

Design Principles for Sensitivity Optimization in Plasmonic Hydrogen Sensors

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ABSTRACT: Palladium nanoparticles have proven to be exceptionally suitable materials for the optical detection of hydrogen gas due to the dielectric function that changes with the hydrogen concentration. The development of a reliable, low-cost, and widely applicable hydrogen detector requires a simple optical readout mechanism and an optimization of the lowest detectable hydrogen concentration. The so-called "perfect absorber"-type structures, consisting of a layer of plasmonic palladium nanoantennas suspended above a metallic mirror layer, are a promising approach to



realizing such sensors. The absorption of hydrogen by palladium leads to a shift of the plasmon resonance and, thus, to a change in the far-field reflectance spectrum. The spectral change can be analyzed in detail using spectroscopic measurements, while the reflectance change at a specific wavelength can be detected with a simple photometric system of a photodiode and a monochromatic light source. Here, we systematically investigate the geometry of cavity-coupled palladium nanostructures as well as the optical system concept, which enables us to formulate a set of design rules for optimizing the hydrogen sensitivity. Employing these principles, we demonstrate the robust detection of hydrogen at concentrations down to 100 ppm. Our results are not limited to hydrogen sensing but can be applied to any type of plasmonic sensor.

KEYWORDS: hydrogen detection, plasmonic sensing, metasurface, perfect absorber, palladium, microspectroscopy, Fourier-plane spectroscopy, tailored disorder

INTRODUCTION

The development of safe, reliable, and low-cost hydrogen detectors is of great importance for widespread usage of hydrogen as an energy carrier, which holds great promise as an alternative to fossil fuels and for energy storage. First, hydrogen detection is needed to address safety issues, considering the explosive nature of H₂ gas at concentrations between 4.2 and 74% in air.¹ This is, for example, necessary to ensure safe working conditions in hydrogen fuel filling stations, and also in nuclear waste repository environments.^{2,3} Second, the detection of trace amounts of H₂ at concentrations down to the 100 ppm range is crucial in process monitoring in, e.g., hydrolysis plants and power transformers.^{4,5}

While hydrogen sensors with an electrical readout employ the change in electrical conductivity upon hydrogen absorption in metals,^{5,6} recent developments have brought forward optical sensing schemes, in which the change in reflectance and/or transmittance of hydrogen-absorbing materials is detected.^{7–9} In such sensors, no electrical contact has to be introduced in the sensing area. A fiber-based readout enables the spatial separation of the sensing substrate and any sensor electronics.^{2,10–13} This is especially important for sensing applications in hazardous areas, where these sensors can be installed without the need for costly and large shielding.

One particularly suitable material for optical hydrogen detection is palladium (Pd). This is due to the formation of

palladium hydride (PdH_r) upon hydrogen exposure, with a composition that reversibly depends on the ambient hydrogen concentration. The change from Pd to PdH_r manifests itself in a change in the dielectric function. At high hydrogen concentrations, when the H atoms not only occupy interstitial lattice sites (α phase) but saturate the Pd lattice (β phase), this is accompanied by an increase of the lattice constant of over 10%.¹⁴ In recent years, different sensor geometries have been investigated, which can mainly be divided into thin films and plasmonic nanoparticles. In the case of Pd thin films, the optical transmittance and/or reflectance can be analyzed as a measure for the hydrogen concentration.^{11,15,16} In Pd nanoparticles, the localized plasmon resonance (LSPR) undergoes a shift upon hydrogen absorption, so that tracking the centroid wavelength via spectroscopic measurements offers another detection method,¹⁷⁻¹⁹ that can even be employed to study the behavior of individual Pd nanoparticles.²⁰⁻²² On the other hand, the relative simplicity of reflectance measurements makes this method more suitable for large-scale, low-cost sensor applications. While both optical readout mechanisms

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can be used to reliably extract the hydrogen concentration, there are significant differences between films and particles from a thermodynamic viewpoint.²²⁻²⁶

The freedom of volumetric expansion and the sensitivity of the plasmonic resonance make nanoantennas preferable over thin films, even though Pd nanoparticles suffer more strongly from undesirable effects such as a hysteresis in the loading and unloading of hydrogen, nonlinear behavior of the sensor response, and deactivation through poisoning by other gases.^{11,17} These challenges can be tackled by, for example, alloying Pd with other metals,^{26–28} protecting the particles with hydrogen-permeable cover layers [e.g., poly-(tetrafluoroethylene) (PTFE),⁷ poly(methyl methacrylate) (PMMA),²⁹ or platinum¹¹], and using lattice-matched substrates (e.g., CaF₂ and MgF₂¹¹). Additionally, one can employ advanced prediction algorithms based on mathematical modeling of the sensor.³⁰ Furthermore, different nanostructure geometries, including stacked structures, have been investigated to enhance the hydrogen sensitivity, both in thin films³¹ and in nanoparticles.^{19,32} Recently, H₂ detection with a combination of nanoantennas and hydrogen-reactive thin films was demonstrated as well.^{33,34}

One highly promising type of sensor geometry is the socalled perfect absorber layout.^{30,35,36} In this design, an array of Pd nanostructures is separated by a dielectric spacer layer from a metallic film, which acts as a mirror (see Figure 1a). Using



Figure 1. (a) Schematic of the plasmonic hydrogen sensor structures considered in this study. Palladium (Pd) nanodisks are separated from a metallic mirror (gold) by a dielectric spacer layer (magnesium fluoride, MgF_2). Upon hydrogen absorption, the dielectric function and the size of the Pd nanodisks change, leading to a change in the reflectance spectrum of the structure. (b) In a hydrogen sensor with an LED and a photodiode, the measured voltage *U* is proportional to the LED intensity *I*, the reflectance *R*, and the readout circuit gain *G*.

this nanostructure layout, it is possible to achieve near-unity absorption through careful tuning of the design parameters (hence the name).^{37–39} One argument for using "perfect absorber" hydrogen sensors is that a very high relative change in the optical reflectance upon H₂ exposure can be obtained.³⁵ This reasoning, however, does not take into account the noise in the sensor response, i.e., in the reflectance $R(\lambda_{,}p_{\rm H_2})$ of the sensor substrate. This is important in the case of a simple, single-wavelength readout scheme based on, e.g., a lightemitting diode (LED) light source and a photodiode,¹³ rather than centroid wavelength tracking in spectroscopic measurements (Figure 1b). To minimize the lowest detectable amount of hydrogen, the signal-to-noise ratio (SNR) of the detected signal must be maximized, since it defines the lowest distinguishable signal. In fact, if the detector output is defined as the voltage *U* generated from the photodiode's photocurrent, which depends on the incoming light intensity *I*, the reflectance *R*, and the readout electronics gain *G* as $U(\lambda, p_{H_2}) = I(\lambda) \cdot R(\lambda, p_{H_2}) \cdot G$, it can be shown that the SNR of the voltage is proportional to the absolute reflectance attenuation $\Delta R_{abs} = R(p_{H_1}) - R_0$

$$\mathrm{SNR} \approx \frac{\Delta R_{\mathrm{abs}}}{\sqrt{2 \cdot \langle \delta R^2 \rangle}} \tag{1}$$

where δR is the uncertainty in the reflectance caused by external influences such as temperature fluctuations, pollution, and fabrication uncertainties. A full derivation of this expression as well as the underlying assumptions can be found in the Supporting Information.

Equation 1 implies that the absolute reflectance difference must be maximized to achieve the highest hydrogen sensitivity. In this work, we thus focus on the question of how a maximum ΔR_{abs} can be achieved through tuning the relevant design parameters. Specifically, we study ensembles of Pd nanodisks on a magnesium fluoride (MgF₂) spacer and a gold mirror as a model system. In the first step, we perform numerical calculations on this system to gain a better understanding of the optical response and the underlying physical principles and to predict an optimum sensor design. We then compare these calculations to microspectroscopic reflectance measurements. As a further step, we extend the measurement setup for Fourier-plane spectroscopy, which enables us to record angleresolved reflectance spectra, and thus to investigate the influence of the readout angle θ on the sensing performance.

NUMERICAL CALCULATIONS

To gain better insight into the optical response of the perfect absorber palladium nanostructures, we carry out numerical calculations using an in-house implementation of the scattering matrix approach, also known as the Fourier modal method or rigorous coupled-wave analysis.⁴⁰ Figure 2a shows a pseudo-color plot of the reflectance as a function of the wavelength λ and the thickness of the spacer layer $t_{\rm spacer}$ at normal incidence. The disk diameter $d_{\rm disk}$ has been fixed at 195 nm. The disk height $h_{\rm disk}$ considered in all calculations is 20 nm, and the structures are periodically arranged with a periodicity *P* of 300 nm.

The shape of the reflectance plot highlights the importance of the spacer thickness, i.e., the coupling distance between the plasmonic nanostructures and the mirror. The dashed white lines show the function $t_{\text{spacer}} = m\lambda/4n$ for different integer values of *m*, with *n* being the refractive index of MgF₂.⁴¹ These lines demonstrate that the reflectance as a function of t_{spacer} exhibits a periodic behavior with a period of $\lambda/2n$, within which one reflectance minimum (perfect absorption) and one reflectance maximum occur. This behavior has been described before in similar coupled antenna–film systems and can be explained by different coupling models, depending on the spacer thickness.^{42–47} At small distances between the disks and the mirror, the plasmon resonance in the nanoantennas induces a mirror plasmon in the metal film, leading to near-



Figure 2. (a) Calculated reflectance spectra for varying spacer thicknesses, for a disk diameter of 195 mm, a disk thickness of 20 nm, and a periodicity of 300 nm. The dashed white lines indicate the spacer thicknesses necessary to fit m/4 wavelengths into the cavity formed by the mirror and the disk array. (b–g) Electric field enhancement distributions for selected wavelengths and spacer thicknesses, indicated by the colored and labeled dots in (a). At a spacer thickness of 20 nm, in the near-field coupling regime, one can observe coupling between the Pd disk and the Au mirror in the field distribution (b, c). Structures with thicker spacers, such as 150 nm (d, e) and 270 nm (f, g), act as cavity resonators. If the disk array is positioned in a minimum of the electric field, practically no plasmon resonance is excited, so that the disk array is effectively transparent and the far-field response of the structure is dominated by the mirror (d, g). If the disk array is in a maximum of the electric field, coupling of the LSPR to the cavity resonance leads to an absorption maximum (e, f).



Figure 3. (a) Calculated reflectance spectra for varying spacer thicknesses for Pd disks with a diameter of 160 nm, at a periodicity of 300 nm. A comparison to the transmittance spectra of a Pd disk array on MgF₂ without a metallic mirror (1D pseudocolor plot) reveals how a substantial reflectance modulation is only achieved in spectral ranges where the Pd disks are plasmonically active. (b) Calculated reflectance spectra for the same structures as in (a), with β phase PdH instead of Pd disks and taking into account a volume expansion of 10%. (c) Plot of the resulting reflectance difference vs spacer thickness and wavelength. The 1D pseudocolor plot shows the corresponding transmittance difference for the case of disks on a substrate. A comparison between these two signals shows how the disk–mirror structure can approximately double the maximum optical response. The positions of some exemplary local maxima of $|\Delta R|$ are indicated in all three plots. These points show that the maximum ΔR value is obtained in areas around but not at the reflectance minima.

field coupling between the plasmon and the mirror plasmon and thus to a spectral shift.⁴² To visualize this, Figure 2b,c depicts the electric field enhancement in a cross-section through one unit cell of the structure for two different wavelengths. These field distributions are obtained from finiteelement simulations using CST Microwave Studio, with light polarized along the *x* axis. A radius of 3 nm is used at the edges of the nanodisks to avoid artifacts due to the sharp corners. The extent of the electric field enhancement reaching from the plasmonic hotspots at the disk to the mirror charges in the Au layer is clearly visible in this case.

At increasing spacer thicknesses, however, a transition to the far-field coupling regime occurs. Here, the structure can be described as a Fabry–Perot cavity with resonating mirrors. The distribution of the electric field enhancement in a thicker spacer (Figure 2d–g) illustrates the mechanism behind the farfield reflectance, as a standing wave occurs within the cavity formed by the plasmonic layer and the mirror. If an electric field minimum exists at the *z* position of the disks, this means that the incident and reflected waves interfere destructively at this position. This renders the nanoantennas practically invisible for the incident light so that the reflectance is effectively determined by the mirror. In the case of a Au mirror, this means that the reflectance approaches unity at $\lambda >$ 600 nm, and the reflectance at lower wavelengths is dominated by the d-band absorption of Au. If the disks are located in an electric field maximum, the resonance conditions for the cavity are met, leading to "perfect absorption" and thus to a reflectance minimum.



Figure 4. (a) Schematic of the microspectroscopy setup, consisting of an inverted microscope and a grating spectrometer (monochromator + CCD camera). Light from a broadband light source is focused on the back focal plane (BFP) of the objective to ensure normal incidence for good comparability with numerical calculations. The sample plane is directly imaged onto the entrance slit of the monochromator (red lines). (b) To record angle-resolved reflectance spectra, the Fourier plane is imaged onto the spectrometer entrance slit using a modified 4-f setup (blue shaded area). In this case, the full BFP is illuminated (BS: beam splitter, TL: tube lens, F-stop: field stop, A-stop: aperture stop, and pol: polarizer).

A detailed description of this multilayer system can be found in the works of Weiss et al.,⁴⁸ Ameling and Giessen,⁴⁴ Bhattarai et al.,⁴⁹ and, more recently, Berkhout and Koenderink.⁴⁷ Essentially, the cavity can be described in terms of the phase shift of the electromagnetic wave while passing through the cavity, which is composed of the phase shifts due to propagation through the spacer ($\Delta \phi_{\rm prop}$), reflection at the mirror–spacer interface ($\Delta \phi_{\rm refl}$), and reflection at the plasmonic layer due to plasmon excitation ($\Delta \phi_{\rm exc}$). This leads to the following expression for the resonance wavelength of the cavity⁴⁴

$$\Delta\phi_{\text{total}} = 2\Delta\phi_{\text{prop}} + \Delta\phi_{\text{refl}} + \Delta\phi_{\text{exc}} \stackrel{!}{=} (m+1) \cdot 2\pi$$
(2)

where $\Delta \phi_{\text{prop}} = 2\pi n_{\text{spacer}} t_{\text{spacer}} \lambda$, and $\Delta \phi_{\text{refl}}$ can be computed via the Fresnel equations. This means that the plasmon resonance in the Pd disks only influences the phase shift upon reflectance at the plasmonic layer, $\Delta \phi_{\text{exc}}$. This shift is a more complex function involving the plasmon resonance wavelength and damping, as well as the filling fraction of plasmonic nanoantennas, through an effective medium model. This model provides an explanation for the shape of the $R(\lambda_i t_{\text{spacer}})$ "landscape", and the deviation from the exact course of the $t_{\text{spacer}} = m\lambda/4n$ lines since an additional, wavelength-dependent phase shift is introduced by the plasmon resonance. This resonance, in turn, is influenced by the size, shape, and arrangement of the nanoparticles (see also Figure S2 of the Supporting Information), as well as their dielectric function.

The next step is to investigate the behavior of the reflectance difference ΔR due to hydrogen absorption. To this end, we perform scattering matrix calculations on the same system as in Figure 1 but with the dielectric function of the Pd disks replaced by β phase PdH.⁵⁰ Furthermore, we take into account the increased lattice constant of PdH compared to Pd, approximated as an isotropic volume expansion of 10%. Since the transition from the α phase to β phase PdH_x typically occurs in particles at H₂ concentrations (in N₂) of around 2%,⁵¹ the system thus represents a Pd perfect absorber structure in the presence of a relatively high concentration of H₂. Figure 3 shows the resulting $R(\lambda, t_{spacer})$ plot for Pd (a) and PdH (b) disks, in this case, with a diameter of 160 nm. Equivalent calculation results for other disk diameters can be found in Figure S2 of the Supporting Information. The optical response of an array of Pd/PdH disks on an infinitely thick

 MgF_2 layer without a mirror, thus without coupling to any cavity, is shown in the one-dimensional (1D) pseudocolor plots below the main plots.

A comparison of the bare disks to the disk-spacer-mirror system reveals how the plasmon resonance influences the behavior of the perfect absorber. Only at wavelengths where the nanoantennas are plasmonically active (thus, inducing a significant transmittance modulation in the absence of a mirror), strong modulation of the reflectance as a function of the spacer thickness is reached. If the plasmon resonance undergoes a shift due to the absorption of hydrogen, the resonance condition (eq 2) is changed, leading to a shifted "landscape" of $R(\lambda, t_{spacer})$, as shown in Figure 3b. The resulting reflectance difference ΔR is displayed in Figure 3c, along with the equivalent ΔT for bare disks. The positions of four exemplary $|\Delta R|$ maxima are indicated in Figure 3c as well as in Figure 3a,b. These positions reveal a key feature of the system: The highest reflectance differences are obtained at points in between the reflectance minima and maxima. This implies that the shifting plasmon resonance has the strongest influence on the far-field reflectance neither at the strongest nor at the weakest interaction between the incoming light and the plasmonic antennas. In other words, when the aim is to maximize $|\Delta R|$ (see eq 1), trying to obtain perfect absorption at the readout wavelength is in fact counterproductive.

Furthermore, a comparison of ΔR with ΔT reveals how the disk-cavity geometry can bring major improvement over a simple transmittive disk array. The maximum $|\Delta R|$ values exceed the maximum $|\Delta T|$ values by almost a factor of 2. An intuitive explanation is that the photonic cavity can strongly enhance the interaction of the light with the nanoantennas, leading to a stronger influence on the amount of light that is reflected. However, the interaction can be decreased as well. This means that the spacer thickness must be chosen carefully, taking into account the envisioned readout wavelength of the sensor. In particular, when a response maximum very close to a region of low response is chosen, a deposition technique with high accuracy is required. The data shown in Figures 3c and S2c provide an important guide to selecting the correct parameters.

EXPERIMENTAL SECTION

To verify the numerical results and study the behavior of perfect absorber hydrogen sensors at different H_2 concentrations, we fabricate

Article



Figure 5. (a) Measured (solid lines) and calculated (dashed lines) reflectance spectra for spacer thicknesses between 60 and 290 nm, at P = 300 nm, in pure N₂ and in an atmosphere of 5% H₂ gas in N₂. The Pd disk diameter is 202 ± 7 nm. The largest reflectance difference is indicated in each plot. (b) Dielectric function of Pd and PdH as used in the calculations. The largest reflectance difference are obtained in the wavelength range where the difference between the dielectric functions is highest. (c) Maximum of the measured reflectance difference vs disk diameter for the five different spacer thicknesses. (d) Reflectance difference obtained at a high (5%) and a low (0.5%) H₂ concentration for spacer thicknesses 60 and 160 nm (disk diameter 174 ± 6 nm). The optimum readout wavelength is not necessarily the same for different concentration ranges of interest.

Pd nanodisk arrays on substrates with an Au mirror and MgF₂ spacers of different thicknesses (60, 110, 160, 210, and 290 nm). The samples are fabricated by evaporating 120 nm of Au, followed by the appropriate thickness of MgF₂ onto plasma-cleaned glass substrates with a Pfeiffer Vacuum PLS 500 electron-beam-assisted evaporation system. These substrates are then spin-coated with resist (PMMA) for patterning in an electron-beam lithography system (RAITH eLINE Plus). After resist development, a 20 nm-thick layer of Pd is evaporated onto all substrates simultaneously, followed by resist liftoff in NEP. The fabricated samples contain nanodisk arrays of $100 \times$ 100 μ m² with different disk diameters and periodicities (see the Supporting Information). The exact disk diameter, which can deviate from the target size, is determined by analysis of scanning electron microscopy (SEM) images of the finished samples. In the last step, a part of each sample is covered and an 80-nm-thick Au layer is deposited on the uncovered part to be used for spectral referencing.

Reflectance measurements in a wavelength range from 400 to 1000 nm are performed in a microspectroscopy setup that consists of a Nikon Eclipse TE2000-U inverted microscope combined with a Princeton Instruments SP2500i grating spectrometer and a PIXIS 256 charge-coupled device (CCD) detector (see Figure 4a). An ultrastable laser-driven white light source (Energetiq EQ-99FC) is used to illuminate the sample via a $60 \times$ microscope objective (NA = 0.7). The light is tightly focused into the center of the back focal plane (BFP) of this objective to ensure near-normal incidence, which is necessary for good comparability to the numerical calculations. A field stop in the illumination path is used to limit the illuminated area to a single 100 \times 100 μ m² array so that no stray light from outside the array can influence the measurement. The collected image is then projected onto the entrance slit of the spectrometer. In a later stage, the setup is extended for angle-resolved reflectance measurements (Figure 4b).

During these optical measurements, the sample is situated in a home-made gas flow cell with thin microscopy windows, which is initially flooded with pure nitrogen at a flow rate of 1 L_n /min (liter normal per minute) at room temperature. Using Bronkhorst mass flow controllers, different concentrations of hydrogen gas can be added to this gas flow, while keeping the total flow rate constant at atmospheric pressure.

REFLECTANCE MEASUREMENTS

Figure 5a shows the measured reflectance spectra for Pd disk arrays with $d_{\text{disk}} = 202 \pm 7$ nm, at a periodicity of 300 nm, for the five different spacer thicknesses. Reflectance measurements were carried out once in pure nitrogen (blue curves) and once at a hydrogen concentration of 5% in N2 (red curves) at atmospheric pressure. The corresponding calculated spectra are displayed as dashed lines, showing excellent overall agreement. In each plot, the wavelength at which the highest reflectance difference is obtained is highlighted. One interesting feature is that the spectral position of $max(|\Delta R|)$ is always achieved in the higher wavelength range, above approximately 700 nm. This effect, which can also be observed in Figure 3, can be explained by looking at the dielectric functions of Pd and PdH, as shown in Figure 5b.⁵⁰ These data reveal that the difference between the dielectric function of Pd and PdH is also highest in this wavelength range, especially in the imaginary part ε_2 . This suggests that to maximize $|\Delta R|$, the readout wavelength should be chosen in a range, where the modulation of the dielectric function due to hydrogen absorption is as high as possible.

Figure 5c depicts the influence of the disk diameter on the maximum reflectance difference for each spacer thickness. Apart from the fact that the highest signal (approx. 17% reflectance difference) is obtained with a spacer thickness of 160 nm, these curves indicate that the disk diameter significantly influences the maximum signal up to around 150 nm, after which increasing the disk diameter further does not yield great improvements anymore. This can be understood by the information presented in Figure S2 of the Supporting Information. If the disks are too small, the plasmon resonance occurs at small wavelengths and does not lead to significant modulation of R due to the strongly decreased scattering cross section. Since the plasmon resonance has only an indirect influence on the cavity resonance condition (eq 2)



H₂ concentrations 5% - 0.5% (50,000 ppm - 5,000 ppm)

Figure 6. (a, b) Measured reflectance differences vs wavelength and time during hydrogen concentration cycles for spacer thicknesses 60 and 160 nm. Hydrogen concentrations are decreasing from 5 to 0.5% (5000 ppm) in N₂. The Pd disk diameter is 174 ± 6 nm. The wavelength of maximum reflectance difference is indicated in each plot. (c) Time traces of measured maximum reflectance differences for both spacer thicknesses, for a simulated spectrally narrow light source with a linewidth of 10 nm. (d, e) Measured reflectance differences vs wavelength and time at hydrogen concentrations decreasing from 0.1% (1000 ppm) to 0.01% (100 ppm). (f) Reflectance difference time traces extracted at optimum readout wavelengths determined for low concentrations.

and is rather broad anyway, changing the disk diameter does not have a very strong influence on ΔR when the disks are plasmonically active in the wavelength range above approx. 700 nm.

Figure 5d displays the spectral shapes of ΔR for spacer thicknesses of 60 and 160 nm, respectively, for a H₂ concentration of 5% as well as 0.5% in N2. At this lower concentration, the Pd lattice is not saturated with hydrogen; instead, isolated hydrogen atoms are located at interstitial lattice sites (α phase). Next to a smaller change in ε , the lattice expansion is much smaller in this case. Interestingly, this does not only lead to a reduced absolute ΔR value but also to a spectral shift of ΔR . This constitutes another important design principle, namely, that the hydrogen concentration range of interest must be taken into account for optimizing the sensor. In a threshold warning sensor that should trigger an alarm when the hydrogen concentration is close to the lower explosion threshold, a different sensor design and/or readout wavelength might be required when compared with a sensor meant to reliably detect trace amounts of H₂ in the sub-100 ppm range.

To study the performance of the different sensor geometries at different hydrogen concentrations, we perform time-resolved reflectance measurements during hydrogen concentration cycling. In a typical hydrogen concentration cycle, hydrogen is mixed into the N₂ gas flow at intervals of several minutes, at decreasing concentrations. Hydrogen exposure periods are always separated by several minutes of pure N₂ flow to ensure that the sample goes back to its original state and to avoid hysteresis effects between the absorption and desorption. Figure 6a,b shows pseudocolor plots of the obtained reflectance difference vs wavelength and time for $t_{\rm spacer}$ values of 60 and 160 nm and $d_{\rm disk} = 174 \pm 6$ nm, at H₂ concentrations decreasing from 5 to 0.5%. The measurement data for the

other spacer thicknesses and disk diameters can be found in Figure S3 of the Supporting Information. The reflectance in the absence of H₂ is determined by averaging over all spectra recorded before the first hydrogen exposure, and this spectrum is subtracted from all measured spectra to obtain ΔR . Background correction is performed by fitting a polynomial surface to all data points in the N2 exposure periods, excluding times with a strong signal change during hydrogen unloading (see the Supporting Information). From these spectral measurements, the optimum readout wavelength is determined. A time trace of the resulting $|\Delta R|$ is displayed in Figure 6c for both spacer thicknesses. A spectrally narrow light source with a linewidth of 10 nm is simulated here, to mimic the behavior of an actual LED-based sensor. The transition from α - to β -phase at a hydrogen concentration of 2% is clearly visible. At higher concentrations, the signal quickly saturates. If required (e.g., in a threshold warning sensor for the lower explosion limit), this saturation level could be raised by increasing the operating temperature of the sensor.³⁰ Another possibility is to use a different sensor material, such as a Pd-Au alloy.^{27,29}

Figure 6d,e depicts spectral measurements of ΔR vs time for the exact same nanodisk arrays, but during a hydrogen cycle at much lower hydrogen concentrations, decreasing from 0.1% (1000 ppm) to 0.01% (100 ppm). Following the insights from Figure 5d, a separate optimum readout wavelength is determined for this concentration range, and the resulting measured signal is displayed in Figure 6f. Interestingly, the difference between the two spacer thicknesses is much lower than for higher H₂ concentrations in this case. A possible explanation is that the actual maximum of $|\Delta R|$ has shifted out of the accessible wavelength range and is thus not recorded. Nevertheless, these measurements prove that even a low hydrogen concentration of 100 ppm can lead to a detectable

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Figure 7. (a) To study the angle- and polarization-dependent sensor response, structures with two different periodicities (300 and 500 nm) are investigated. Reflectance spectra measured in pure N₂, and the resulting reflectance differences for 5% H₂ in N₂, are plotted vs the incidence angle θ for s and p polarization for $t_{\text{spacer}} = 60$, 160, and 290 nm at P = 300 nm (b–d). A reflectance blueshift occurs for higher angles. The obtained ΔR values shift along with the reflectance spectrum, while the maximum $|\Delta R|$ value hardly changes or even increases. At P = 500 nm (e–g), waveguide–plasmon–polariton modes, SPP modes, and Rayleigh anomalies lead to sharp features in the reflectance, which also shows up in the sensor signal.

optical signal, with a $|\Delta R|$ in the order of 10^{-3} . It is important to note that the signal noise in the data shown here originates purely from the used measurement setup. It has nothing to do with the signal-to-noise ratio in an actual LED-based sensor and thus does not define any lower limit for the detectable hydrogen concentration.

ANGLE-RESOLVED MEASUREMENTS

So far, we have discussed the influence of important structure parameters, namely, the spacer thickness and the disk diameter, and of the hydrogen concentration range of interest. We have, however, not yet taken into account the optical readout angle θ (see Figure 1a), which is another important parameter in real-world sensor realizations. In particular, when lattice diffraction effects play a role, the angle can significantly influence the detected signal.

To perform angle-resolved reflectance measurements, we adapt the microspectroscopy setup for Fourier-plane imaging spectroscopy (Figure 4b). A modified 4-f setup projects the Fourier plane [which is conjugated to the objective back focal plane (BFP)] instead of the image plane onto the entrance slit of the spectrometer.^{52,53} The illumination geometry is modified to illuminate the full objective BFP. The CCD camera of the spectrometer records a wavelength-resolved image of the central slice through the Fourier plane, which means that a reflectance spectrum is obtained for each collection angle in one shot. The highest collection angle is

defined by the objective NA of 0.7, which corresponds to $\theta_{\text{max}} \approx 44^{\circ}$. Polarization-resolved measurements are recorded by inserting a linear polarizer behind the objective.

The results of angle-dependent reflectance measurements are shown in Figure 7 for Pd disk arrays with a period P of 300 nm and 500 nm, for s and p polarization (Figure 7a). Pseudocolor plots of the reflectance in pure N₂ are displayed for three different spacer thicknesses (60, 160, and 290 nm) in Figure 7b–g, along with the reflectance difference ΔR obtained at a H₂ concentration of 5%. The reflectance plots at P = 300nm clearly show how the reflectance spectrum undergoes a blueshift when the angle increases, which is to be expected for Fabry-Perot-like cavity resonators. The effect is most pronounced for the thickest spacer, which can be understood by the far-field coupling that dominates the reflectance behavior, while for thinner spacers, near-field coupling effects play a dominating role. The ΔR plots show two important features. The shape of the ΔR spectrum follows the shape of *R*, meaning that the highest signal is also obtained at shifted (in general shorter) wavelengths. The maximum value of $|\Delta R|$, however, does not change significantly. This implies that the readout angle of an optical hydrogen sensor can in principle be chosen arbitrarily for a fixed structure geometry, as long as the readout wavelength is adjusted accordingly.

A vastly different picture arises when the periodicity of the structures is increased, as indicated in Figure 7e–g. At a periodicity of 500 nm, strongly angle- and polarization-



Figure 8. Comparison of square nanodisk arrays and disordered ensembles. The disordered patterns are defined using randomized positions with a minimum interparticle spacing s_{min} , chosen such that the density of nanodisks per unit area is maintained for P = 300 nm (a) and P = 500 nm (b). Plots of the measured ΔR vs. wavelength and $\theta(t_{spacer} = 160 \text{ nm})$ prove that the diffraction effects are suppressed when disordered structures are used, yielding a much more uniform response as a function of θ and thus a robustness against changes in the angle of incidence (c, d). On the other hand, a comparison between the P = 500 nm grid and the corresponding disordered ensemble indicates that the array effects can in fact be used to enhance the sensor response if the readout wavelength and angle of incidence are chosen accordingly (d).

dependent features occur in the reflectance spectrum. These features can be attributed to waveguide–plasmon–polariton modes in the spacer layer and SPP modes at the MgF₂–Au interface, and, to a lesser degree, to the Rayleigh anomaly of the two-dimensional (2D) lattice.^{54–59} Detailed analysis can be found in the Supporting Information. These grating effects strongly influence ΔR as well. This is potentially destructive for robust sensor design, as the sensor response becomes strongly angle-dependent. In particular, at or very close to the grating modes, the obtained signal can be significantly decreased. An intuitive way to understand this is that at these modes, the farfield response of the structure is not dominated by the localized plasmon resonance of the nanoantennas, but rather by their arrangement, which remains unchanged. At the same time, local maxima in $|\Delta R|$ also seem to occur close to the grating modes.

Lattice effects can be suppressed using a disordered arrangement of the nanoparticles. In a real-world sensor, the type of arrangement depends on the nanofabrication process. Many large-scale nanopatterning processes, for example, laser-interference lithography, produce highly periodic patterns,³⁶ while processes such as hole-mask colloidal lithography⁶⁰ and colloidal etching lithography³⁹ produce disordered structures that exhibit only short-range order, thus suppressing far-field interaction between individual particles.

To study the effect of a disordered arrangement on the angle-dependent behavior of our Pd-based sensor structures, we also fabricate disordered structures using electron-beam lithography. We generate a set of randomized positions using a simplified version of the so-called random sequential adsorption (RSA) model, which can be used to simulate the effect of colloidal fabrication processes.⁶¹ In our implementation of the model, particles are placed at randomized (x,y) coordinates, under the conditions that a predefined minimum spacing s_{min} between the adjacent particles is maintained. The value of s_{min} is chosen such that the number of particles per unit area is the same as in the ordered case, as shown in Figure 8a,b.

Figure 8c shows an example of $\Delta R(\theta, \lambda)$ for P = 300 nm at $t_{\text{spacer}} = 160$ nm, alongside the corresponding disordered realization ($s_{\min} = 250$ nm). Almost no difference between the

ordered and the disordered case can be identified, especially not in the higher wavelength range, where the highest sensitivity is obtained. At such subdiffraction nanostructure densities, there is thus no clear advantage in using either lattice-based or disordered fabrication methods. In contrast, a comparison between P = 500 nm and the corresponding disordered arrangement with $s_{\min} = 420$ nm clearly reveals how the previously observed lattice diffraction effects are suppressed (Figure 8d). This leads again to a highly angleindependent sensor response. However, Figure 8d also reveals another interesting feature of the large-periodicity sensor arrangement. Close to the observed waveguide and SPP modes, the sensor signal $|\Delta R|$ can actually be *higher* than in the corresponding disordered case, by a factor of more than two. This indicates that the interaction between the incoming light and the Pd nanodisks can not only be suppressed but also enhanced. In other words, a disordered nanoparticle arrangement is clearly advantageous when a highly angle-independent sensor response is required, but if careful tuning of the readout wavelength and the incidence angle is possible, lattice effects can be exploited to enhance the sensor response.⁶

CONCLUSIONS

In this work, we have presented a systematic study of the design parameters for perfect absorber-type plasmonic hydrogen sensors and their influence on the sensor signal. We have shown that the system can be described as a plasmonic cavity generated by the metal mirror and the layer of plasmonic nanoantennas and that reflectance maxima and minima can be obtained by tuning the cavity length, i.e., the spacer thickness. Based on our numerical calculations as well as our measurements, we are able to formulate a set of design principles for maximizing the sensitivity of the sensors. First, the obtained signal ΔR , and thus, the SNR, at a certain wavelength, can be maximized by careful tuning of the spacer thickness and is obtained at neither of the reflectance extrema. The disk diameter has only a limited influence. Second, the readout wavelength should not be chosen entirely at random but should be in the wavelength range where the change in the dielectric function of Pd due to hydrogen incorporation is highest. Third, the concentration range of interest must be taken into account when choosing a readout wavelength, as the shape of $\Delta R(\lambda)$ can vary significantly between low and high concentrations. This can be explained by the transition from α to β -phase PdH_x and the corresponding volume expansion. A readout at several wavelengths simultaneously can of course be advantageous. Fourth, when lattice effects do not play a role in the reflectance spectrum, a slightly angle-dependent reflectance spectrum is obtained. This is not necessarily a disadvantage since the maximum sensor signal is hardly affected. Finally, at increased periodicities, grating effects such as the Rayleigh anomaly and waveguide-plasmon-polariton modes in the spacer layer lead to a highly angle-dependent sensor response. This can be suppressed by employing disordered instead of periodic structures. However, it is also possible to use the lattice effects to enhance the sensor response at specific combinations of the readout wavelength and the incidence angle.

Using all of these insights, we were able to demonstrate a nanoplasmonic hydrogen sensor with a detectable signal at a H_2 concentration of 100 ppm. This is entirely based on a single-wavelength reflectance readout. The use of dedicated, stabilized readout electronics can enable the reliable detection of even lower concentrations. At this point, we would like to stress that the insights presented here are not limited to Pd-based plasmonic hydrogen sensors. For any other choice of H_2 -sensing material, as well as a spacer and/or mirror material, the design principles listed above remain valid. The perfect absorber geometry can furthermore be applied to any other type of plasmonic sensor as well, such as indirect nanoplasmonic sensing or refractive-index sensing. We thus believe that our work can be beneficial for a broad range of plasmonic sensor applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssensors.9b02436.

Derivation of the signal-to-noise ratio (SNR) in a singlewavelength optical plasmonic hydrogen sensor; additional calculated R and ΔR spectra as a function of spacer thickness for different disk diameters; exemplary microscope photographs of the fabricated structures; description of the drift correction applied to the time trace data; additional time trace data for gas cycles at H₂ concentrations from 0.5 to 5% for different spacer thicknesses and disk diameters; additional angle-dependent reflectance measurements for different spacer thicknesses; detailed analysis of the angle-dependent behavior of the reflectance and its physical origins (PDF)

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Notes

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REFERENCES

 Patnaik, P. A Comprehensive Guide to the Hazardous Properties of Chemical Substances, 3rd ed.; John Wiley & Sons, Inc.: 2007; p 1059.
 Aleixandre, M.; Corredera, P.; Hernanz, M. L.; Gutierrez-Monreal, J. Development of fiber optic hydrogen sensors for testing nuclear waste repositories. Sens. Actuators, B 2005, 107, 113–120.

(3) Xu, T.; Senger, R.; Finsterle, S. Corrosion-induced gas generation in a nuclear waste repository: Reactive geochemistry and multiphase flow effects. *Appl. Geochem.* **2008**, *23*, 3423–3433.

(4) Bodzenta, J.; Burak, B.; Gacek, Z.; Jakubik, W. P.; Kochowski, S.; Urbańczyk, M. Thin palladium film as a sensor of hydrogen gas dissolved in transformer oil. *Sens. Actuators, B* **2002**, *87*, 82–87.

(5) Yang, F.; Jung, D.; Penner, R. M. Trace detection of dissolved hydrogen gas in oil using a palladium nanowire array. *Anal. Chem.* **2011**, *83*, 9472–9477.

(6) Hübert, T.; Boon-Brett, L.; Black, G.; Banach, U. Hydrogen sensors - A review. Sens. Actuators, B 2011, 157, 329-352.

(7) Slaman, M.; Westerwaal, R.; Schreuders, H.; Dam, B. Optical hydrogen sensors based on metal-hydrides. *Proc. SPIE* **2012**, *8368*, No. 836805.

(8) Ngene, P.; Radeva, T.; Slaman, M.; Westerwaal, R. J.; Schreuders, H.; Dam, B. Seeing hydrogen in colors: Low-cost and highly sensitive eye readable hydrogen detectors. *Adv. Funct. Mater.* **2014**, *24*, 2374–2382.

(9) Nasir, M. E.; Dickson, W.; Wurtz, G. A.; Wardley, W. P.; Zayats, A. V. Hydrogen detected by the naked eye: Optical hydrogen gas sensors based on core/shell plasmonic nanorod metamaterials. *Adv. Mater.* **2014**, *26*, 3532–3537.

(10) Butler, M. A. Fiber Optic Sensor for Hydrogen Concentrations near the Explosive Limit. J. Electrochem. Soc. **1991**, 138, L46–L47.

(11) Strohfeldt, N.; Tittl, A.; Giessen, H. Long-term stability of capped and buffered palladium-nickel thin films and nanostructures for plasmonic hydrogen sensing applications. *Opt. Mater. Express* **2013**, *3*, 194–204.

(12) Miliutina, E.; Guselnikova, O.; Chufistova, S.; Kolska, Z.; Elashnikov, R.; Burtsev, V.; Postnikov, P. S.; Svorcik, V.; Lyutakov, O. Fast and All-Optical Hydrogen Sensor Based on Gold-Coated Optical Fiber Functionalized with Metal-Organic Framework Layer. *ACS Sens.* **2019**, *4*, 3133–3140.

(13) Herkert, E.; Sterl, F.; Strohfeldt, N.; Walter, R.; Giessen, H. Low-cost hydrogen sensor in the ppm range with purely optical readout. *ACS Sens.* **2020**.

(14) Flanagan, T.; Oates, W. The Palladium-Hydrogen System. Annu. Rev. Mater. Sci. 1991, 21, 269–304.

(15) Avila, J. I.; Matelon, R. J.; Trabol, R.; Favre, M.; Lederman, D.; Volkmann, U. G.; Cabrera, A. L. Optical properties of Pd thin films exposed to hydrogen studied by transmittance and reflectance spectroscopy. J. Appl. Phys. **2010**, 107, No. 023504.

(16) She, X.; Shen, Y.; Wang, J.; Jin, C. Pd films on soft substrates: a visual, high-contrast and low-cost optical hydrogen sensor. *Light: Sci. Appl.* **2019**, *8*, No. 4.

(17) Langhammer, C.; Zorić, I.; Kasemo, B.; Clemens, B. Hydrogen storage in Pd nanodisks characterized with a novel nanoplasmonic sensing scheme. *Nano Lett.* **2007**, *7*, 3122–3127.

(18) Wadell, C.; Syrenova, S.; Langhammer, C. Plasmonic Hydrogen Sensing With Nanostructured Metal Hydrides. *ACS Nano* **2014**, *8*, 11925–11940.

(19) Strohfeldt, N.; Zhao, J.; Tittl, A.; Giessen, H. Sensitivity engineering in direct contact palladium-gold nano-sandwich hydrogen sensors. *Opt. Mater. Express* **2015**, *5*, 2525–2535.

(20) Liu, N.; Tang, M. L.; Hentschel, M.; Giessen, H.; Alivisatos, A. P. Nanoantenna-enhanced gas sensing in a single tailored nanofocus. *Nat. Mater.* **2011**, *10*, 631–636.

(21) Shegai, T.; Langhammer, C. Hydride formation in single palladium and magnesium nanoparticles studied by nanoplasmonic dark-field scattering spectroscopy. *Adv. Mater.* **2011**, *23*, 4409–4414.

(22) Syrenova, S.; Wadell, C.; Nugroho, F. A. A.; Gschneidtner, T. A.; Diaz Fernandez, Y. A.; Nalin, G.; Świtlik, D.; Westerlund, F.; Antosiewicz, T. J.; Zhdanov, V. P.; Moth-Poulsen, K.; Langhammer, C. Hydride formation thermodynamics and hysteresis in individual Pd nanocrystals with different size and shape. *Nat. Mater.* 2015, *14*, 1236–1244.

(23) Pivak, Y.; Gremaud, R.; Gross, K.; Gonzalez-Silveira, M.; Walton, A.; Book, D.; Schreuders, H.; Dam, B.; Griessen, R. Effect of the substrate on the thermodynamic properties of PdH_x films studied by hydrogenography. *Scr. Mater.* **2009**, *60*, 348–351.

(24) Griessen, R.; Strohfeldt, N.; Giessen, H. Thermodynamics of the hybrid interaction of hydrogen with palladium nanoparticles. *Nat. Mater.* **2016**, *15*, 311–317.

(25) Wagner, S.; Pundt, A. Quasi-thermodynamic model on hydride formation in palladium-hydrogen thin films: Impact of elastic and microstructural constraints. *Int. J. Hydrogen Energy* **2016**, *41*, 2727–2738.

(26) Bannenberg, L. J.; Nugroho, F. A. A.; Schreuders, H.; Norder, B.; Trinh, T. T.; Steinke, N. J.; Van Well, A. A.; Langhammer, C.; Dam, B. Direct Comparison of PdAu Alloy Thin Films and Nanoparticles upon Hydrogen Exposure. *ACS Appl. Mater. Interfaces* **2019**, *11*, 15489–15497.

(27) Wadell, C.; Nugroho, F. A. A.; Lidström, E.; Iandolo, B.; Wagner, J. B.; Langhammer, C. Hysteresis–Free Nanoplasmonic Pd– Au Alloy Hydrogen Sensors. *Nano Lett.* **2015**, *15*, 3563–3570.

(28) Nugroho, F. A. A.; Darmadi, I.; Zhdanov, V. P.; Langhammer, C. Universal Scaling and Design Rules of Hydrogen-Induced Optical Properties in Pd and Pd-Alloy Nanoparticles. *ACS Nano* **2018**, *12*, 9903–9912.

(29) Nugroho, F. A. A.; Darmadi, I.; Cusinato, L.; Susarrey-Arce, A.; Schreuders, H.; Bannenberg, L. J.; da Silva Fanta, A. B.; Kadkhodazadeh, S.; Wagner, J. B.; Antosiewicz, T. J.; Hellman, A.; Zhdanov, V. P.; Dam, B.; Langhammer, C. Metal–polymer hybrid nanomaterials for plasmonic ultrafast hydrogen detection. *Nat. Mater.* **2019**, *18*, 489–495.

(30) Teutsch, T.; Strohfeldt, N.; Sterl, F.; Warsewa, A.; Herkert, E.; Paone, D.; Giessen, H.; Tarin, C. Mathematical Modeling of a Plasmonic Palladium-Based Hydrogen Sensor. *IEEE Sens. J.* 2018, *18*, 1946–1959.

(31) ElKabbash, M.; Sreekanth, K. V.; Alapan, Y.; Kim, M.; Cole, J.; Fraiwan, A.; Letsou, T.; Li, Y.; Guo, C.; Sankaran, R. M.; Gurkan, U. A.; Hinczewski, M.; Strangi, G. Hydrogen Sensing Using Thin-Film Perfect Light Absorber. *ACS Photonics* **2019**, *6*, 1889–1894.

(32) Wadell, C.; Antosiewicz, T. J.; Langhammer, C. Optical absorption engineering in stacked plasmonic Au-SiO₂-Pd nanoantennas. *Nano Lett.* **2012**, *12*, 4784–4790.

(33) Tittl, A.; Yin, X.; Giessen, H.; Tian, X.-D.; Tian, Z.-Q.; Kremers, C.; Chigrin, D. N.; Liu, N. Plasmonic smart dust for probing local chemical reactions. *Nano Lett.* **2013**, *13*, 1816–1821.

(34) Beni, T.; Yamasaku, N.; Kurotsu, T.; To, N.; Okazaki, S.; Arakawa, T.; Balčytis, A.; Seniutinas, G.; Juodkazis, S.; Nishijima, Y. Metamaterial for Hydrogen Sensing. *ACS Sens.* **2019**, *4*, 2389–2394.

(35) Tittl, A.; Mai, P.; Taubert, R.; Dregely, D.; Liu, N.; Giessen, H. Palladium-based plasmonic perfect absorber in the visible wavelength range and its application to hydrogen sensing. *Nano Lett.* **2011**, *11*, 4366–4369.

(36) Bagheri, S.; Strohfeldt, N.; Sterl, F.; Berrier, A.; Tittl, A.; Giessen, H. Large-Area Low-Cost Plasmonic Perfect Absorber Chemical Sensor Fabricated by Laser Interference Lithography. *ACS Sens.* **2016**, *1*, 1148–1154.

(37) Liu, N.; Mesch, M.; Weiss, T.; Hentschel, M.; Giessen, H. Infrared perfect absorber and its application as plasmonic sensor. *Nano Lett.* **2010**, *10*, 2342–2348.

(38) Tittl, A.; Harats, M. G.; Walter, R.; Yin, X.; Schäferling, M.; Liu, N.; Rapaport, R.; Giessen, H. Quantitative Angle-Resolved Small-Spot Reflectance Measurements on Plasmonic Perfect Absorbers: Impedance Matching and Disorder Effects. *ACS Nano* **2014**, *8*, 10885–10892.

(39) Walter, R.; Tittl, A.; Berrier, A.; Sterl, F.; Weiss, T.; Giessen, H. Large-Area Low-Cost Tunable Plasmonic Perfect Absorber in the Near Infrared by Colloidal Etching Lithography. *Adv. Opt. Mater.* **2015**, *3*, 398–403.

(40) Weiss, T.; Granet, G.; Gippius, N. A.; Tikhodeev, S. G.; Giessen, H. Derivation of plasmonic resonances in the Fourier modal method with adaptive spatial resolution and matched coordinates. *J. Opt. Soc. Am. A* **2009**, *17*, 238–244.

(41) Dodge, M. J. Refractive properties of magnesium fluoride. *Appl. Opt.* **1984**, 23, 1980–1985.

(42) Taubert, R.; Ameling, R.; Weiss, T.; Christ, A.; Giessen, H. From near-field to far-field coupling in the third dimension: Retarded interaction of particle plasmons. *Nano Lett.* **2011**, *11*, 4421–4424.

(43) Schmidt, M. A.; Lei, D. Y.; Wondraczek, L.; Nazabal, V.; Maier, S. A. Hybrid nanoparticle-microcavity-based plasmonic nanosensors with improved detection resolution and extended remote-sensing ability. *Nat. Commun.* **2012**, *3*, No. 1108.

(44) Ameling, R.; Giessen, H. Microcavity plasmonics: Strong coupling of photonic cavities and plasmons. *Laser Photonics Rev.* 2013, 7, 141–169.

(45) James, T. D.; Mulvaney, P.; Roberts, A. The Plasmonic Pixel: Large Area, Wide Gamut Color Reproduction Using Aluminum Nanostructures. *Nano Lett.* **2016**, *16*, 3817–3823.

(46) Kwadrin, A.; Osorio, C. I.; Koenderink, A. F. Backaction in metasurface etalons. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, 93, No. 104301.

(47) Berkhout, A.; Koenderink, A. F. Perfect Absorption and Phase Singularities in Plasmon Antenna Array Etalons. *ACS Photonics* **2019**, *6*, 2917–2925.

(48) Weiss, T.; Gippius, N. A.; Granet, G.; Tikhodeev, S. G.; Taubert, R.; Fu, L.; Schweizer, H.; Giessen, H. Strong resonant mode coupling of Fabry-Perot and grating resonances in stacked two-layer systems. *Photonics Nanostruct.—Fundam. Appl.* **2011**, *9*, 390–397.

(49) Bhattarai, K.; Silva, S.; Song, K.; Urbas, A.; Lee, S. J.; Ku, Z.; Zhou, J. Metamaterial Perfect Absorber Analyzed by a Meta-cavity Model Consisting of Multilayer Metasurfaces. *Sci. Rep.* **2017**, *7*, No. 10569.

(50) Von Rottkay, K.; Rubin, M.; Duine, P. A. Refractive index changes of Pd-coated magnesium lanthanide switchable mirrors upon hydrogen insertion. *J. Appl. Phys.* **1999**, *85*, 408–413.

(51) Khanuja, M.; Mehta, B. R.; Agar, P.; Kulriya, P. K.; Avasthi, D. K. Hydrogen induced lattice expansion and crystallinity degradation

in palladium nanoparticles: Effect of hydrogen concentration, pressure, and temperature. *J. Appl. Phys.* **2009**, *106*, No. 093515.

(52) Wagner, R.; Heerklotz, L.; Kortenbruck, N.; Cichos, F. Back focal plane imaging spectroscopy of photonic crystals. *Appl. Phys. Lett.* **2012**, *101*, No. 081904.

(53) Kurvits, J. A.; Jiang, M.; Zia, R. Comparative analysis of imaging configurations and objectives for Fourier microscopy. *J. Opt. Soc. Am.* A **2015**, 32, 2082–2092.

(54) Christ, A.; Zentgraf, T.; Kuhl, J.; Tikhodeev, S. G.; Gippius, N. A.; Giessen, H. Optical properties of planar metallic photonic crystal structures: Experiment and theory. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2004**, *70*, No. 125113.

(55) Christ, A.; Zentgraf, T.; Tikhodeev, S. G.; Gippius, N. A.; Kuhl, J.; Giessen, H. Controlling the interaction between localized and delocalized surface plasmon modes: Experiment and numerical calculations. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2006, 74, No. 155435.

(56) Etchegoin, P. G.; Le Ru, E. C.; Meyer, M. An analytic model for the optical properties of gold. *J. Chem. Phys.* **2006**, *125*, No. 164705.

(57) Kichin, G.; Weiss, T.; Gao, H.; Henzie, J.; Odom, T. W.; Tikhodeev, S. G.; Giessen, H. Metal-dielectric photonic crystal superlattice: 1D and 2D models and empty lattice approximation. *Phys. B* **2012**, *407*, 4037–4042.

(58) 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*, No. 237401.

(59) 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**, *96*, No. 045129.

(60) Fredriksson, H.; Alaverdyan, Y.; Dmitriev, A.; Langhammer, C.; Sutherland, D. S.; Zäch, M.; Kasemo, B. Hole-mask colloidal lithography. *Adv. Mater.* **2007**, *19*, 4297–4302.

(61) Piechulla, P. M.; Muehlenbein, L.; Wehrspohn, R. B.; Nanz, S.; Abass, A.; Rockstuhl, C.; Sprafke, A. Fabrication of Nearly-Hyperuniform Substrates by Tailored Disorder for Photonic Applications. *Adv. Opt. Mater.* **2018**, *6*, No. 1701272.

(62) 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.