency for Plasmonic Sensing. *Nano Lett.* **2010**, *10*, 1103–1107.

(21) Zhang, S.; Bao, K.; Halas, N. J.; Xu, H.; Nordlander, P. Substrate-induced Fano resonances of a plasmonic nanocube: a route to increased-sensitivity localized surface plasmon resonance sensors revealed. *Nano Lett.* **2011**, *11*, 1657–63.

(22) Zhan, Y.; Lei, D. Y.; Li, X.; Maier, S. A. Plasmonic Fano Resonances in Nanohole Quadrumers for Ultra-sensitive Refractive Index Sensing. *Nanoscale* **2014**, *6*, 4705–4715.

(23) Butet, J.; Martin, O. J. F. Refractive index sensing with Fano resonant plasmonic nanostructures: a symmetry based nonlinear approach. *Nanoscale* **2014**, *6*, 15262–15270.

(24) Gallinet, B.; Siegfried, T.; Sigg, H.; Nordlander, P.; Martin, O. J. F. Plasmonic Radiance: Probing Structure at the ngstrm Scale with Visible Light. *Nano Lett.* **2013**, *13*, 497–503.

(25) Granet, G.; Plumey, J.-P. Parametric formulation of the Fourier modal method for crossed surface-relief gratings. *J. Opt. A* 2002, *4*, 145–149.

(26) Weiss, T.; Granet, G.; Gippius, N. A.; Tikhodeev, S. G.; Giessen, H. Matched coordinates and adaptive spatial resolution in the Fourier modal method. *Opt. Express* **2009**, *17*, 8051–8061.

(27) Muljarov, E. A.; Langbein, W.; Zimmermann, R. Brillouin-Wigner perturbation theory in open electromagnetic systems. *Europhys. Lett.* **2010**, *92*, 50010.

(28) Doost, M. B.; Langbein, W.; Muljarov, E. A. Resonant-state expansion applied to three-dimensional open optical systems. *Phys. Rev. A: At., Mol., Opt. Phys.* **2014**, *90*, 013834.

(29) Armitage, L. J.; Doost, M. B.; Langbein, W.; Muljarov, E. A. Resonant-state expansion applied to planar waveguides. *Phys. Rev. A: At., Mol., Opt. Phys.* **2014**, *89*, 053832.

(30) Weiss, T.; Mesch, M.; Schäferling, M.; Giessen, H.; Langbein, W.; Muljarov, E. A. From dark to bright: First-order perturbation theory with analytical mode normalization for plasmonic nanoantenna arrays applied to refractive index sensing. *Phys. Rev. Lett.* **2016**, *116*, 237401.

(31) Weiss, T.; Schäferling, M.; Giessen, H.; Gippius, N. A.; Tikhodeev, S. G.; Langbein, W.; Muljarov, E. A. Analytical normalization of resonant states in photonic crystal slabs and periodic arrays of nanoantennas at oblique incidence. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2017**, 1 DOI: 10.1103/PhysRevB.96.045129.

(32) Yang, J.; Giessen, H.; Lalanne, P. Simple analytical expression for the peak-frequency shifts of plasmonic resonances for sensing. *Nano Lett.* **2015**, *15*, 3439–3444.

(33) Arnold, S.; Khoshsima, M.; Teraoka, I.; Holler, S.; Vollmer, F. Shift of whispering-gallery modes in microspheres by protein adsorption. *Opt. Lett.* **2003**, *28*, 272–274.

(34) Unger, A.; Kreiter, M. Analyzing the Performance of Plasmonic Resonators for Dielectric Sensing. *J. Phys. Chem. C* **2009**, *113*, 12243–12251.

(35) Zhang, W.; Martin, O. J. F. A universal law for plasmon resonance shift in biosensing. ACS Photonics **2015**, *2*, 144–150.

(36) Perrin, M. Eigen-energy effects and non-orthogonality in the quasi-normal mode expansion of Maxwell equations. *Opt. Express* **2016**, *24*, 27137–27151.

(37) Liu, N.; Langguth, L.; Weiss, T.; Kästel, J.; Fleischhauer, M.; Pfau, T.; Giessen, H. Plasmonic analogue of electromagnetically induced transparency at the Drude damping limit. *Nat. Mater.* **2009**, *8*, 758–762.

(38) Rapp, P.; Mesch, M.; Giessen, H.; Tarìn, C. Regression methods for ophthalmic glucose sensing using metamaterials. *Journal of Electrical and Computer Engineering* **2011**, 2011, 953064.

(39) Sauvan, C.; Hugonin, J. P.; Maksymov, I. S.; Lalanne, P. Theory of the spontaneous optical emission of nanosize photonic and plasmon resonators. *Phys. Rev. Lett.* **2013**, *110*, 237401.

(40) Bai, Q.; Perrin, M.; Sauvan, C.; Hugonin, J. P.; Lalanne, P. Efficient and intuitive method for the analysis of light scattering by a resonant nanostructure. *Opt. Express* **2013**, *21*, 27371–27382.

(41) Purcell, E. M. Spontaneous emission probabilities at radio frequencies. *Phys. Rev.* **1946**, *69*, 681.

(42) Muljarov, E. A.; Langbein, W. Exact mode volume and Purcell factor of open optical systems. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *94*, 235438.

(43) Sherry, L. J.; Chang, S.-h.; Schatz, G. C.; Van Duyne, R. P.; Wiley, B. J.; Xia, Y. Localized Surface Plasmon Resonance Spectroscopy of Single Silver Nanocubes. *Nano Lett.* **2005**, *5*, 2034–2038.

(44) Gallinet, B.; Martin, O. J. F. Refractive Index Sensing with Subradiant Modes: A Framework To Reduce Losses in Plasmonic Nanostructures. *ACS Nano* **2013**, *7*, 6978–6987.